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Synthesis of Chain End Functionalized Fluoropolymers by Functional Borane Initiators and Application in the Exfoliated Fluoropolymer/Clay Nanocomposites

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Introduction. Fluoropolymers are commonly used in high-end applications, such as aerospace and microelectronics. They exhibit a unique combination of properties,[1] including thermal stability, chemical inertness, self-extinguishing, and peculiar surface and electric properties. However, fluoropolymers also have some drawbacks, including poor adhesion to substrates and inertness to chemical modification, which limit their interactive and reactive properties. Unfortunately, the functionalization of fluoropolymers has been a constant research challenge in the past. Most research approaches have been focusing on the copolymerization of fluorinated monomers with functional comonomers to form functional fluoro-copolymers containing pendent functional groups.[2] Few reports discussed the preparation of telechelic fluoropolymers[3] containing terminal functional groups. The chemistry involves the use of functional initiators, including diester peroxides and diiodo initiators. Recently, Saint-Loup et al.[4] prepared telechelic VDF/HFP elastomers containing two opposing hydroxy terminal groups by using hydrogen peroxide as an initiator. However, many side reactions occurred in this polymerization, and the final product contained not only hydroxy terminal groups but also carboxylic acid terminal groups as well as some unsaturated terminal groups.

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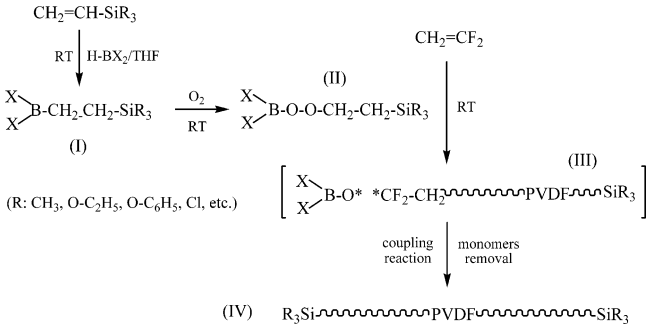
Scheme 1



A few years ago, we reported a borane/oxygen radical initiator system[5] that carries out a control radical polymerization of acrylic monomers in bulk and in solution at ambient temperature. The chemistry provides an effective route in the preparation of functional polyolefins (i.e., PE, PP) and block/graft copolymers.[6] The unexpected performance of good control in the radical chain extension prompted us to examine the scope and limitations of this radical initiator system and its reaction mechanism. The same borane initiators were effective for fluoromonomers, such as vinylidene fluoride (VDF), trifluoroethylene (TrFE), and chlorotrifluoroethylene (CTFE), which prepare the fluoropolymer and random copolymers in mild reaction conditions. The resulting VDF/TrFE/CTFE terpolymers exhibit interesting dielectric, ferroelectric, and capacitor properties.[7] Recently, we further extended the chemistry to functional borane initiators with the objective of preparing chain end functional fluoropolymers.[8] The silane-terminated fluoropolymers exhibit very high surface activity on the silicate clay surfaces to exfoliate the clay interlayer structure, even when using the pristine clay materials.

Experimental Details. *Synthesis of $[(C_2H_5O)_3SiCH_2CH_2]_3B$ Functional Initiator.* In a 500 mL flame-dried flask, equipped with a magnetic stir bar, 250 mL of dry THF and 35 g (180 mmol) of vinyltriethoxylsilane were injected under argon. After cooling the solution to 0 °C, 60 mL of BH_3 in THF (1.0 M) was added. The mixture was stirred at 0 °C for 4 h and then was warmed to ambient temperature for 1 h to ensure a complete hydroboration reaction. After solvent removal, the product was

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Table 1. Summary of Chain End Functionalized PVDF Polymers Prepared by Functional Borane Initiators[a]

						end groups (NMR)					GPC	
run	initiator (mmol)	O_2 (mL)	temp (°C)	time (h)	conv (%)	CF_2H (%)	CH_3 (%)	SiR_3 (%)	M_n[b] (NMR) (g/mol)	M_n[c] (NMR) (g/mol)	M_n (g/mol)	PDI
A-1	B−Si(OEt)$_3$ (1.0)	25	0	16	32.1	32.5	9.5	58.0	22 100	38 100	N.A	N.A
A-2	B−Si(OEt)$_3$ (1.0)	25	25	5	30.6	35.1	13.0	51.9	15 500	29 800	N.A	N.A
A-3	B−Si(OEt)$_3$ (1.0)	25	60	5	39.6	40.2	10.1	49.7	12 100	24 700	N.A	N.A
A-4	B−Si(OEt)$_3$ (1.0)	25	25	21	51.5	33.2	13.3	54.5	22 900	42 400	N.A	N.A
A-5	B−Si(OEt)$_3$ (3.0)	60	25	21	65.7	27.6	9.8	62.6	13 300	21 500	N.A	N.A
B-1	B−SiMe$_3$ (3.0)	40	25	5	10.1	26.4	5.3	68.3	12 500	18 400	17 500	1.4
B-2	B−SiMe$_3$ (3.0)	60	25	5	11.2	19.3	7.9	72.8	10 500	14 600	14 500	1.6
B-3	B−SiMe$_3$ (3.0)	80	25	5	10.2	25.4	6.3	68.3	12 900	19 000	18 200	1.4
C-1	B−Si(OEt)Me$_2$ (1.0)	25	25	5	30.8	38.3	11.3	50.4	18 500	37 000	N.A	N.A
C-2	B−Si(OEt)Me$_2$ (1.0)	25	25	17	53.3	34.4	7.0	58.6	30 000	51 700	N.A	N.A
C-3	B−Si(OEt)$_2$Me (2.0)	50	25	17	38.8	29.8	6.8	63.4	19 600	31 100	N.A	N.A
C-4	B−O−SiMe$_3$ (3.0)	50	25	14	53.0	31.3	8.4	60.3	10 500	17 500	N.A	N.A
C-5	B−SiCl$_3$ (2.0)	40	25	19	34.3	N.A	N.A	N.A	N.A	N.A	N.A	N.A

[a] Polymerization conditions: 75 mL reactor; 20 mL of VDF; solvent: acetonitrile 30 mL. [b] Estimated from chain end analysis (including three end groups) by ^{1}H NMR spectra. [c] Estimated from chain end analysis (only silane end groups) by ^{1}H NMR spectra.

subjected to vacuum distillation at 170 °C to obtain 23.4 g of the tris(triethoxylethylsilyl)borane product. The ^{1}H NMR spectrum indicates that the hydroboration reaction involves, mainly, an anti-Markovnikov addition (>90%). Both ^{1}H and ^{13}B NMR spectra of tris(triethoxylsilylethyl)borane are shown in Figure S2 (Supporting Information).

Synthesis of PVDF Polymers with A Terminal $(C_2H_5O)_3Si$ Group. In a typical reaction (run A-2 in Table 1), 0.6 g of $[(C_2H_5O)_3SiCH_2CH_2]_3B$ (1 mmol) was dissolved in 30 mL of CH_3CN in a dry box. The reactor was then connected to a vacuum line, and 20 mL (13.4 g) of VDF (210 mmol) was condensed into an autoclave reactor under vacuum by liquid nitrogen. VDF has a vapor pressure of ~40 atm at 25 °C. About 25 mL of O_2 was charged into the reactor to oxidize borane moiety and initiate the polymerization that was carried out at ambient temperature for 5 h. After releasing the pressure, the mixture was transferred into a flask containing 100 mL of hexane. After stirring for 30 min, the polymer powder was filtered, washed, and then dried under vacuum at ambient temperature for 6 h. About 4.1 g of polymer was obtained with a yield of 30.6%. The resulting polymer was characterized by GPC (M_n) and ^{1}H NMR measurements.

Preparation of PVDF/Clay Nanocomposite Using PVDF-t-Si(OR)$_3$ Interfacial Agent. The silane-terminated PVDF polymers [PVDF-t-Si(OR)$_3$] were used as interfacial agents in the preparation of exfoliated PVDF/clay nanocomposites by a melt blending process. In a typical example, a PVDF-t-Si(OR)$_3$ polymer containing a terminal Si(OR)$_3$ group (T_m = 168 °C, M_n = 22 100 g/mol) was mixed with pristine Na^+-montmorillonite clay (Na^+-mmt), which has an ion-exchange capacity of ca. 90 mequiv/100 g (WM). Static melt intercalation was employed by, first, mixing and grinding PVDF-t-Si(OR)$_3$ dried powder and Na^+-mmt with a 90/10 weight ratio in a mortar and pestle at ambient temperature. The mixed powder was then heated at 200 °C for 3 h under nitrogen to result in the exfoliated PVDF-t-Si(OR)$_3$/Na^+-mmt nanocomposite. The resulting binary PVDF-t-Si(OR)$_3$/Na^+-mmt exfoliated nanocomposite was further melted by mixing it (50/50 weight ratio) with commercial neat PVDF (M_n = 70 000 and M_w = 180 000 g/mol). First, the PVDF-t-Si(OR)$_3$/Na^+-mmt exfoliated nanocomposite and neat PVDF with 50/50 weight ratio were ground together in a mortar and pestle at ambient temperature. The mixed powder was then heated at 200 °C for 3 h under nitrogen to form a ternary PVDF/PVDF-t-Si(OR)$_3$/Na^+-mmt nanocomposite.

Results and Discussion. In this paper, we discuss a new class of borane initiators that contain functional groups, such as OH and silane groups, which are stable during the borane oxidation and polymerization processes at ambient temperature. Scheme 1 illustrates an example, in which the silane-terminated poly(vinylidene fluoride) is prepared by using a silane containing borane initiator at ambient temperature. (Detailed information on other PVDF co- and terpolymers and various functional groups are provided in the Supporting Information.) Overall, this method offers a convenient and effective route to prepare a broad range of chain end functionalized fluoropolymers under mild reaction conditions.

The functional borane initiator (I), containing a silane group, was quantitatively prepared by a well-known hydroboration reaction[9] of vinylsilane (commercial available) with a borane compound containing at least one B−H group at ambient temperature. The subsequent mono-oxidation reaction of the functional borane initiator with a control quantity of oxygen occurs spontaneously at room temperature to form the corresponding peroxylborane (II) for initiating polymerization.[10] This oxidation reaction can be carried out in situ during the control radical polymerization with the presence of VDF monomers. The propagating PVDF chain (III) contains a terminal silane group in the beginning of polymer chain and a propagating radical at the other chain end. The propogating radical at the end of the polymer chain is capped with a borinate radical (*O−BX_2) in order to prolong the propagation reaction.[8,10] Upon releasing VDF monomer gas, the radical coupling reaction takes place to obtain telechelic silane-terminated PVDF polymer (IV).

Table 1 summarizes the experimental conditions and results of PVDF polymers prepared by various borane initiators. The first set (runs A-1 to A-5) compares VDF homopolymerization reactions using tris(triethoxylethylsilyl)borane under various reaction conditions. Comparing runs A-1, A-2, and A-3, the reaction temperature seems to have a relatively small effect to the polymer yield. Both the instantaneous oxygen autooxidation of B−C moieties in the borane initiator and the subsequent radical addition reaction with the fluoromonomer are very effective at ambient temperature, even at 0 °C (run A-1). In comparing runs A-2 and A-4, note that the polymer yield and molecular weight are positively correlated with the monomer conversion. The resulting PVDF-t-Si$(OC_2H_5)_3$ polymer is sensitive to moisture and becomes insoluble upon heating. The second set (runs B-1 to B-3) prepares trimethylsilane-terminated PVDF polymers (PVDF-t-Si$(CH_3)_3$) using the tris(trimethylethylsilyl)borane initiator, with various amounts of O_2 activator ([borane]/[O_2] = 2/1−1/1) at ambient temperature. The resulting PVDF-t-Si$(CH_3)_3$ polymers are moisture stable and suitable for

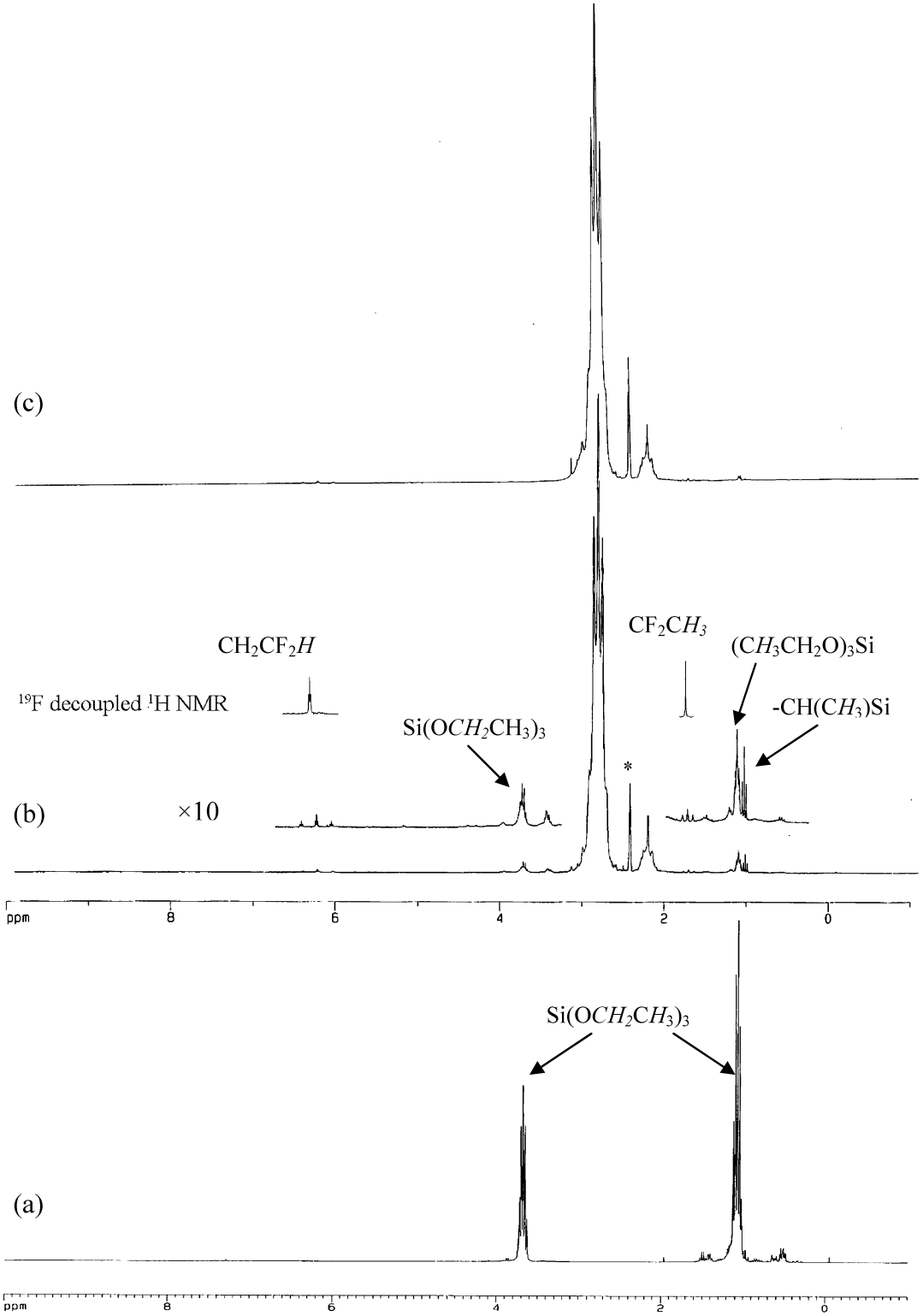

Figure 1. ^1H NMR spectra of (a) $[(C_2H_5O)_3SiCH_2CH_2]_3B$ initiator, (b) PVDF-t-$Si(OC_2H_5)_3$ polymer (run A-3), and (c) its corresponding hydrolyzed PVDF-t-$Si(OH)_3$ polymer.

structure analyses, especially in analyzing end groups and molecular weight. The chain end structures were determined by the ^1H NMR spectrum, and the estimated polymer molecular weight from the silane end group analysis is consistent with the GPC result using a universal calibration curve.[11] As will be discussed later, the combined results indicate that most polymer chains contain two terminal silane groups.

Basically, the functional initiators behave similarly with their corresponding trialkylborane initiators[10] during the initiation and propagation steps. The relatively stable propagating radicals slowly increase polymer molecular weight with monomer conversion and maintain a relatively narrow molecular weight distribution. The slurry reaction condition, due to the insolubility of PVDF (high crystallinity and high melting temperature) in acetonitrile, may also contribute to the slowdown of the polymerization rate. Note that the relatively slow propagating rate, compared to that of the regular free radical polymerization mechanism, removes the safety concern for heat transport and

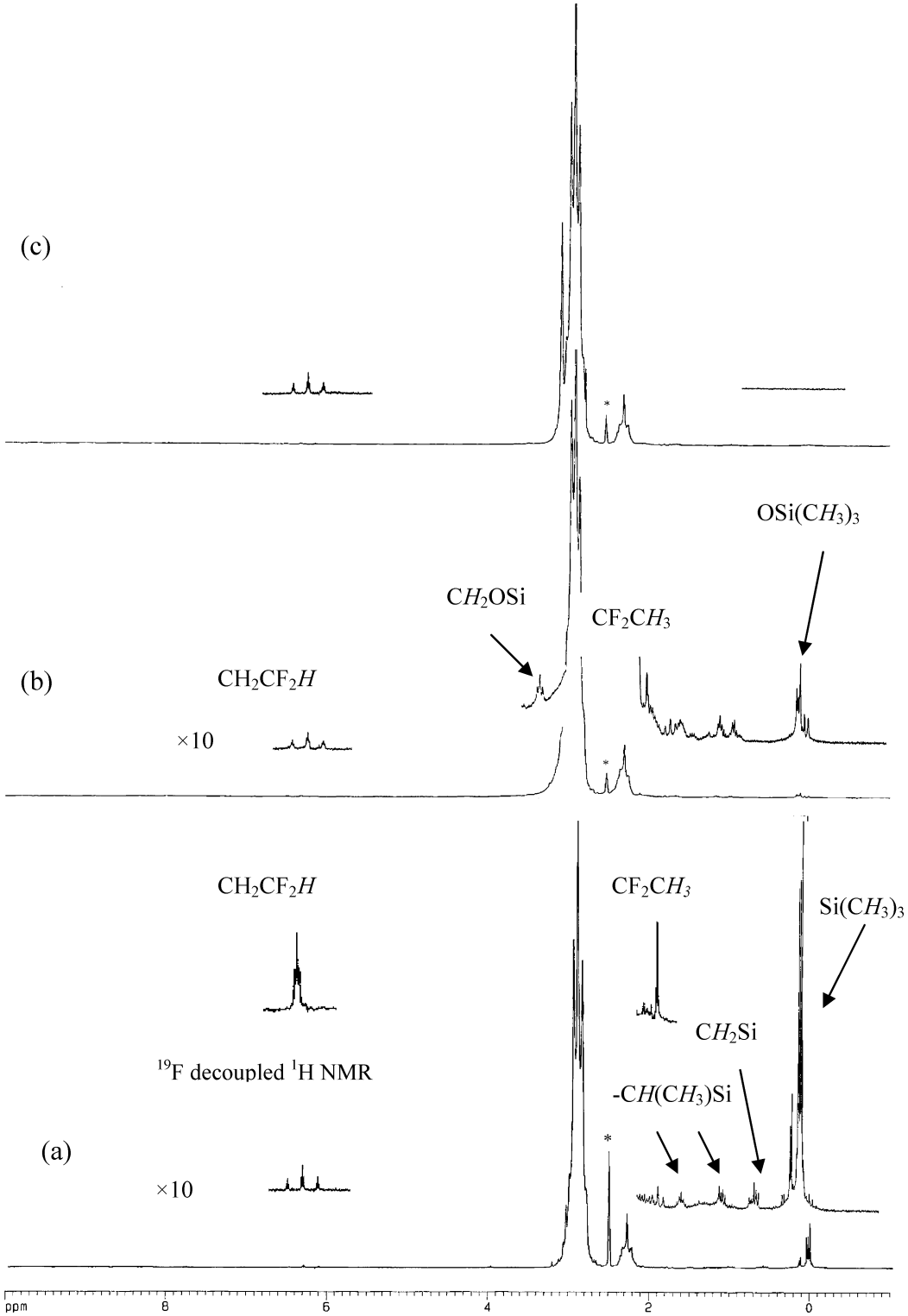

Figure 2. ^{1}H NMR spectra of three chain end functionalized PVDF polymers, including (a) PVDF-t-SiMe$_3$ (run B-2), (b) PVDF-t-O−SiMe$_3$ (run C-4), and (c) its corresponding PVDF-t-OH.

temperature control usually associated with bulk or solution polymerization of fluoromonomers.

Figure 1 compares the ^{1}H NMR spectra of a PVDF-t-Si-$(OC_2H_5)_3$ polymer (run A-3) with the corresponding functional borane initiator containing triethoxyl groups and its hydrolyzed PVDF-t-Si$(OH)_3$ polymer. Insets of the expanded regions exhibit chain end structures and a selected ^{19}F decoupled chemical shift. In Figure 1b, the PVDF-t-Si$(OC_2H_5)_3$ polymer exhibits two chemical shifts at 2.9 and 2.3 ppm, corresponding to the CH_2 units with 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 in the PVDF backbone, respectively. In the expanded regions, there are two dominate chemical shifts at 1.15 ppm (CH_3) and 3.75 ppm (OCH_2), which are almost identical with those in Figure 1a of the $[(C_2H_5O)_3SiCH_2CH_2]_3B$ initiator. They represent the existence of terminal $(C_2H_5O)_3Si$ silane groups in the PVDF polymer chain end. After hydrolysis by exposing PVDF-t-Si$(OC_2H_5)_3$ polymer in water, the resulting PVDF-t-Si$(OH)_3$ shows almost a complete disappearance of $(C_2H_5O)_3Si$ groups (Figure 1c). Both PVDF-t-Si$(OEt)_3$ and PVDF-t-Si$(OH)_3$ polymers are very

reactive. Upon drying in vacuum, both polymers become insoluble (cross-linked) networks.

One advantage of the borane initiator is its continence in regards to the incorporation of organic functional groups, by the hydroboration reaction of B−H with the α-olefin containing functional group at ambient temperature, as illustrated in Scheme 1. In addition, most of the functional groups (and their derivatives) are stable throughout the borane-mediated radical polymerization process. As discussed, the PVDF-t-Si(OEt)$_3$ polymer is sensitive to moisture. The PVDF-t-Si(OEt)Me$_2$ (runs C-1 and C-2) and PVDF-t-Si(OEt)$_2$Me (run C-3) are easier to handle, but the PVDF-t-SiCl$_3$ (run C-5) is extremely sensitive to moisture, a characteristic that makes it very difficult to maintain good solubility in organic solvents. On the other hand, the PVDF-t-SiMe$_3$ polymers (runs B-1 to B-3) are very stable and are used in examining the polymerization mechanism and the resulting polymer structure. Figure 2a shows the ^{1}H NMR spectrum of a PVDF-t-SiMe$_3$ polymer (run B-2), with insets showing the expanded regions and chemical shift assignments that are associated with three terminal groups (−Si(CH$_3$)$_3$, −CH$_2$CF$_2$H, and −CF$_2$CH$_3$). Two selected ^{19}F decoupled chemical shifts (changing from a triplet−triplet to a triplet peak at 6.3 ppm and from a triplet to a singlet peak at 1.8 ppm) confirm the existence of two end group structures (−CH$_2$CF$_2$H, and −CF$_2$CH$_3$). Pianca[12] assigned these two groups as the side chain end groups, formed by intrachain chain transfer reactions. These transfer reactions involve −CH$_2$CF$_2$* (major) and −CF$_2$-CH$_2$* (minor) propagating sites with a 1,5-hydrogen shift after a head-to-head monomer addition. As discussed in Table 1, the PVDF-t-SiMe$_3$ polymer molecular weight, estimated from the concentration of two Si(CH$_3$)$_3$ chain end groups (determined by ^{1}H NMR), is similar to that of the GPC result, indicating the existence of the telechelic PVDF polymer structure with two terminal silane groups.

Figure 2b,c shows the ^{1}H NMR spectra of the end functional PVDF polymers, containing O−SiMe$_3$ (run C-4) and its corresponding OH group (after hydrolysis). The PVDF-t-O−SiMe$_3$ polymer is quantitatively hydrolyzed to form the desirable hydroxyl group-terminated PVDF (PVDF-t-OH). Essentially, the same reaction mechanism was observed in each reaction with the incorporation of a functional group in the beginning of the polymer chain. The free radical coupling reaction (termination) took place after monomer removal in order to form the polymer with two terminal functional groups. Similar results were also observed in the copolymers and terpolymers, which are discussed in the Supporting Information.

One interesting feature of the chain end functionalized fluoropolymer, having the reactive terminal groups (anchor sites), is its high interfacial activity in the composite materials. Resembling the chain end functionalized polypropylene,[13] the chain end functionalized fluoropolymer shows an effective dispersion (stabilization) of inorganic particles in the polymer matrix. Figure 3 shows the X-ray results of one set of PVDF/clay samples, in which the PVDF-t-Si(OEt)Me$_2$ containing the reactive Si(OEt)Me$_2$ terminal group (run B-3; T_m = 170 °C, M_n = 30 000 g/mol) was mixed with pristine Na$^+$-mmt clay (without treatment with organic surfactants or acids). Static melt intercalation was employed by, first, mixing and grinding PVDF-t-Si(OEt)Me$_2$ dried powder and Na$^+$-mmt with a 90/10 weight ratio in a mortar and pestle at ambient temperature. The XRD pattern (Figure 3a) of this simple mixture shows a (001) peak at $2\theta \sim 7$, corresponding to the Na$^+$-mmt interlayer structure with a *d*-spacing of 1.45 nm. The mixed powder was then heated at 200 °C for 3 h under a nitrogen condition. The

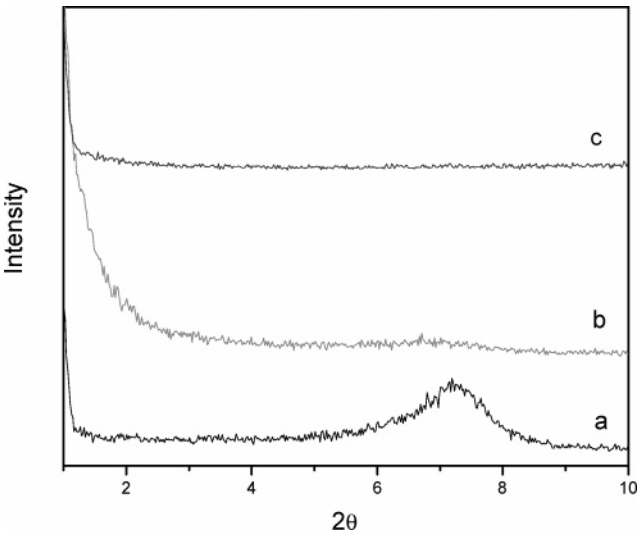

Figure 3. X-ray diffraction patterns of (a) physical mixture of PVDF-t-Si(OEt)Me$_2$ and pristine Na$^+$-mmt clay (90/10 weight ratio), (b) the same mixture after static melt intercalation, and (c) the 50/50 mixture by weight of exfoliated PVDF-t-Si(OEt)Me$_2$/ Na$^+$-mmt structure (from b) and neat PVDF.

resulting PVDF-t-Si(OEt)Me$_2$/Na$^+$-mmt nanocomposite shows a featureless XRD pattern (Figure 3b), indicating the formation of an exfoliated clay structure. Apparently, the reactive Si(OEt)-Me$_2$ terminal group may react with the Si−OH group on the clay surfaces to form a Si−O−Si bond at the interface between clay interlayers. The anchored hydrophobic and oleophobic fluoropolymer chains—disliking the hydrophilic clay surfaces—exfoliate the clay layer structure.

The resulting binary PVDF-t-Si(OEt)Me$_2$/Na$^+$-mmt exfoliated nanocomposite was further melted by mixing (50/50 weight ratio) with a commercial neat PVDF (M_n = 70 000 and M_w = 180 000 g/mol). First, the PVDF-t-Si(OEt)Me$_2$/Na$^+$-mmt exfoliated nanocomposite and neat PVDF, with a 50/50 weight ratio, were ground together in a mortar and pestle at ambient temperature. The mixed powder was then heated at 200 °C for 3 h under a nitrogen condition. The resulting ternary PVDF/PVDF-t-Si(OEt)Me$_2$/Na$^+$-mmt nanocomposite also shows a featureless XRD pattern (Figure 3c), indicating that the stable exfoliated structure in the binary PVDF-t-Si(OEt)Me$_2$/Na$^+$-mmt exfoliated nanocomposite is maintained after further mixing with PVDF that is compatible with the backbone of PVDF-t-Si(OEt)-Me$_2$.

Conclusion. We have developed a new synthesis route through the combination of functional borane initiators, control radical polymerization, and termination by radical coupling reaction, which produces telechelic fluoropolymers containing two terminal functional groups. This chemistry is advantaged by its simplicity and mild reaction condition and is applicable to a broad range of fluoromonomers, including VDF, TrFE, CTFE, HFP, etc. (in Supporting Information). The formed chain end functionalized fluoropolymer is an effective polymeric surfactant, which shows high interfacial activity in the exfoliated fluoropolymer/clay nanocomposites. The functional group anchors the polymer chain to the clay interface, and the rest of the unperturbed high molecular weight hydrophoblic and oleophobic fluoropolymer chain—disliking the hydrophilic clay surfaces—exfoliates the clay layer structure. This disordered clay structure is maintained even after further mixing with a neat (unfunctionalized) fluoropolymer that is compatible with the backbone of the chain end functionalized fluoropolymer.

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Supporting Information Available: Detailed experimental procedures to prepare functional borane initiators and chain end functionalized PVDF, VDF/CTFE, and VDF/HFP copolymers; ^{1}H and ^{13}B NMR spectra of functional broane initiators; ^{1}H and ^{19}F NMR spectra of the chain end functionalized PVDF, VDF/CTFE, and VDF/HFP copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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