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High Dielectric VDF/TrFE/CTFE Terpolymers Prepared by Hydrogenation of VDF/CTFE Copolymers: Synthesis and Characterization

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Introduction. A few years ago, we reported a new family of ferroelectric and high dielectric fluoro-terpolymers[1] comprised of vinylidene difluoride (VDF), trifluoroethylene (TrFE), and a chlorine-containing monomer, such as chlorodifluorethylene (CDFE) and chlorotrifluoroethylene (CTFE). The slightly bulky chlorine atom serves as a kink in the polymer chain, which alters the chain conformation and reduces the crystalline domain size, but not overall crystallinity. The combination moves the ferroelectric−paraelectric phase transition to near ambient temperature with a very small energy barrier. In some specific terpolymer compositions, we observed a high dielectric constant (>70) and a large electrostrictive response (>4%) at ambient temperature.[2] Overall, the terpolymer exhibits desirable ferroelectric relaxor behaviors with a broad dielectric peak that shifts toward higher temperatures as the frequency increases and has a slim polarization hysteresis loop at near the dielectric peak (around ambient temperature) that gradually evolves into a normal ferroelectric polarization hysteresis loop with reduced temperature.

The VDF/TrFE/CTFE terpolymers were prepared by a direct terpolymerization process using a control borane/oxygen radical initiator[3,4] in solution or bulk (homogeneous solution) at ambient temperature. Different from the conventional emulsion and suspension (heterogeneous) processes at elevated temperatures,[5−7] the resulting VDF/TrFE/CTFE terpolymers show narrower molecular weight and composition distributions and high purities, without any contaminants from surfactants or suspension agents, which are difficult to remove but detrimental in electric applications. However, one major concern in this direct process is the limited supply of TrFE monomer that is dangerous[8] in transport and storage and is very costly. In this paper, we will discuss a new chemical route to prepare VDF/TrFE/CTFE terpolymer, which involves two reaction steps: copolymerization of VDF/CTFE and partial hydrogenation of CTFE units.[9,10] The resulting VDF/TrFE/CTFE terpolymer shows similarities and differences from the corresponding terpolymer prepared by the direct polymerization process.

Experimental Details. a. Synthesis of VDF/CTFE Copolymer. In a typical copolymerization (run 4 in Table 1), 0.10 g (1.0 mmol) of triethylboron initiator was added into a 75 mL stainless steel autoclave equipped with a magnetic stirrer under an argon atmosphere. The autoclave was then cooled by liquid nitrogen before vacuum distilling in 19 g (0.59 mol) of VDF and 7.1 g (0.061 mol) of CTFE monomers. The mixture was warmed to ambient temperature, and 0.27 mmol of oxygen was introduced into the autoclave to oxidize organoborane and initiate polymerization. This bulk polymerization was continued at ambient temperature for 5 h before venting any unreacted monomers. The resulting copolymer (11.3 g) was recovered, washed with methanol, and dried in a vacuum oven at 70 °C for 8 h. According to chlorine analysis and ^{1}H NMR measurements, the copolymer composition was comprised of 80.8 mol % VDF and 19.2 mol % CTFE.

Table 1. Summary of VDF/CTFE Copolymers Prepared by Borane/Oxygen Initiator and Bulk Polymerization Process[a]

run	monomer ratio (mol %) VDF	CTFE	yield (%)	composition (mol %) VDF	CTFE	M_n ($\times 10^4$ g/mol)[b]	T_m (°C)	ΔH (J/g)
1	97.0	3.0	32	91.4	8.6	-[c]	126.3	20.5
2	96.2	3.8	35	86.8	13.2	2.2	99.4	13.6
3	93.8	6.2	47	83.4	16.6	2.1	77.9	3.2
4	90.6	9.4	45	80.8	19.2	2.5	n.d.[d]	n.d
5	89.5	10.5	34	75.7	24.3	2.1	n.d.	n.d
6	81.5	18.5	62	71.3	28.7	2.7	n.d.	n.d
7	77.9	22.1	65	64.7	35.3	2.3	n.d	n.d

[a] Polymerization condition: 1.0 mmol of triethylborane, 25 °C, 5 h. [b] Measured by GPC. [c] The product is insoluble in THF. [d] Rubbery product.

Table 2. Summary of Thermal Transition Temperatures of VDF/TrFE/CTFE Terpolymers Prepared by Hydrogenation of VDF/CTFE (80.8/19.2) Copolymer

run	hydrogenation (%)	copolymer composition VDF/TrFE/CTFE (mole ratio)	T_m (°C)	T_c (°C)
4		80.8/0/19.2	rubbery	
4-1	36	80.8/6.9/12.3	rubbery	
4-2	58	80.8/11.2/8.0	100	39
4-3	65	80.8/12.5/6.7	110	54
4-4	82	80.8/15.9/3.4	128	63
4-5	100	80.8/19.2/0	146	96

b. Hydrogenation of VDF/CTFE Copolymer. About 1 g of the resulting VDF/CTFE copolymer (80.8/19.2 mol %) was dissolved in 25 mL of THF, and then 0.206 mL (0.77 mmol) of tri(*n*-butyl)tin hydride and 0.015 g (0.091 mmol) of AIBN were added to the copolymer solution. The hydrogenation reaction took place at 60 °C for 12 h. After the solvent was evaporated, the resulting VDF/TrFE/CTFE terpolymer was washed with a large quantity of methanol and dried. According to the chlorine analysis and ^{1}H NMR measurements, the terpolymer composition was comprised of 80.8 mol % VDF, 11.2 mol % TrFE, and 8.0 mol % CTFE (run 4-2 in Table 2).

c. Dielectric Measurement. For electrical measurements, polymer films (∼30 μm thickness) were prepared either by solution-casting on a glass slide from *N*,*N*-dimethylformamide solution containing 8−10 wt % polymer or melt-pressing polymer powder at 200 °C. The polymer films were annealed at 110 °C under vacuum for 5 h. Gold (<1 μm thickness) was sputtered onto both surfaces of the polymer film. The dielectric constant was measured by an HP multifrequency LCR meter equipped with a temperature chamber.

Results and Discussion. The new chemical route involves two reaction steps, as illustrated in Scheme 1. First is the copolymerization of VDF and CTFE monomers (easily available) using solution (or bulk) radical polymerization process. The resulting VDF/CTFE copolymer is then subjected to partial hydrogenation to form a VDF/TrFE/CTFE terpolymer that exhibits desirable dielectric properties.

Table 1 summarizes the experimental results of VDF/CTFE copolymers prepared by a borane/oxygen control radical initia-

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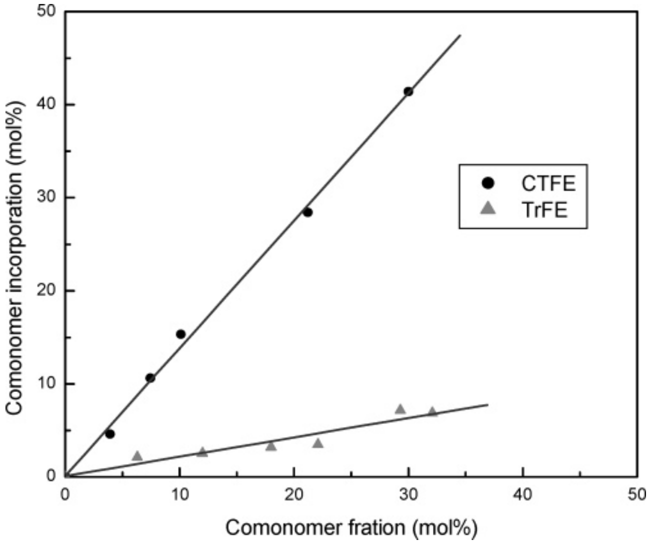
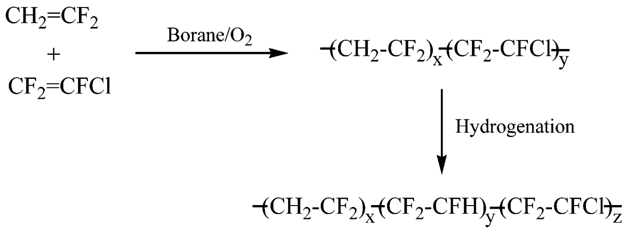


Figure 1. Plots of the incorporation of CTFE and TrFE comonomer units vs comonomer feed ratios during the copolymerization with VDF monomers.

Scheme 1



tor. The reaction is carried out in solution or bulk at ambient temperature. The propagating copolymer increases in molecular weight with reaction time and monomer conversion but maintains a relatively narrow molecular weight distribution. The polymer molecular weight reaches $M_n > 20\,000$ g/mol (measured by GPC) 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.

Figure 1 shows the plot of CTFE incorporation in the VDF/CTFE copolymer vs CTFE comonomer feed ratio during triethylborane/O_2 mediated control radical copolymerization, which is also compared with that of the corresponding VDF/TrFE copolymerization. To ensure a constant monomer feed ratio during copolymerization, all reactions were terminated at a low monomer conversion ($<10\%$). Note that CTFE shows similar (slightly higher) reactivity with VDF, but TrFE exhibits much lower reactivity than VDF. In other words, compared with the VDF/TrFE copolymer prepared under the same batch copolymerization condition, the VDF/CTFE copolymer maintains relatively narrow copolymer composition distribution even with a high monomer conversion, and the copolymer composition is easily controlled by the comonomer feed ratio. As shown in the Supporting Information, the homogeneity of the VDF/CTFE copolymer is evidenced by sharp thermal transition temperatures in the DSC curve.

Figure 2 compares ^1H and ^{19}F NMR spectra of a VDF/CTFE copolymer (run 4) and its corresponding VDF/TrFE copolymer after complete hydrogenation. In the ^1H NMR spectrum of the VDF/CTFE copolymer (Figure 2, left, a), there are only two chemical shifts at 2.9 and 2.3 ppm for VDF 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, respectively. There is no proton chemical shift for CTFE units. Therefore, the VDF/CTFE copolymer composition (80.8/19.2 mol %) was determined by the ^{19}F NMR spectrum (Figure 2, right, a), which shows three major chemical shifts at 91−96, 109−111, and 120−122 ppm, corresponding to three fluorine species ($CH_2-C\mathbf{F}_2$, $C\mathbf{F}_2-C\mathbf{F}Cl$), respectively. The copolymer composition was determined by their intensity ratio and the number of fluorine atoms each unit represents. The detail chemical shift assignments and the calculation of copolymer composition are discussed in the Supporting Information. After hydrogenation, all ^{19}F chemical shifts associated with CTFE units disappear, and a new $C\mathbf{F}CH-CF_2$ chemical shift at ∼200 ppm is observed (Figure 2, right, b). It is easier to determine the VDF/TrFE composition by the

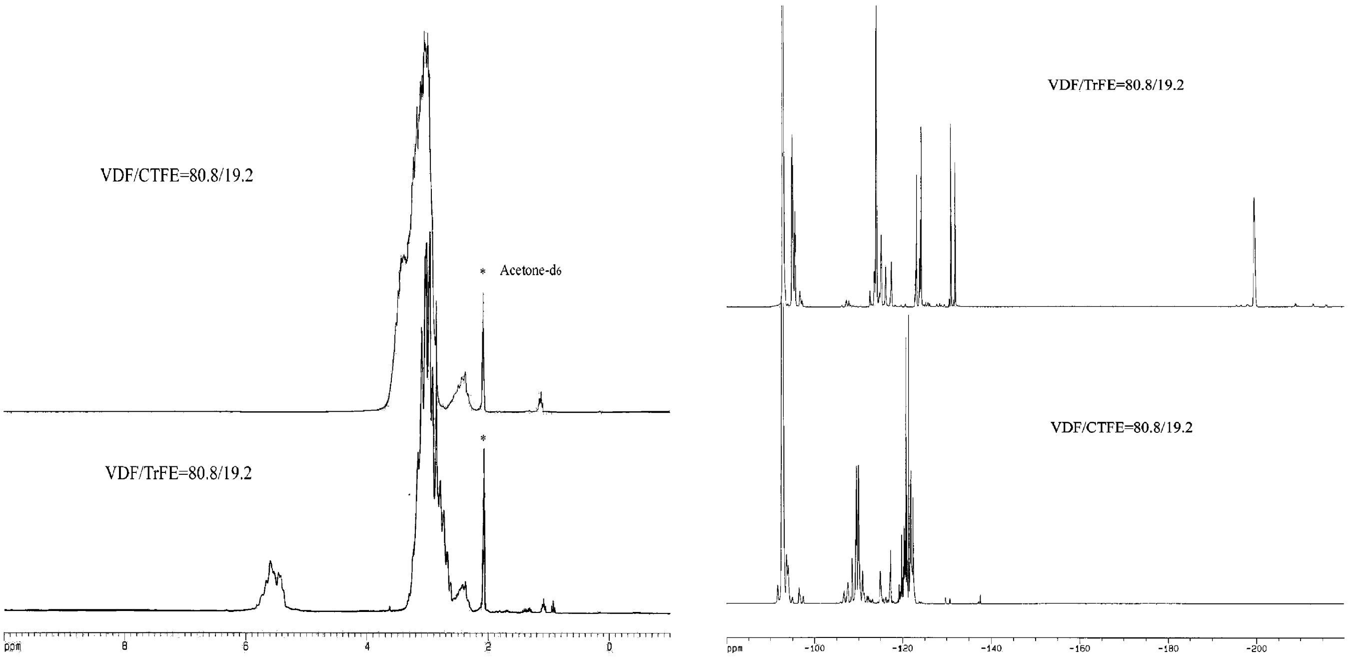
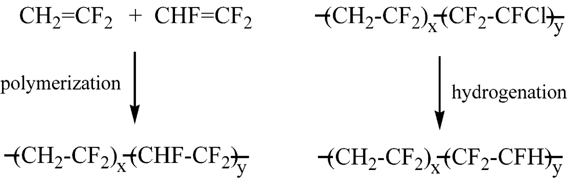


Figure 2. ^1H and ^{19}F NMR spectra of a VDF/CTFE (80.8/19.2 mole ratio) copolymer and its corresponding VDF/TrFE copolymer after complete hydrogenation (solvent: acetone-d_6).

Scheme 2



^{1}H NMR spectrum (Figure 2, left, b), with a distinctive new chemical shift at 5.3−5.7 ppm corresponding to C**H**F−CF$_2$ units in the presence of two chemical shifts at 2.8−3.4 and 2.3−2.6 ppm for (−C**H**$_2$−CF$_2$−) units with head-to-tail and head-to-head sequences, respectively. The resulting VDF/TrFE mole ratio in the copolymer was determined by the intensity ratio and the number of hydrogen atoms in each units. Overall, the copolymer composition before and after hydrogenation is quite consistent, and the hydrogenation of the VDF/CTFE copolymer to the VDF/TrFE copolymer using the combination of tri(*n*-butyl)tin hydride and AIBN radical initiator[9,10] is quantitative.

A DSC measurement was used to examine the crystalline structure of the copolymers before and after hydrogenation. As shown in Table 1, both melting temperature and crystallinity systematically decrease with the increase of the incorporated CTFE units due to the bulky Cl atom. The VDF/CTFE copolymer containing more than 16.6 mol % CTFE units becomes completely amorphous. On the other hand, the hydrogenation to remove Cl atoms results in the VDF/TrFE copolymers with semicrystalline structure in all compositions.[11−14] Several DSC curves (melting−crystallizing cycle) of the resulting VDF/TrFE copolymers are shown in the Supporting Information. It is clear that a cocrystallization takes place between TrFE and VDF units. It is interesting to note that the resulting VDF/TrFE copolymer reaches the lowest melting temperature (~145 °C) at about an 80/20 mole ratio, which is about 5 °C below than that of the corresponding VDF/TrFE copolymer[15] prepared by direct copolymerization process, indicating some subtle difference in the semicrystalline structure of VDF/TrFE copolymer.

Some of the resulting VDF/TrFE copolymers show a ferroelectric−paraelectric (Curie) phase transition, which is associated with the crystalline phase change from polar (β) phase to nonpolar (α) phase and the polymer chain conformation change from all-trans to trans-gauche.[16,17] As expected, the Curie temperature (T_c) reduces with the increase of TrFE content in the PVDF chain. However, it reaches a lowest point (~96 °C) after incorporating about 20 mol % of TrFE units, which is a dramatic difference from the VDF/TrFE copolymers prepared by the direct polymerization process, in which the Curie temperature of similar copolymer composition is higher than 130 °C and continuously decreases to ~65 °C for the VDF/TrFE copolymer (60/40 mole ratio)[18,19] before reaching a constant. On the other hand, the similar VDF/TrFE (64.7/35.3) copolymer, prepared by hydrogenation of the corresponding VDF/CTFE copolymer, shows a much higher Curie temperature at ~120 °C. There is a significant change in the polymer chain microstructure in the current VDF/TrFE copolymer. As illustrated in Scheme 2, compared with the VDF/TrFE copolymer by direct process, a completely reverse VDF−TrFE (head-to-head) sequence exists in the VDF/TrFE copolymer prepared by hydrogenation of the VDF/CTFE copolymer, which is prepositioned CF$_2$−CF$_2$ sequences during the VDF/CTFE copolymerization step. Although a small portion of CF$_2$−CF$_2$ sequences may also originate from head-to-head regio-defective VDF units[10] during the polymerization, which is only less than 6% of VDF units and happens in both cases.

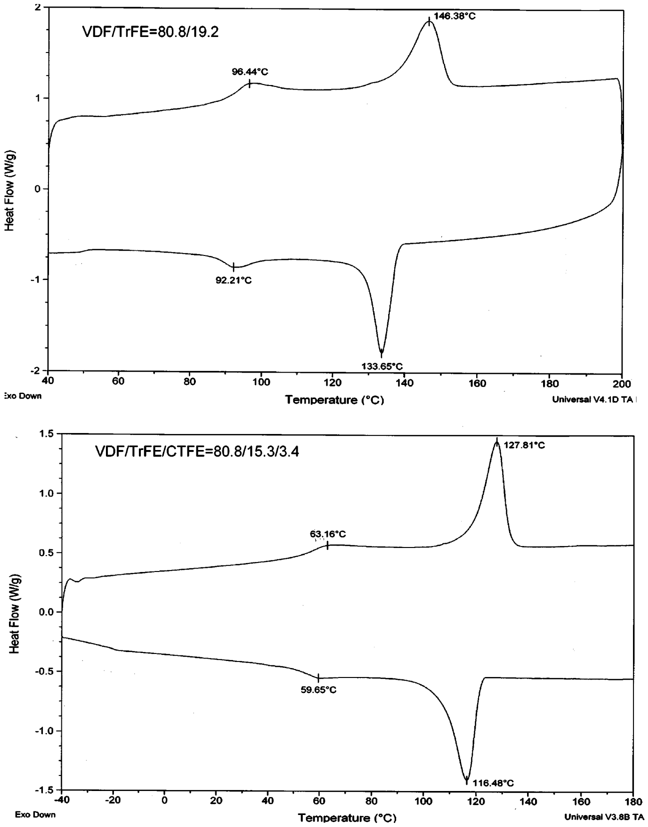


Figure 3. DSC heating−cooling curves of (bottom) a partially hydrogenated VDF/TrFE/CTFE terpolymer (80.8/15.3/3.4 mol %) and (top) a completely hydrogenated VDF/TrFE (80.8/19.2 mol %) copolymer.

It is logical to further manipulate the VDF/TrFE (80/20 mol %) copolymer microstructure to reduce its F−P phase transition temperature. The goal is to achieve the desirable ferroelectric relaxor behaviors with an F−P phase transition at ambient temperature, low activation energy in phase transition, and a slim polarization hysteresis loop. As shown in our previous papers,[1−3] the incorporation of few percentages of CTFE units in the VDF/TrFE copolymer is very effective in altering the Curie temperature and the activation energy for the F−P phase transition, without significant reduction of overall crystallinity and dielectric constant. Therefore, we carried out a systematic study by partial hydrogenation of the VDF/CTFE (80/20 mol %) copolymer to form VDF/TrFE/CTFE terpolymers with various concentrations of CTFE units.

Figure 3 compares DSC (heating−cooling) curves of a partially hydrogenated VDF/TrFE/CTFE terpolymer (80.8/15.3/3.4 mol %) and a completely hydrogenated VDF/TrFE (80.8/19.2 mol %) copolymer. Both semicrystalline polymers are prepared from the same amorphous VDF/CTFE (80.8/19.2 mol %) copolymer. All thermal transitions (Curie, crystallization, and melting) are sharp, indicating a homogeneous polymer microstructure and semicrystalline morphology, which should be attributed to an effective copolymerization and hydrogenation reaction. Table 2 summarizes melting (T_m) and Curie (T_c) temperatures of several VDF/TrFE/CTFE terpolymers with two corresponding VDF/CTFE and VDF/TrFE copolymers. The starting amorphous VDF/CTFE (80.8/19.2 mol %) copolymer changes to semicrystalline after reducing CTFE content to about 8.0 mol %. A new T_m at 100 °C and a new T_c at 39 °C are observed for this VDF/TrFE/CTFE (80.8/11.2/8.0 mol %) terpolymer. Both T_m and T_c continuously increase with the reduction of CTFE content. After complete hydrogenation, the resulting VDF/TrFE (80.8/19.2) copolymer shows the highest

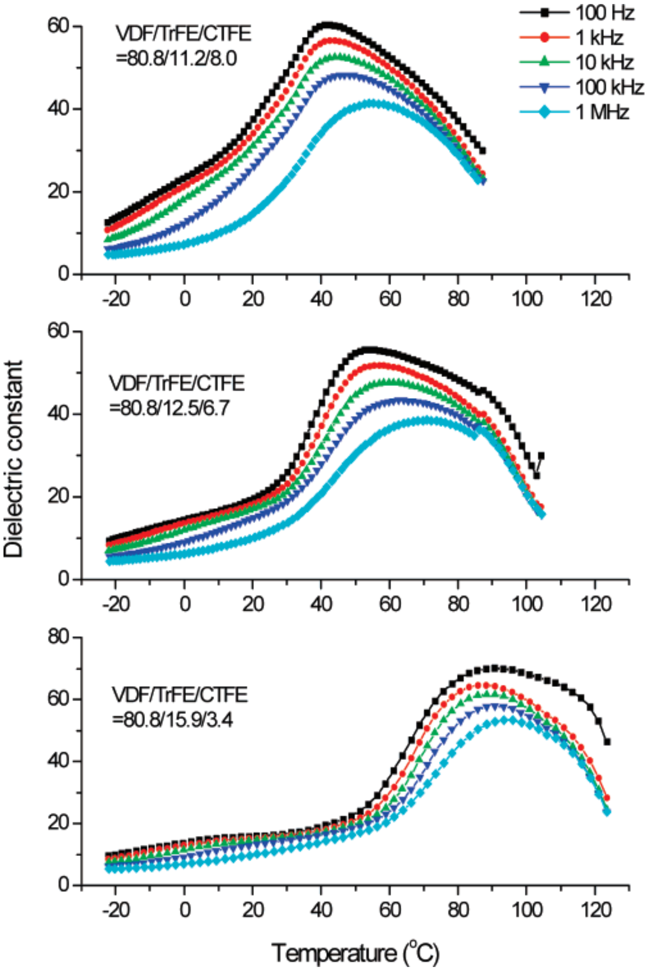
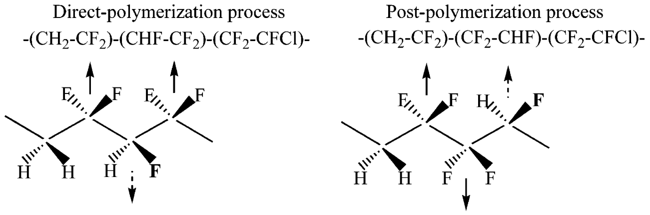


Figure 4. Dielectric constant vs temperature and frequency for three VDF/TrFE/CTFE terpolymers: (a) 80.8/15.9/3.4 mol %, (b) 80.8/12.5/6.7 mol %, and (c) 80.8/11.2/8.0 mol %.

T_m and T_c at 146 °C and 116 °C, respectively. The CTFE unit with a bulky Cl atom serves as a kink to shorten the VDF/TrFE sequence and to prevent the extension of crystallization, which results in the reduction of the lamella thickness of the crystal and the energy for changing polymer chain conformation.

Figure 4 shows the dielectric constant vs temperature and frequency for three resulting VDF/TrFE/CTFE terpolymers (runs 4-2, 4-3, and 4-4 in Table 2). In general, the terpolymers exhibit common ferroelectric relaxor behaviors with a broad dielectric peak that shifts toward higher temperatures as the frequency increases. The dielectric peak moves to a lower temperature with increasing CTFE content and reaches to near ambient temperature for the VDF/TrFE/CTFE (80.8/11.2/8.0 mol %) terpolymer, which is consistent with the Curie temperature measured by the DSC method. Overall, the highest dielectric constant is between 60 and 40 in the frequency range 100 Hz−1 MHz, which is well below that observed in the corresponding terpolymers prepared by the direct polymerization process.[2,3] The head-to-head sequence between VDF and TrFE units, illustrated in Scheme 3, results in opposite dipole orientation and reduces the overall dielectric constant in the VDF/TrFE/CTFE terpolymer prepared by the postpolymerization process.

Scheme 3



Conclusion. This paper discusses a new chemical route involving VDF/CTFE copolymerization and partial hydrogenation of CTFE units to prepare VDF/TrFE/CTFE terpolymers that exhibit several common features of a typical relaxor ferroelectric behavior, such as a diffuse phase transition, high dielectric constant at ambient temperature, and dielectric relaxation (large frequency dependence). In addition, we also observed the similar bulky CTFE effect in the VDF/TrFE/CTFE terpolymer, with the reduction of melting and Curie temperatures (relative to the thickness of ferroelectric crystalline domains). However, the microstructure of this terpolymer with a head-to-head VDF-TrFE sequence is very different from that of a head-to-tail VDF-TrFE sequence in the corresponding terpolymer prepared by direct terpolymerization. Consequently, the dielectric constant and Curie temperature vs terpolymer composition are very different. The overall dielectric constant is significantly reduced in the current terpolymer.

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Supporting Information Available: GPC curves of VDF/CTFE copolymers, chemical shift assignments of ^{19}F NMR and composition determination of the VDF/CTFE copolymer, DSC curves of VDF/TrFE copolymers, and FTIR spectra of VDF/CTFE and VDF/TrFE copolymers. This material is available free of charge via Internet at http://pubs.acs.org.

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