Synthesis and Properties of Ferroelectric Fluoroterpolymers with Curie Transition at Ambient Temperature

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ABSTRACT: This paper discusses a new family of ferroelectric polymorphic fluoroterpolymers comprosed of vinylidene difluoride (VDF), trifluoroethylene (TrFE), and a chloro-containing third monomer, such as chlorodifluoroethylene (CDFE), and chlorotrifluoroethylene (CTFE), which feature relatively narrow molecular weight and composition distributions. The terpolymers were prepared by a bulk reaction process with a low temperature free radical initiator, i.e., the oxidation adducts of trialkylborane and oxygen. The slightly bulky chlorine atom serves as a kink in the polymer chain, which spontaneously alters the chain conformation and crystalline structure. Compared to the corresponding VDF/TrFE copolymer (>20 mol % of TrFE), the slowly increasing chlorine content (<8 mol % of termonomer) gradually changes the all-trans ($t_{m>4}$) chain conformation (β-phase) to $tttg^+tttg^-$ conformation (γ-phase) without significant reduction of overall crystallinity. The Curie (ferroelectric−paraelectric) phase transition temperature between the mixed ferroelectric β- and γ-phases and paraelectric α-phase (tg^+tg^- conformation) also gradually reduced to near ambient temperature with very small activation energy. Consequently, the terpolymers show high dielectric constant (>70), slim polarization hysteresis, and large electrostrictive response (>4%) at ambient temperature and exhibit common ferroelectric relaxor behaviors with a broad dielectric peak that shifted toward higher temperatures as the frequency increased.

Introduction

Materials exhibiting electromechanical responses are useful in many important applications, such as transducers, actuators, and sensors. Traditional ceramic-based materials, such as piezoceramics and magnetrostrictives, have suffered from low strain response (<0.5%)[1] despite their high dielectric constants and fast electric responses (low hysteresis). Recently, polymer materials have attracted a great deal of attention due to many desirable properties, such as flexibility, lightweight, low cost, good stability under stress, ease of processability in large area films, and ability to be molded into a desirable configuration. In addition, the combination of high electromechanical coupling and low acoustic impedance in the polymers permits their use in ultrasonic transducer applications and medical instruments.

Poly(vinylidiene fluoride) (PVDF)[2,3] and its copolymers,[4−7] especially vinylidiene fluoride/ trifluoroethylene (VDF/TrFE), are the most investigated ferroelectric polymer system with high piezoelectricity and pyroelectricity. Their interesting electric properties originate from the strong dipole in the constituted CF_2 units along the polymer chain and the orientation of dipoles in some of the crystalline phases (such as β- and γ-phases).[8,9] They exhibit polymorphic structure across the whole composition range, with high crystallinity and only slight differences in the melting temperature. Although, the crystallization of PVDF homopolymer from the melt form trans−gauche (tg^+tg^-) polymer chain conformation, which results in a paraelectric phase (α-phase), the VDF/TrFE copolymer with > 20% TrFE units changes to all-trans ($t_{m>4}$) chain conformation with a ferroelectric phase (β-phase). The extra fluorine atoms in TrFE comonomers prevent the polymer chain from adopting trans−gauche (tg^+tg^-) conformation and result in an extended planar zigzag all-trans conformation. The ferroelectricity in the copolymer was strongly evidenced by the existence of Curie (ferroelectric−paraelectric) phase transition temperature (T_c). In this transition, the all-trans polymer chain conformation in the ferroelectric β-phase changes to trans−gauche chain conformation in paraelectric α-phase. One major drawback is the relatively high Curie temperature. Although it is very dependent on the copolymer composition, the lowest T_c observed is >60 °C in VDF/TrFE (55/45) copolymer,[10] which is well above ambient temperature (the most convenient application temperature). Therefore, the dielectric response of the dipoles to the electric field is very small at ambient temperature despite the VDF/TrFE copolymer exhibiting a high piezoelectric constant ($d_{31} = 15-30$ pC/N).[11] The small response to the electric field is also revealed in a low dielectric constant and a large polarization hysteresis loop[12,13] due to the high energy barrier of switching the dipole direction at ambient temperature.

In the past decade, many researchers have devoted their efforts related to PVDF and VDF/TrFE copolymers to the general goal of reducing the Curie transition temperature, narrowing the polarization hysteresis loop, and generating a large electromechanical response at ambient temperature. The direct correlation between the reduced polar domain size and lower energy barrier, shown in ferroelectric ceramic materials,[14] led to many attempts to alter copolymer morphology. The methods include mechanical deformation,[15] electron irradiation,[16,17] uniaxial drawing,[18] crystallization under high pressure,[19] and crystallization under high electric field.[20]

In our previous paper,[21] we introduced a new chemical approach by incorporating some slightly bulky chlorotrifluoroethylene (CTFE) units into the VDF/TrFE copolymer structure. The resulting VDF/TrFE/CTFE terpolymers were solution and melt processable and

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formed a stable ferroelectric phase with reduced Curie temperature and small energy barrier for the phase transition. Some VDF/TrFE/CTFE terpolymers exhibited a slim polarization hysteresis loop and large electrostrictive response ($\sim$4%) at ambient temperature.

In this study, we concentrated on the correlation between the improved electric properties and the changes of molecular structure, such as polymer chain conformation, crystallinity, etc., due to the incorporated termonomer units. To gain a better understanding on the structure−property relationship, a systematical study was performed to synthesize and examine a broad range of terpolymers containing various bulky termonomer units. It was expected that a certain content of slightly bulky groups (in termonomer units) homogeneously distributed along the polymer chain would reduce Curie temperature and activation energy in phase transition without significant reduction of overall crystallinity and dielectric constant.

Experimental Details

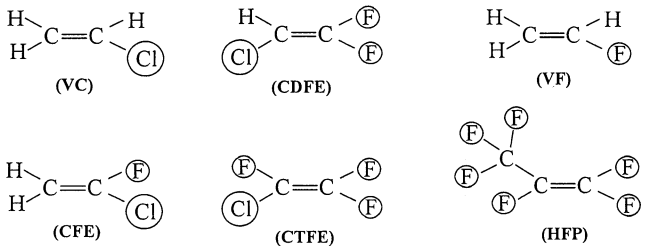
The terpolymers were prepared by a combination of the bulk polymerization process and an oxygen-activated organoborane initiator[17−19] at ambient temperature. This chemistry produces high terpolymers that have uniform molecular structure and few impurities. In a typical example of preparing a VDF/TrFE/CTFE (72.2/17.8/10.0) terpolymer, 0.1 g of a tributylboron initiator was added into a 75-mL autoclave under argon atmosphere. The reactor was then cooled from outside by liquid nitrogen and 16.7 g of VDF, 7.6 g of TrFE, and 1.7 g of CTFE were distilled into the reactor. After a known amount of oxygen (0.5:1 of oxygen:boron) was introduced, the reactor was warmed to ambient temperature. The bulk polymerization took place at this temperature for 5 h before vacuum-distilling the unreacted monomers. The resulting terpolymer (6.5 g) was recovered, washed with methanol, and dried.

The composition of the terpolymer was determined by a combination of ^{1}H NMR spectrum recorded on a Bruker AM-300 spectrometer and an elemental analysis provided by Galbraith Laboratories, Inc. The molecular weight was determined using a Waters 150C that was operated at 135 °C. The columns used were mStyragel HT of 10^6, 10^5, 10^4, and 10^3 Å. A flow rate of 0.7 mL/min was used, and the mobile phase was trichlorobenzene. Narrow molecular weight distribution polystyrene samples were used as standards. Differential scanning calorimetry (DSC) was measured (with a heating rate of 20 °C/min) on a Perkin-Elmer DSC-7, TAC-7 instrument controller.

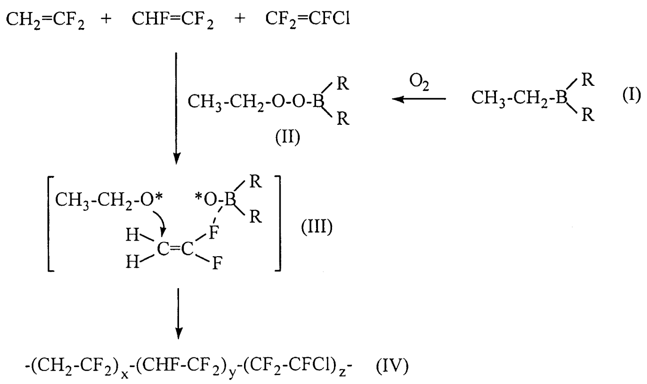
For electrical measurements, polymer films ($\sim$30 μm thickness) were prepared by solution casting on a glass slide from a *N*,*N*-dimethylformamide solution containing 8−10 wt % polymer. The polymer films were annealed at 110 °C under vacuum for 5 h. Gold ($<$1 μm thickness) was sputtered on both surfaces of the polymer film. The dielectric constant was measured by a HP multifrequency LCR meter equipped with a temperature chamber. The electric field-induced longitudinal strain was measured by the displacement of the polymer film thickness using a modified Sawyer−Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research Systems, model SR830). Electric fields ranging from 20 to 150 MV/m were applied across the polymer film using an amplified ramp waveform at 1 Hz. Because of the softness of polymer material (comparing with ceramics), the stress from the sample holders affects the strain of the polymer. Thus, the stain under each electric field was determined by extrapolating strain vs stress line to zero stress.

Results and Discussion

Scheme 1



Scheme 2



In this paper, we will discuss a family of ferroelectric terpolymers composed of VDF, TrFE, and a chloro-containing third monomer (illustrated in Scheme 1), including vinyl chloride (VC), 1,1-chlorofluoroethylene (CFE), chlorodifluoroethylene (CDFE), and chlorotrifluoroethylene (CTFE), which feature relatively narrow molecular weight and composition distributions. Two reference terpolymers containing a smaller size vinyl fluoride (VF) and a larger size hexafluoropropylene (HFP) units, respectively, were also prepared for comparison.

As will be discussed, the slightly bulky chlorine atoms (radii of F and Cl are 1.19 and 1.67 Å, respectively) homogeneously located along the VDF/TrFE polymer chain introduce the kinks (with gauche conformation) into the otherwise planar zigzag all-trans chain conformation. As a result, they spontaneously alter the crystalline phase from ferroelectric β-phase ($t_{m>4}$) toward another ferroelectric γ-phase ($ttt g^+ ttt g^-$ conformation) without significant reduction of overall crystallinity. The shortened trans sequence in the polymer chain significantly reduces the activation energy of the Curie phase transition, and the terpolymers show high dielectric constant, strong ferroelectricity, and large electromechanical response at ambient temperature.

Synthesis of Terpolymers. Traditionally, the polymerization of fluoromonomers was carried out in emulsion or suspension (heterogeneous) reaction conditions[22−25] using inorganic or organic peroxides as initiators at elevated temperatures. High monomer pressure is usually required to ensure a sufficient fluoromonomer (gas) diffusion through the aqueous media to the active site. In this study, we have adopted a bulk (homogeneous) polymerization process, in which all three monomers were condensed into liquid phase and mixed with a low-temperature free radical initiator—an oxidation adduct of trialkylborane and oxygen.[26,27] The homogeneous solution may provide better reaction conditions to achieve an uniform terpolymer structure. As expected, the homogeneously distributed termonomer units are crucial to regulate the polymer chain conformation and crystalline phases. Scheme 2 illustrates the possible reaction mechanism.

Upon exposure to a controlled quantity of oxygen, alkylborane (**I**) is autoxidized at the linear alkyl group

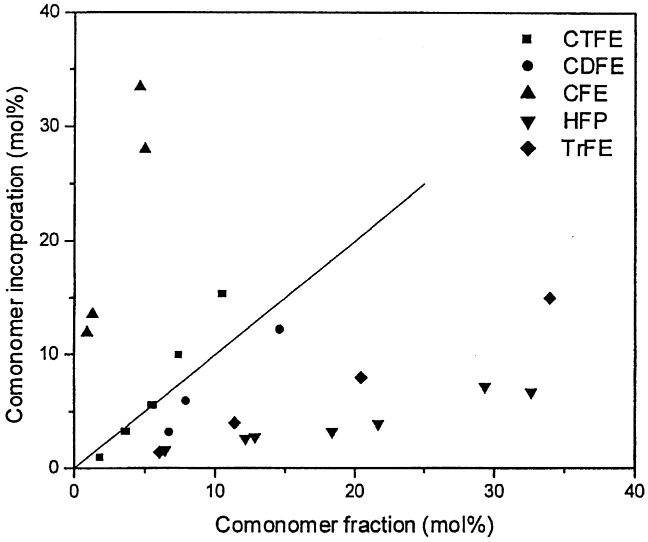


Figure 1. Fluorocomonomer content in the copolymer vs the comonomer feed ratio in the copolymerization reaction with VDF. (The line indicates the identical comonomer incorporation vs comonomer fraction.)

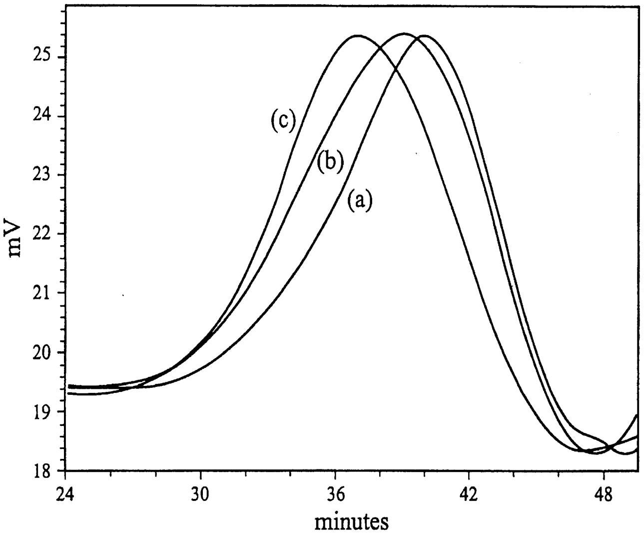


Figure 2. GPC curves of three VDF/TrFE/CTFE terpolymers prepared by a borane/oxygen initiator and various reaction times: (a) 4, (b) 7, and (c)10 h.

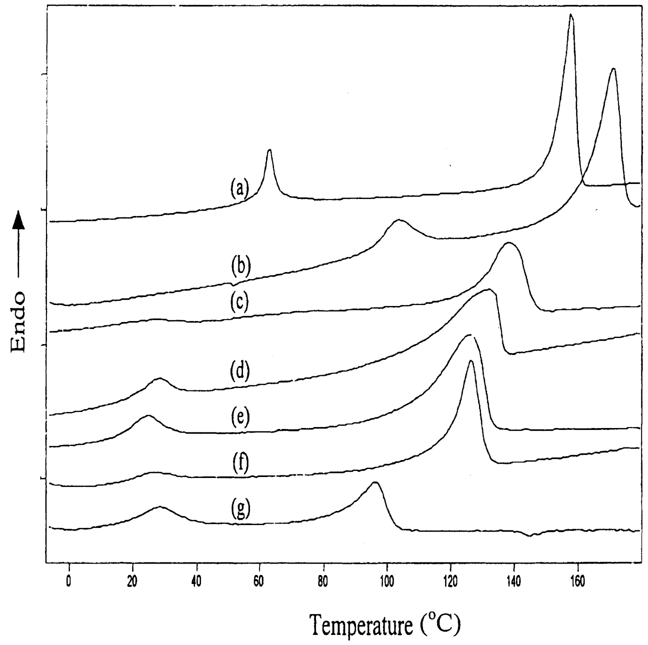


Figure 3. DSC curves of (a) a VDF/TrFE (60/40 mole ratio) copolymer and six terpolymers containing various termonomer units, including (b) VDF/TrFE/VF (53.8/38.8/7.4; sample E-2), (c) VDF/TrFE/CFE (62.4/29.8/7.8; sample D-2), (d) VDF/TrFE/VC (58.3/34.7/7) (sample C-2), (e) VDF/TrFE/CDFE (62.5/30.9/6.6; sample B-3), (f) VDF/TrFE/CTFE (59.3/32.9/7.8, sample A-3), and (g) VDF/TrFE/HFP (63.1/29.9/7.0; sample F-2).

to produce ethylperoxyborane (**II**). The peroxyborane (**II**) behaves very differently from regular benzoyl peroxides, which can initiate free radical polymerization at ambient temperature with a relatively "stable" polymerization process. In this case, the peroxyborane (**II**) may subsequently interact with fluoromonomer and cleavage peroxide bond to an alkoxy radical (C−O*) and a borinate radical (B−O*) in the intermediate (**III**) at ambient temperature. The alkoxyl radical initiates the radical polymerization. On the other hand, the borinate radical, which is relatively stable due to the back-donating of electron density to the empty p-orbital of boron, may form a weak and reversible bond with the growing chain end and provide stability to the active site. The B−F acid−base interaction in the intermediate (**III**) may not only facilitate the insertion of monomers but also provide a relatively equal chance for the different incoming fluoromonomers in approaching the active site.

To understand the relative reactivity of each fluoromonomer in the bulk process, a series of copolymerization reactions between VDF and various fluoromonomers were examined using a tributylborane/oxygen initiator at ambient temperature. Figure 1 shows the fluoromonomer incorporation in the copolymer with the comonomer feed ratio. All reactions were terminated at low monomer conversion (<10%) to ensure a constant monomer feed ratio during the copolymerization. In general, the fluoromonomers containing a chlorine atom show high reactivity, especially the CFE with a small molecular size. On the other hand, the bulky HFP with no chlorine atom exhibits poor incorporation. Two most interesting CDFE and CTFE monomers show comparable reactivity with VDF and a comonomer incorporation ratio that is close to the comonomer feed ratio.

Figure 2 shows the GPC curves of a series of VDF/TrFE/CTFE terpolymers that increase their molecular weight with the conversion of monomers. The long-life propagating site leads to a linear polymer structure with a molecular weight distribution $M_w/M_n \sim 2.5$. In addition to the relatively narrow molecular weight and composition distributions, this bulk process also produces fewer impurities (boric acid and butanol) that can be easily removed by methanol washing. The composition of the terpolymer was determined by the combination of its ^{1}H NMR spectrum and elemental analysis. Two major chemical shifts were observed at 2.8−3.2 ppm ($-C\mathbf{H}_2-CF_2-$) and 5.3−5.7 ppm ($-C\mathbf{H}F-CF_2-$), and their intensity ratio and the number of protons each unit represents determine the VDF/TrFE mole ratio in the terpolymer. On the other hand, chlorine elemental analysis provides the concentration of the termonomer. The detailed experimental results are summarized in Table 1. All terpolymers are high molecular weight (>20 000) polymers that are completely soluble in common organic solvents and melt processable at >150 °C.

Table 1. Summary of the Terpolymers Containing VDF, TrFE, and Termonomers

	composition (mol %)			melting temp		Curie temp		dielectric 1 kHz	
run no.	VDF	TrFE	termonomer	T_m (°C)	ΔH (J/g)	T_c (°C)	ΔH (J/g)	DK	peak (°C)
	55.0	45.0	0.0	150.0	25.4	64.0	10.0	80	65.0
A-1	60.0	36.0	CTFE/4.0	140.9	25.7	43.8	6.5	80	42.0
A-2	58.0	35.1	CTFE/6.9	126.6	21.0	33.5	1.6	70	38.5
A-3	59.3	32.9	CTFE/7.8	125.1	20.3	24.8	1.4	72	32.5
A-4	57.3	31.2	CTFE/11.5	111.1	14.8	none	none	51	25.3
A-5	63.1	25.4	CTFE/11.5	113.7	18.5	none	none	61	27.1
A-6	66.0	22.5	CTFE/11.5	117.2	21.6	25.2	2.5	72	33.2
A-7	72.2	17.8	CTFE/10.0	107.8	17.8	25.0	0.4	61	38.5
B-1	63.6	31.4	CDFE/5.0	135.8	24.5	36.9	6.9	91	40
B-2	64.5	30.2	CDFE/5.3	128.7	26.0	31.6	5.5	82	34
B-3	62.5	30.9	CDFE/6.6	126.0	24.6	24.2	3.9	92	30
B-4	69.0	21.2	CDFE/9.8	111.0	20.4	17.9	1.5		
B-5	72.1	21.3	CDFE/6.6	123.7	23.4	24.0	2.5	65	36.3
B-6	73.2	21.6	CDFE/5.2	131.4	24.6	31.8	2.8	64	50.2
B-7	77.6	16.2	CDFE/6.1	126.2	24.0	35.5	3.4	61	50.5
C-1	55.1	33.1	VC/11.8	103.0	18.2	14.0	2.1	83	35.4
C-2	58.3	34.7	VC/7.0	132.8	25.3	27.7	4.5		
D-1	60.1	29.3	CFE/10.6	115.1	24.5	11.3	1.8	37	26
D-2	62.4	29.8	CFE/7.8	138.5	18.5	25.2	1.6	39	62
E−1	66.7	30.5	VF/2.8	161.1	29.9	81.1	16.4	80	86.5
E−2	53.8	38.8	VF/7.4	171.2	27.9	103.3	9.0		>100
F-1	55.2	42.4	HFP/2.5	129.1	15.6	35.6	2.6		
F-2	63.1	29.9	HFP/7.0	96.3	6.8	28.5	3.3		

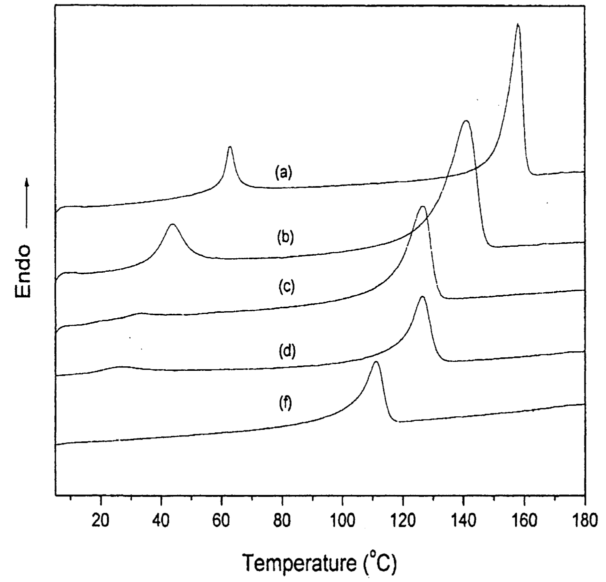


Figure 4. DSC curves of (a) a VDF/TrFE (60/40) copolymer and three VDF/TrFE/CTFE terpolymers with (b) 60/36/4 (sample A-1), (c) 60/35.1/6.9 (sample A-2), (d) 59.3/32.9/7.8 (sample A-3), and (e) 57.3/31.2/11.5 (sample A-4) mole ratios.

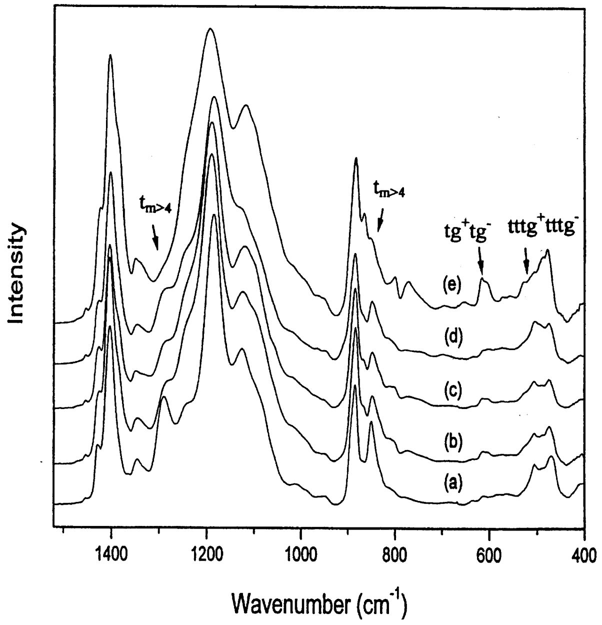


Figure 5. FTIR spectra of (a) a VDF/TrFE (60/40 mole ratio) copolymer and various terpolymers including (b) VDF/TrFE/VC (58.3/34.7/7.0) (sample C-2), (c) VDF/TrFE/CDFE (62.5/30.9/6.6; sample B-3), (d) VDF/TrFE/CTFE (59.3/32.9/7.8, sample A-3), and (e) VDF/TrFE/CFE (62.4/29.8/7.8; sample D-2).

Thermal Transitions. Figure 3 shows the DSC curves of several terpolymers containing similar VDF and TrFE contents and about 7 mol % of various termonomers and a reference VDF/TrFE (60/40 mole ratio) copolymer that has the lowest Curie temperature. The detailed DSC data are summarized in Table 1. The smaller fluoroethylene (VF) termonomer fails to reduce the Curie temperature. In fact, both the melting and Curie temperatures increase with the addition of VF units. On the other hand, the large HFP units destroy most of the crystallinity, and the VDF/TrFE/HFP terpolymer (>7 mol % HFP) becomes an amorphous elastomer. The suitable termonomers seem to be vinyl chloride (VC), 1,1-chlorofluoroethylene (CFE), chlorodifluoroethylene (CDFE), and chlorotrifluoroethylene (CTFE) containing a slightly larger size of chlorine atom. About 7 mol % of the randomly distributed chorine atoms in the polymer chain clearly reduce both the melting and Curie temperatures and diminish the activation energy for the phase transition. Despite changing the crystalline phase (as will be discussed later), the incorporated chorine atoms (up to 7 mol %) did not significantly reduce the overall crystallinity.

It is interesting to understand the effect of the termonomer concentration on the thermal transition temperatures. Figure 4 shows the DSC curves of three VDF/TrFE/CTFE terpolymers (samples A-1, A-2, A-3, and A-4 in Table 1) compared to that of a reference VDF/TrFE (55/45 mole ratio) copolymer. The relatively sharp

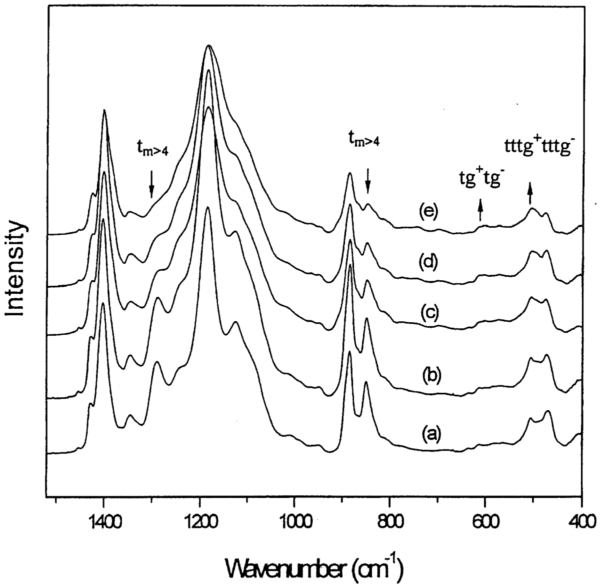


Figure 6. FTIR spectra of (a) a VDF/TrFE (60/40 mole ratio) copolymer and four VDF/TrFE/CTFE terpolymers with (b) 60/36/4 (sample A-1), (c) 60/35.1/6.9 (sample A-2), (d) 59.3/32.9/7.8 (sample A-3), and (e) 57.3/31.2/11.5 (sample A-4) mole ratios.

melting and Curie phase transitions imply a relatively uniform molecular structure and polymer morphology. With the increase of CTFE units, the Curie temperature of the terpolymer gradually shifts to ambient temperature and the intensity becomes smaller and broader; whereas the transition temperature in Figure 4f almost disappears, which indicates a very small energy barrier in the phase transition. The results are consistent with the electric responses of the terpolymer under an electric field (this will be discussed later).

Molecular Structure. The changes that occur in the polymer structure (chain conformation and crystalline structure) due to the termonomers are very curious. Figure 5 compares the infrared spectra of several terpolymers containing similar VDF (~60 mol %) and TrFE contents and about 7 mol % of various termonomers to a reference VDF/TrFE (60/40 mole ratio) copolymer at ambient temperature. In general, two strong absorption bands at 1288 and 850 cm^{-1}, intrinsic to the CF$_2$ vibration and CH$_2$ rocking modes[28-30] of the all-trans ($t_{m>4}$) conformation in the β-phase, significantly reduce their intensities. On the other hand, two weak absorption bands centered at 614 and 505 cm^{-1}, corresponding to the CF$_2$ vibration bands of tg^+tg^- conformation in the α-phase and $tttg^+tttg^-$ conformation in the γ-phase, respectively, become more visible. It is interesting to note that the most profound conformation change in the VDF/TrFE/CFE terpolymer with 7.8 mol % CFE (Figure 5e) shows an intense 614 cm^{-1} band (tg^+tg^- conformation) and an almost complete disappearance of all 1288, 850, and 505 cm^{-1} bands ($t_{m>4}$ and $tttg^+tttg^-$ conformations).

Figure 6 compares the infrared spectra of a series of VDF/TrFE/CTFE terpolymers with about 60 mol % VDF content and various TrFE/CTFE mole ratios. With the increase of termonomer content, the absorption bands (1288 and 850 cm^{-1}) for the all-trans conformation gradually decrease and the CF$_2$ vibration bands (614 and 505 cm^{-1}) for the tg^+tg^- and $tttg^+tttg^-$ conformations increase in relative intensity. At about 11.5 mol % CTFE units, the vibration bands for all-trans conformation are almost completely absent. The general trend

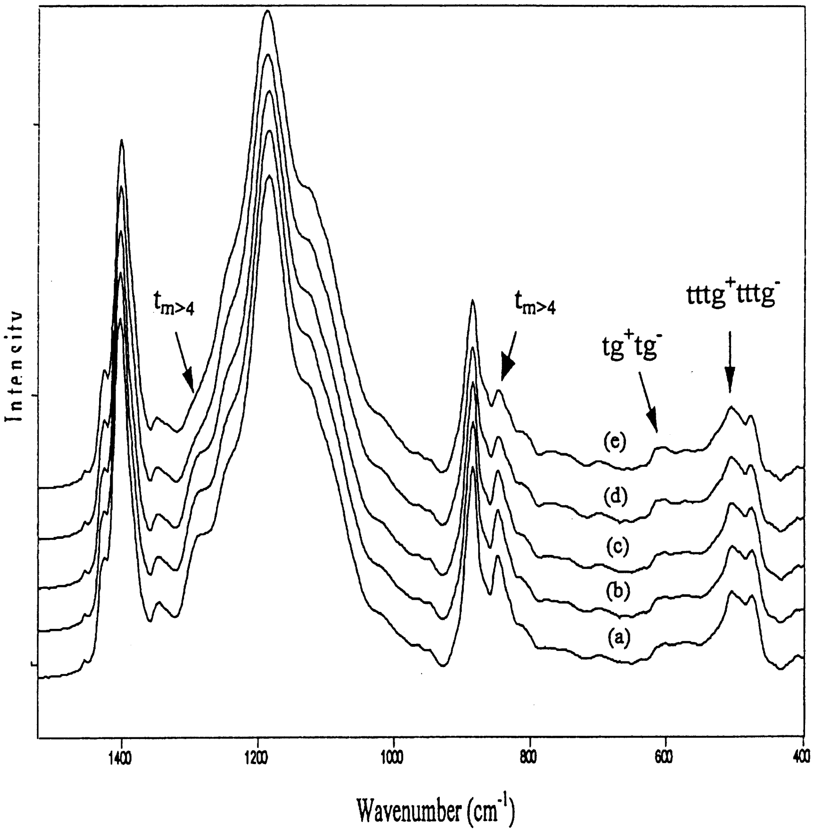


Figure 7. FTIR spectra of a VDF/TrFE/CTFE terpolymer 59.3/32.9/7.8 (sample A-3) annealed at various temperatures: (a) 20, (b) 25, (c) 30, (d) 40, and (e) 50 °C.

was also observed in other terpolymers containing VC, CFE, and CDFE termonomer units. The incorporated termonomer units seem to create kinks (with gauche conformation) along the otherwise all-trans zigzag polymer chain conformation. It is very interesting to note that the gradual shift from all-trans confromation (β-phase) to tttg$^+$tttg$^-$ conformation (γ-phase) coincides with the gradual reduction of Curie temperature and activation energy in phase transition. The correlation implies that the length of the all-trans sequence between the two gauche structures plays a key role in crystalline phase transition. With the proper choice of termonomer content, we will be able to control the Curie phase transition at the application temperature.

It is also very interesting to study the thermal effect on the chain conformation of the terpolymer, especially around the Curie temperature. Figure 7 shows a series of infrared spectra of a VDF/TrFE/CTFE terpolymer film (with 7.8 mol % CTFE) annealed at various temperatures. As the annealing temperature increases to near the Curie transition temperature (T_c is about 25 °C as determined by DSC), the all-trans conformation bands (1288 and 850 cm^{-1}) gradually decrease in intensity whereas the tttg$^+$tttg$^-$ band (505 cm^{-1}) and the tg$^+$tg$^-$ band (614 cm^{-1}) gradually increase in intensity. These slow changes indicate the gradual process of the phase transition in terpolymer. At about 50 °C, all trans sequences are completely transformed to the mixtures of tttg$^+$tttg$^-$ and tg$^+$tg$^-$ sequences. It is interesting to note that the whole spectral pattern is reversible during heating and cooling cycles, with very slim hysteresis. The overall results indicate the reversible process of polymer chain conformation at the Curie temperature, from predominately low temperature mixed β- and γ-phases to high temperature mixed α- and γ-phases in this VDF/TrFE/CTFE (59.3/32.9/7.8) terpolymer.

Electric Properties. The electric properties of the terpolymers were evaluated by dielectric constant and electric field induced strain response at ambient temperature. Figure 8 shows the dielectric constants of two typical samples VDF/TrFE/CDFE with 62.5/30.9/6.6 (sample B-3) and VDF/TrFE/CTFE terpolymers with 59.3/32.9/7.8 (sample A-3), respectively. In general, the dielectric constant hysteresis during heating–cooling cycles gradually decreases with increasing termonomer content, and the curve of the dielectric constant becomes broader and the peak moves to lower temperature with some reduction of the peak dielectric constant. In addition to the diffuse dielectric peak, the dielectric constant peak also shifts toward higher temperature as the frequency increases—a common feature of relaxor ferroelectric.

In general, the terpolymer containing $\sim$7 mol % termonomer content exhibits very slim polarization hysteresis with high dielectric constant, and the dielectric peak (as well as Curie temperature) shows at near 25 °C—well below the dielectric peak observed in the 55/45 VDF/TrFE copolymer ($>$60 °C) with a big hysteresis loop. The detailed comparison shows some dielectric constant dependence on the termonomer used. The dielectric constant peak of $>$90 was observed in some VDF/TrFE/CDFE and VDF/TrFE/CFE terpolymers. Although only a few mole percent of termonomer units were present in the terpolymer structure, the positive dipole contributions from the CFE and CDFE units (compared to almost no net dipole in the CTFE unit) are reflected in slightly higher dielectric constants. The mechanical stretching of the polymer film, usually very important for increasing the dielectric constant in VDF/TrFE copolymers, is not necessary in these terpolymers. The effective orientation of dipoles under an electric field may be attributed to the low phase transition energy, which occurs at near ambient temperature.

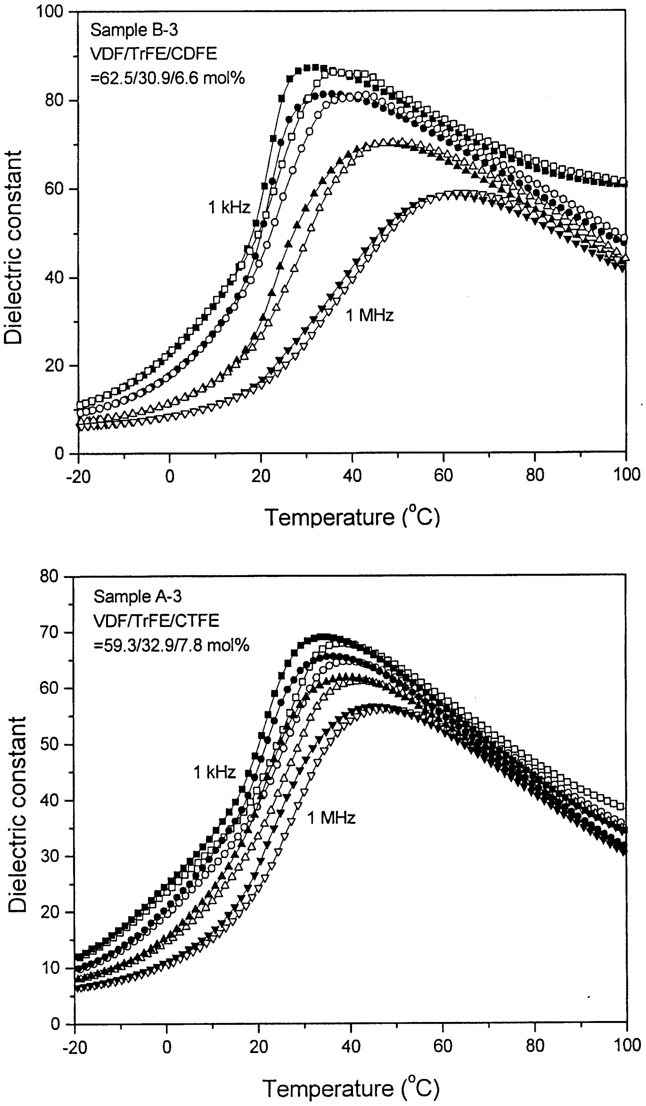


Figure 8. Temperature dependence of dielectric constant in two terpolymers, VDF/TrFE/CDFE (62.5/30.9/6.6; sample B-3) and VDF/TrFE/CTFE (59.3/32.9/7.8; sample A-3), during heating–cooling cycles and frequency range. Symbols for frequency in heating cycles are (□) 1 kHz, (○) 10 kHz, (△) 100 kHz, and (▽) 1 MHz. Symbols for frequency in cooling cycles are (■) 1 kHz, (●) 10 kHz, (▲) 100 kHz, and (▼) 1 MHz.

The electric field-induced strain was measured at ambient temperature in the field range of 0–150 MV/m using a bimorph-based strain sensor. Figure 9 shows three samples A-1, A-3, and A-4 having VDF/TrFE/CTFE mole ratios of 60.0/35.1/6.9, 59.3/32.9/7.8, and 57.3/31.2/11.5, respectively. At ambient temperature, the longitudinal strain reached about 4.5% for sample A-3 under an electric field of 130 MV/m.

Conclusions

This paper has shown a novel chemical method that combines a borane/oxygen low temperature initiator and a bulk reaction process to prepare a new family of

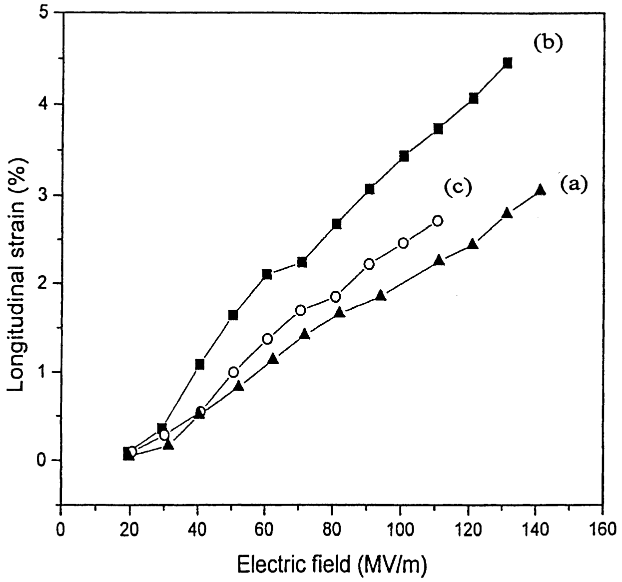


Figure 9. Electric field-induced strain of three VDF/TrFE/CTFE samples with (a) 60/36/4 (sample A-1), (b) 59.3/32.9/7.8 (sample A-3), and (c) 57.3/31.2/11.5 (sample A-4) mole ratios, respectively.

ferroelectric polymorphic fluoroterpolymers composed of VDF, TrFE, and a chloro-containing third monomer. Similar reactivity ratios between VDF and termonomers, especially chlorodifluoroethylene (CDFE) and chlorotrifluoroethylene (CTFE), produce terpolymers with relatively narrow molecular weight and composition distributions. The experimental results demonstrated that the homogeneously incorporated chlorine atoms in the VDF/TrFE chain with a controlled quantity ($\sim$7 mol % of termonomer units) alters the ferroelectric phase from the β-phase (t$_{m>4}$ conformation) to the γ-phase (tttg$^+$tttg$^-$ conformation), without significant reduction of overall crystallinity. The stable ferroelectric γ-phase in the terpolymer results in a low Curie phase transition temperature with a low energy barrier. Consequently, the terpolymers exhibit several common behaviors of a typical relaxor ferroelectric, such as diffuse phase transition, slim polarization hysteresis loop, high dielectric constant at ambient temperature, and dielectric relaxation (large frequency dependence). The expansion and contraction of these crystalline domains under an external electric field, coupled with the large difference in the lattice strain between the polar and nonpolar crystal phases, generates a large strain response.

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