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The Structure−Property Relationship of Poly(vinylidene difluoride)-Based Polymers with Energy Storage and Loss under Applied Electric Fields

Zhicheng Zhang and T. C. Mike Chung*

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

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ABSTRACT: This paper systematically examines the family of poly(vinylidene difluoride) (PVDF)-based fluoropolymers, including homo-, co-, and terpolymers containing vinylidene fluoride (VDF), trifluorethylene (TrFE), and chlorotrifluoroethylene (CTFE) units, with the objective of tuning the polymer chain conformation and crystal structure in order to identify the most suitable polymer for energy storage (capacitor) applications. All polymers have high molecular weight, uniform composition distribution, semicrystallinity, and high purity. They were prepared by a borane/oxygen control radical initiator in a homogeneous solution at ambient temperature. The resulting polymers were solution-cased, then melt-conditioned into uniform (defect-free) thermoplastic thin films (thickness 10−20 μm). The combination of thermal, dielectric, and uni- and bipolar charge displacements reveals their polarization profiles, which are dependent on chain conformation, crystal phase, crystal size, Curie temperature, and ac and dc fields. Ferroelectric VDF/TrFE copolymers, having all-trans chain conformation and polar β-phase crystals, exhibiting huge remnant polarization, are not suitable for energy storage (capacitor) applications. Some poled PVDF homopolymer and VDF/CTFE copolymers with γ-phase crystals show potential for dc (not ac) powered applications. The most suitable polymer is the VDF/TrFE/CTFE terpolymer having a TTTG chain conformation, small polar γ-phase crystals, relaxed dielectric properties, and a Curie transition at near ambient temperature, providing both ac and dc powered capacitors with a balance of properties, high-energy density and low-energy loss.

Introduction

Energy storage has long been a scientifically challenging and technologically important area[1] and is an essential element to energy utilization. The battery and capacitor are the two best known energy storage devices, but both fall short in many applications. Opposite to batteries, which have high-energy density and low power density, capacitors[2,3] exhibit high power density but very low-energy density. It is very desirable to increase the energy density of the capacitors, which is governed by the dielectric material that separates the opposite static charges between two surfaces. In the past decade, the metallized polymer film capacitors,[4,5] using semicrystalline thermoplastic films as the dielectric materials, have attracted a great deal of attention due to their desirable properties, such as light weight, low cost, and excellent processibility for forming thin film with a large surface area. They also demonstrate flexibility and toughness under stress and the ability to be packaged into a desirable configuration. Some advanced capacitors using biaxial oriented polypropylene (BOPP) thin film[6,7] show noticeably high dielectric strength (breakdown electric field > 600 MV/m) and self-healing[8] after a puncture, which merely results in a gradual loss of capacitance, so that they can be operated near the breakdown voltage. However, these metallized polymer film capacitors generally suffer from low-energy density (0.5−1.5 J/cm^3) due to their low dielectric constant ($\epsilon < 3$).

It is very interesting to study high dielectric poly(vinylidene difluoride) (PVDF)-based fluoropolymers[9] that are also semicrystalline thermoplastics with strong dipole CF$_2$ repeating units along the polymer chain, which potentially offers high dielectric constants ($\epsilon > 60$) with high breakdown strength and dramatically increasing capacitor energy density. However, several prior reports showed limited success. One[10] reported the energy density of 2.4 J/cm^3 in the PVDF capacitor, but the combination of a nonlinear response to the voltage, high remnant polarization, and high-energy loss makes the PVDF capacitor performance difficult to predict. Another report showed poor performance in the VDF/TrFE copolymer[11] with low-energy density (<1 J/cm^3) and very high-energy loss. After proton irradiation, the VDF/TrFE copolymer slightly improved its energy density and energy loss. Better results were shown in the corresponding irradiated composite material,[11] containing a VDF/TrFE copolymer and a high dielectric ceramic ferroelectric relaxor with a 60/40 volume ratio, which showed that the energy density increases to about 1.8 J/cm^3 at a relatively low electric field (80 MV/m). A new report showed high-energy density in a VDF/CTFE (91/9 mol %) copolymer[12] with nonspecific energy loss and remnant polarization. Recently, we reported a VDF/TrFE/CTFE terpolymer[13] exhibiting a high breakdown electric field, high-energy density, relatively small energy loss, and almost no remnant polarization at zero electric field. The somewhat contradicted results may be associated with the fact that the PVDF-based polymers existed in many forms of polymer chain conformations and crystal structures.[9] It is worthwhile to systematically examine this family of fluoropolymers side-by-side, with the objectives of understanding their structure−property relationship and identifying the desirable polymer structure that could exhibit a polarization profile for high-energy density capacitor applications.

In chemistry, a few years ago we reported a new borane/oxygen control radical initiator system[14−16] that provides an effective route to prepare high quality fluoro-copolymers in

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* Author to whom all correspondences should be addressed. E-mail: chung@ems.psu.edu.

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Table 1. Summary of the Polymerization of VDF, TrFE, and CTFE Monomers Using a Triethylborane/Oxygen Radical Initiator

	reaction conditions				reaction products			
run	TEB/O_2 (mmol)	VDF/TrFE/CTFE (mL)	time (h)	cov (%)	VDF/TrFE/CTFE (%)	T_m[a] (°C)	T_c[b] (°C)	ΔH[a] (J/g)
control		PVDF			100/0.0/0.0	167.3		33.2
A-1	0.3/0.4	25.0/0.0/0.3	5	26	95.4/0.0/4.6	155.7		31.5
A-2	1.0/0.8	25.0/0.0/1.5	2	30	92.2/0.0/7.8	146.1		25.9
A-3	2.4/2.0	25.0/0.0/2.5	2	37	88.0/0.0/12.0	132.8		22.9
A-4	1.0/0.8	25.0/0.0/10.0	1	33	84.0/0.0/16.0	87.2		6.3
B-1	1.2/1.0	20.0/5.0/0.0	1.5	35	81.7/18.3/0.0	146.4	117.7	35.2
B-2	1.2/1.0	20.0/10.0/0.0	1	34	72.1/27.9/0.0	148.9	106.4	31.2
B-3	1.2/1.0	20.0/18.0/0.0	1	38	63.3/36.7/0.0	151.7	89.4	30.1
C-1	1.2/1.0	20.0/20.0/1.5	1	34	58.3/37.4/4.3	134.6	38.1	23.3
C-2	0.3/0.4	20.0/20.0/2.0	3	22	56.2/37.0/6.8	121.3	27.2	21.3
C-3	0.3/0.4	20.0/18.0/2.0	3	25	58.4/34.2/7.4	121.5	25.9	19.6
C-4	0.3/0.4	20.0/20.0/2.5	3	21	57.1/31.4/11.5	106.4	18.1	19.0
C-5	0.3/0.4	20.0/10.0/1.0	3	30	67/3/27.2/5.5	127.1	37.4	25.1
C-6	1.2/1.0	20.0/11.6/1.5	1	38	65.6/26.7/7.7	123.6	30.2	21.0
C-7	0.3/0.4	20.0/10.0/1.5	3	32	68.2/22.5/9.3	112.6	20.4	21.1
C-8	0.3/0.4	25.0/4.0/1.0	4	32	81.5/9.9/8.6	118.6		30.8
C-9	0.3/0.4	25.0/4.2/1.0	4	31	81.3/11.3/7.4	119.3		31.1
C-10	0.3/0.4	25.0/4.3/1.0	4	32	80.7/11.6/7.7	119.2		29.2

[a] T_m and ΔH are measured by DSC in the second heating cycle at a heating rate of 10 °C/min. [b] T_c is determined by dielectric constant vs temperature study at 100 Hz and a heating rate of 2 °C/min.

solution or bulk (homogeneous solution) at ambient temperature. Different from the conventional emulsion and suspension (heterogeneous solutions) processes at elevated temperatures, the resulting VDF/TrFE/CTFE terpolymers[17] 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. In this study, this chemical route was employed to prepare a wide range of fluoropolymers.

Experimental Details

Materials and Instrumentation. Triethylboron (TEB) was purchased from Aldrich and used as received. Tetrahydrofuran (THF) was dried and distilled from sodium benzophenone ketyl under nitrogen. VDF and CTFE monomers were purchased from SynQuest Laboratory Inc., and the TrFE monomer was purchased from Halocabon Inc. All monomer gases were purified and quantified in a freeze−thaw process prior to use.

^{1}H and ^{19}F NMR spectra were recorded on a Bruker AM-300 spectrometer instrument. The thermal transition data was obtained with a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min. The dielectric constant was measured with a HP multifrequency LCR meter (HP 4284A), equipped with a temperature chamber. 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.

Synthesis of Fluoro-Co- and Terpolymers Using Borane/Oxygen Initiator.[15−17] The polymerization reactions were carried out in a 75 mL stainless steel autoclave equipped with a magnetic stirrer. In a typical reaction, 0.3 mmol of triethylboron initiator and 30 mL of acetonitrile solvent were added into the autoclave under an inert atmosphere. The autoclave was then cooled by liquid nitrogen before vacuum distilling in certain amounts of monomers. About 0.4 mmol of oxygen was introduced into the autoclave in order to oxidize organoborane and initiate polymerization before the mixture was warmed to the ambient temperature. Then the mixture was stirred constantly for a certain period of time at the ambient temperature before the reaction was terminated via venting the unreacted monomers. The resulting polymer was obtained by removing the solvent under a vacuum and subsequently purified by precipitating from the polymer solution in acetone with excess hexane. It was washed three more times with hexane and finally dried in a vacuum oven at 70 °C for 8 h.

To obtain high quality co- and terpolymers with high purity and narrow molecular weight and composition distributions, the polymerization reactions were usually terminated at a low monomer conversion (<30%) to ensure a constant monomer feed ratio during the polymerization. Note that CTFE shows similar (slightly higher) reactivity with VDF, but TrFE exhibits a significantly lower reactivity than VDF. Overall, the borane/oxygen mediated fluoromonomer polymerization was effective to obtain high-molecular weight polymers, and it was easy to control their co- and terpolymer compositions by the monomer feed ratios. The productivity of the polymerizations was also proportional to the quantity of the borane/oxygen initiator used. The detailed experimental results will be discussed in Table 1.

Thin Film Preparation and D−E Measurements. The polymer thin films were prepared by two steps. First, the polymer film (thickness = 30−40 μm) was obtained by a solution casting method, in which the copolymer or terpolymer (8−10 wt %) was dissolved in acetone and cased on a glass slide. After evaporation of the solvent at the ambient temperature overnight, the resulting film was annealed in a vacuum oven at the melting temperature for 2−3 h to obtain a uniform thin film (thickness = 10−20 μm).

For the dielectric constant and *D*−*E* polarization−depolarization cycle measurements, gold electrodes (thickness = 50 nm) were sputtered on both surfaces of the polymer film. The electric displacement-electric field was measured by a modified Sawyer−Tower circuit and a linear variable differential transducer (LVDT), driven by a lock-in amplifier (Stanford Research Systems, model SR830). Electric fields ranging from 50 to 600 MV/m were applied across the polymer film using an amplified ramp waveform at 10 Hz.

Results and Discussion

Characterization of Fluoropolymers. For the systematic structure−property relationship study and identification of the most suitable fluoropolymer for energy storage (capacitor) applications, we have prepared a family of VDF-based polymers with narrow molecular weight and composition distributions and high purities. Table 1 summarizes several comparative sets of PVDF homopolymer, VDF/TrFE and VDF/CTFE copolymers, and VDF/TrFE/CTFE terpolymers, with a systematic variation of TrFE and CTFE contents. Their thermal transition data (T_m, T_c, and ΔH) was determined by DSC and dielectric constant measurements. Several representative DSC curves and dielectric constant profiles (vs temperature) of PVDF homopolymer, VDF/TrFE and VDF/CTFE copolymers, and VDF/TrFE/CTFE ter-

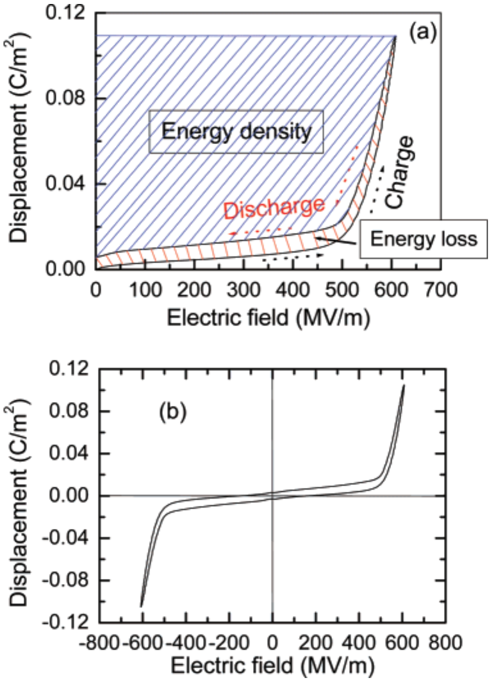

Figure 1. An ideal $D-E$ curve pattern showing (a) unipolar and (b) bipolar polarization−depolarization cycles with the shady areas showing releasing energy and energy loss during discharging.

polymers (runs in Table 1) are shown in Figures 1S and 2S, respectively, in the Supporting Information.

As previously reported,[18] the VDF/TrFE copolymers (runs B-1−B-3) show a semicrystalline structure in all compositions. On the other hand, both melting temperature and crystallinity of the VDF/CTFE copolymers systematically decrease with the increase of the incorporated CTFE units (runs A-1−A-4). The VDF/CTFE copolymer containing more than 16 mol % CTFE units becomes completely amorphous. The bulky Cl atoms interrupt the crystallization of the VDF sequences. With comparison of the VDF/TrFE/CTFE terpolymers (runs C-1−C-4) with similar VDF and TrFE contents and a gradual increase of the CTFE mol %, the melting temperature slowly reduces but maintains a high heat of fusion (ΔH) that starts its diametrical descent after the CTFE content reaches >8 mol %. In other words, the terpolymers with less than 8 mol % of CTFE units maintain an overall high crystallinity, despite the reduction of their crystalline domain size.

As expected, all three VDF/TrFE copolymers (runs B-1−B-3) show a Curie temperature (T_c)[19] at the maximum dielectric constant, which systematically decreases with the TrFE content.[20,21] The TrFE units alter the PVDF chain from trans-gauche (TGTG′) conformation (α-phase crystal)[22−24] to an all-trans (TTTT) zigzag structure (β-phase crystal).[25−27] The lowest T_c observed is about 65 °C in the VDF/TrFE (55/45) copolymer,[28] which is well above ambient temperature. There is no Curie temperature (T_c) observed in PVDF (control) and all VDF/CTFE copolymers (runs A-1−A-4). The incorporated CTFE units do not effect PVDF chain conformation and crystalline structure. As shown in our previous paper,[29,30] the incorporation of bulky CTFE units into the VDF/TrFE copolymer results in a TTTG chain conformation and adopts a γ-phase crystalline phase. The resulting VDF/TrFE/CTFE terpolymer moves T_c to a lower temperature with a small reduction of the peak dielectric constant. The VDF/TrFE/CTFE (65.6/26.7/7.7) terpolymer (run C-6) shows a sharp dielectric peak ($\epsilon \sim 65$ at 100 Hz) at 30.2 °C.

Table 2. Theoretical Estimate of Energy Density under Several Hypothetic Conditions

dielectric constant (ϵ)	film thickness (μm)	applied voltage (kV)	applied field (MV/m)	energy density (J/cm^3)
2.2	20	5	250	0.6
2.2	10	5	500	2.4
60	20	5	250	17
60	10	5	500	66

Ideal Dielectric Behaviors. On the basis of the energy density equation (J/cm^3) $= {}^1/_2\epsilon E^2 = {}^1/_2\epsilon(V/d)^2$, Table 2 shows estimates of ideal energy densities under several hypothetical conditions. A defect-free polymer thin film with a dielectric constant ($\epsilon = 2.2$ in PP case), thickness ($d = 10$ μm), and an applied voltage $V = 5$ kV ($E = 500$ MV/m) can offer a maximum energy density of 2.4 J/cm^3 at the material level. A further increase of the polymer dielectric constant to $\epsilon = 60$ (in the range of this fluoropolymer case) with $d = 20$ and 10 μm can result in a theoretical energy density of 17 and 66 J/cm^3, respectively. In other words, it is theoretically possible to increase more than 20-fold the energy density of the current state-of-the-art metallized polymer (BOPP) film capacitors if we could develop an ideal fluoropolymer dielectric that shows several characteristics. These include good processibility in forming defect-free thin films ($d = 20-10$ μm), a high dielectric constant ($\epsilon > 60$), a high breakdown strength ($E > 500$ MV/m), and a polarization−depolarization profile (Figure 1) without early dielectric saturation at low-electric fields.

Figure 1 shows the ideal $D-E$ (charge displacement vs applied electric field) curves during uni- and bipolar polarization−depolarization (charging−discharging) cycles. The dipoles in the polymer chains (or crystals) are polarized by an external electric field at a high field condition (before breakdown voltage) and are completely reversible (very low hysteresis) in their dipole orientation under both ac and dc conditions. Ideally, there is no conduction loss, no remnant polarization at $E = 0$, and no coercive electric field at $D = 0$. The combination provides maximum energy density during the discharging cycle with minimum energy loss. The total energy density (U_{charge}) charged to the capacitor is estimated by integrating the area $U_{\mathrm{charge}} = \int E\, \mathrm{d}D_{\mathrm{charge}}$ (E, applied electric field; D_{charge}, charge displacement in the charging cycle). The energy density ($U_{\mathrm{discharge}}$) of the capacitor is the total energy released during the discharging cycle, by integrating the area $U_{\mathrm{discharge}} = \int E\, \mathrm{d}D_{\mathrm{discharge}}$ ($D_{\mathrm{discharge}}$, charge displacement in the discharging cycle). The difference, $U_{\mathrm{l}} = U_{\mathrm{charge}} - U_{\mathrm{discharge}}$, is the energy loss ($U_{\mathrm{l}}$), which is equal to the area enclosed by the charging and discharging cycle.

Bipolar $D-E$ Curves. Figure 2 compares bipolar $D-E$ hysteresis loops of four representative semicrystalline fluoropolymers, including the PVDF homopolymer (control), VDF/CTFE (92.2/7.8 mol %) copolymer (run A-2), VDF/TrFE (63.3/36.7 mol %) copolymer (run B-3), and VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer (run C-6). A sinusoidal ac electric field (50 Hz) was applied across the polymer film with an initial amplitude of 50 MV/m, then increasing 50 MV/m intervals until reaching 300 MV/m. In parts a and b of Figure 2, both the PVDF and VDF/CTFE (92.2/7.8 mol %) copolymer show similar (oval-shaped)[31] $D-E$ hysteresis loops, and remnant polarization (at $E = 0$) and a coercive field (at $P = 0$) gradually enlarge with the increasing field amplitude. Under the low applied electric fields (<150 MV/m), some of the CF_2 groups in the trans-gauche (TGTG′) polymer chain conformation were aligned with the field, which might result in the change of the α-phase crystal into a slightly polar δ-phase crystal.[32,33] Both α and δ crystals have identical unit cell and chain conformations, but the δ-phase

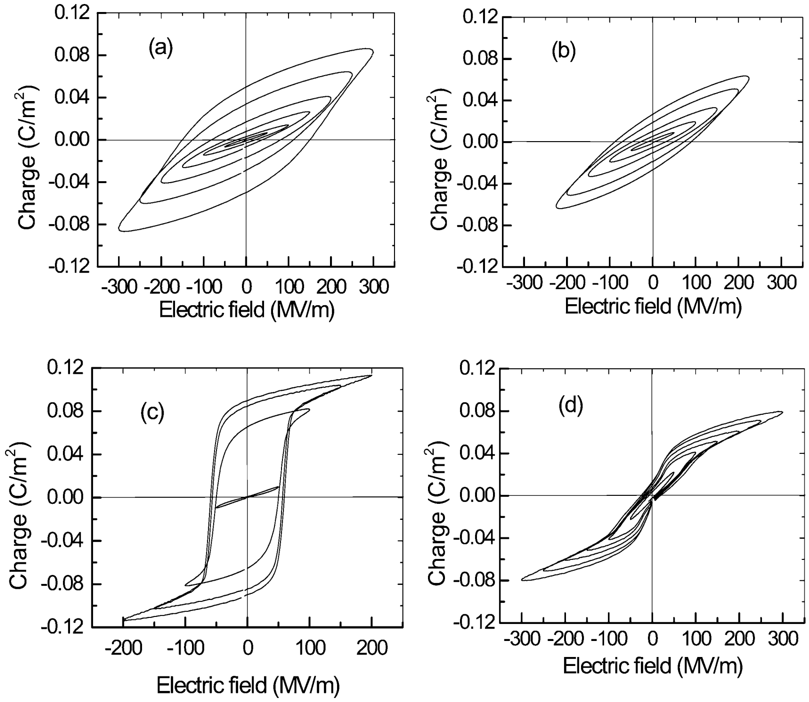

Figure 2. Bipolar $D-E$ hysteresis loops of (a) PVDF homopolymer (control), (b) VDF/CTFE (92.2/7.8 mol %) copolymer (run A-2), (c) VDF/TrFE (63.3/36.7 mol %) copolymer (run B-3), and (d) VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer (run C-6).

crystal contains two parallel polymer chains in each unit cell instead of two antiparallel polymer chains in an α-phase crystal. This crystalline phase transition requires only low activation energy. Above 200 MV/m in Figure 2a and 150 MV/m in Figure 2b, the polarization curves show a slight but noticeable up-turn trend, which may be associated with the poling effect to alter the chain conformation from TGTG′ to TTTG and also to alter the crystalline phase from a δ-phase to a polar γ-phase.[34] The hysteresis loop also expends with the increase of remnant polarization and the coercive field. This poling effect is much more obvious in unipolar polarization curves (discussed later). With a further increase in the electric field (>350 MV/m),[34] the polymer chain conformation eventually becomes an all-trans (TTTT) conformation with β-phase crystals that exhibit an even larger hystersis loop.

Generally speaking, the addition of a small amount of CTFE units in the PVDF polymer reduces its crystal size and activation energy for dipole alignment. This is reflected by the slight increase of the polarization slope and reduction of the hysteresis loop in the VDF/CTFE copolymers. However, with too many CTFE units (>10 mol %), the copolymer starts to lose crystallinity and the hysterysis loop broadens again with a large dielectric loss (discussed later). Overall, both PVDF polymers and VDF/CTFE copolymers, with large energy loss (>70%), are not suitable for ac capacitor applications.

Figure 2c shows a large (square-shaped) $D-E$ hysterisis loop for the VDF/TrFE (63.3/36.7 mol %) copolymer, with a large coercive field ($E_{\mathrm{coe}} \sim 50$ MV/m) and remnant polarization ($P_{\mathrm{rem}} = 0.08$ C/m^2) that is only slightly smaller than the maximum polarization ($P_{\max} = 0.11$ C/m^2) at $E = 200$ MV/m. The strong irreversibility of the polar β-phase crystals result in huge energy loss (>90%) during the polarization−depolarization cycles, which prevents any consideration in ac capacitor applications. On the other hand, the VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer (Figure 2d) has a similar VDF content but contains few bulky Cl atoms along the polymer chain, which reduce the crystalline size and change the all-trans (TTTT) chain conformation (β-phase crystal) to a TTTGTTTG′ conformation (γ-phase crystal). The terpolymer exhibits common relaxed ferroelectric behaviors with a Curie temperature (maximum dielectric constant) at near ambient temperature. Consequently, the terpolymer shows a slim $D-E$ hysteresis loop with very small remnant polarization ($P_{\mathrm{rem}} < 0.01$ C/m^2 at $E = 0$) and coercive field ($E_{\mathrm{coe}} < 10$ MV/m at $P = 0$) even after applying $E = 300$ MV/m. Overall, the polar γ-phase crystals are easily aligned with the applied electric field to a high polarization level ($P_{\max} = 0.078$ C/m^2 at $E = 200$ MV/m). This reversible bipolar polarization−depolarization is essential in the ac capacitors with high-energy density and low-energy loss.

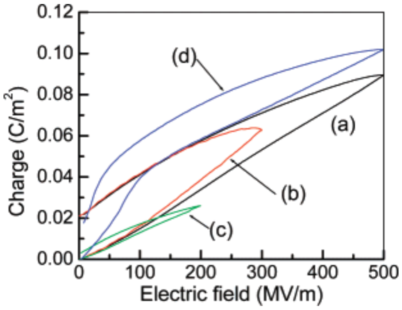

Figure 3. Unipolar $D-E$ hysteresis loops (before breakdown) of (a) PVDF homopolymer (control), (b) VDF/CTFE (92.2/7.8 mol %) copolymer (run A-2), (c) VDF/TrFE (63.3/36.7 mol %) copolymer (run B-3), and (d) VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer (run C-6).

Unipolar $D-E$ Curves. The unipolar polarization−depolarization cycles were also first applied in the dc field to 50 MV/m, then increased in 50 MV/m intervals until the breakdown electric field was reached. Figure 3 compares the last unipolar $D-E$ hysteresis loops before the breakdown of the same set of the PVDF homopolymer (control), VDF/CTFE (92.2/7.8 mol %) (run A-2) and VDF/TrFE (63.3/36.7 mol %) (run B-3) copolymers, and the VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer (run C-6). Since unipolar measurement does not require the dipole to flip into the opposite direction, the remnant polarization at zero field becomes a permanent (saturated) dipole

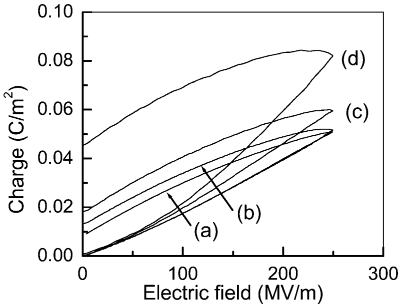

Figure 4. Comparison of unipolar *D*−*E* hysteresis loops ($E = 250$ MV/m) between (a) PVDF homopolymer (control) and three VDF/CTFE copolymers containing (b) 4.6 (run A-1), (c) 7.8 (run A-2), and (d) 12.0 (run A-3) mol % of CTFE contents.

and is not involved in the subsequent polarization−depolarization (charging−discharging) cycles. Therefore, there is no coercive field observed in all unipolar *D*−*E* curves.

A noticeable difference between unipolar and bipolar *D*−*E* curves was observed in the VDF/TrFE (63.3/36.7 mol %) copolymer (run B-3), a thin and small unipolar *D*−*E* loop in Figure 3c in contrast with the wide and large bipolar *D*−*E* loops in Figure 2c. Because of the large remnant polarization, only a small portion of CF_2 dipoles in the VDF/TrFE copolymer responds to the unipolar electric field. This inherent irreversibility of polarization makes VDF/TrFE copolymers almost impossible for any capacitor applications. The contrast between unipolar and bipolar *D*−*E* curves is significantly less in PVDF and VDF/CTFE (92.2/7.8 mol %) copolymer, due to smaller remnant polarization. Both polymers also show similar unipolar *D*−*E* loops in parts a and b of Figure 3, with some reduction of the breakdown strength in the copolymer. A detailed comparison was carried out to understand the effect of CTFE units in the PVDF polymer, which is known to reduce the crystal size without altering the TGTG′ chain conformation and α-crystal. Figure 4 shows the unipolar *D*−*E* loops of the PVDF homopolymer (control) and three VDF/CTFE copolymers containing 4.6, 7.8, and 12 mol % of CTFE contents (runs A-1−A-3), under a 250 MV/m electric field. Initially, the addition of a small amount of CTFE units seems to have only a small effect on the *D*−*E* loop, with a slight increase of the polarization slope and hysteresis. However, as the CTFE content reaches to 12 mol %, the VDF/CTFE copolymer dramatically reduces its crystallinity, and the high amorphous phase results in a high dielectric loss (Figure 4d) through the conducting mechanism.

Figure 3d shows the most desirable unipolar *D*−*E* loop that is almost overlapped within the upper half of the corresponding bipolar *D*−*E* curve in Figure 2d. The relaxed ferroelectric VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer shows almost no remnant polarization and a high breakdown electric field at >500 MV/m. The electric displacement reached to about 0.1 C/m^2 at $E = 500$ MV/m. Compared to the theoretical electric displacement of 0.13 C/m^2 for the fully polarized (β-phase) PVDF homopolymer,[35] this terpolymer almost reached its limit with almost all CF_2 dipoles in VDF and TrFE units oriented along the electric field and disoriented after the removal of the applied electric field. The desirable features in VDF/TrFE/CTFE terpolymers prompted us to systematically examine the whole series of terpolymer compositions in order to understand the structure−property relationship and to identify the most suitable material for dc capacitor applications.

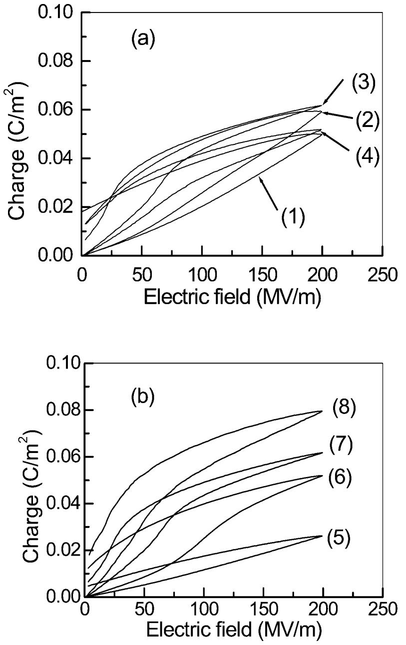

Figure 5. Comparison of unipolar *D*−*E* hysteresis curves of two sets of VDF/TrFE/CTFE terpolymers that contain (a) a fixed CTFE content (∼7.5 mol %) and various VDF/TrFE mole ratios, including (1) 92.2/0 (run A-2), (2) 80.7/11.6 (run C-10), (3) 65.6/26.7 (run C-6), and (4) 58.4/34.2 mol % (run C-3), and (b) a fixed VDF content (∼65 mol %) and various TrFE/CTFE mole ratios, including (5) 36.7/0 (run B-3), (6) 27.2/5.5 (run C-5), (7) 26.7/7.7 (run C-6), and (8) 22.5/9.3 mol % (run C-7).

Figure 5 compares unipolar *D*−*E* hysteresis loops ($E = 200$ MV/m) of two terpolymer sets, one set having a fixed CTFE content and a varying VDF/TrFE mole ratio and the other set having a fixed VDF content and a varying TrFE/CTFE mole ratio. Figure 5a shows *D*−*E* loops of four VDF/TrFE/CTFE terpolymers that have ∼7.5 mol % CTFE content (crystal defects) and various TrFE content from 0, 11.6, 26.7, and 34.2 mol % (runs A-2, C-10, C-6, and C-3), respectively. Two VDF/TrFE/CTFE terpolymers (having 65.6/26.7/7.7 and 58.4/34.2/7.4 mol %) are spontaneously adopted in the polar γ-crystalline phase. The other two nonpolar polymers, VDF/CTFE (92.2/7.8 mol %) copolymer and VDF/TrFE/CTFE (80.7/11.6/7.7 mol %) terpolymer, were poled at 350 MV/m to form a primarily polar γ-crystalline phase. Overall, the increase of the TrFE content seems to have a relatively small effect on the *D*−*E* hysteresis loops. In detail, the VDF/TrFE/CTFE (65.6/26.7/7.7) terpolymer, with the Curie temperature at around 30 °C, shows the slimmest *D*−*E* hysteresis loop with the lowest energy loss (discussed later). In further increasing the TrFE content (>30%), the *D*−*E* loop of the VDF/TrFE/CTFE (58.4/34.2/7.4) terpolymer broadens again with significantly higher energy loss. In addition, the polarization seems to be saturated at 200 MV/m, which results in the limited overall energy density.

Figure 5b compares another four terpolymers (runs B-3, C-5, C-6, and C-7), containing ∼65 mol % VDF and varying CTFE content from 0 to 9.3 mol % (systematically reducing crystal size). They are all polar polymers with either a TTTT conformation (β-phase) or TTTG conformation (γ-phase). It becomes very clear that the crystal size has a big effect on the unipolar *D*−*E* loop. As discussed, the VDF/TrFE (63.3/36.7 mol %) copolymer, adopting a TTTT chain conformation and big polar β-phase crystals, forms huge remnant polarization after the first cycle. Most of the polar CF_2 groups in β-phase crystals cannot contribute to the unipolar charging−discharging cycles, therefore resulting in very low polarization intensity. The increase of the incorporated CTFE units (crystal defects) reduces the crystal size, altering the polymer chain from a TTTT to TTTG conformation and the crystals from a β- to γ-phase. The defects in the crystalline phase increase the reversibility of the

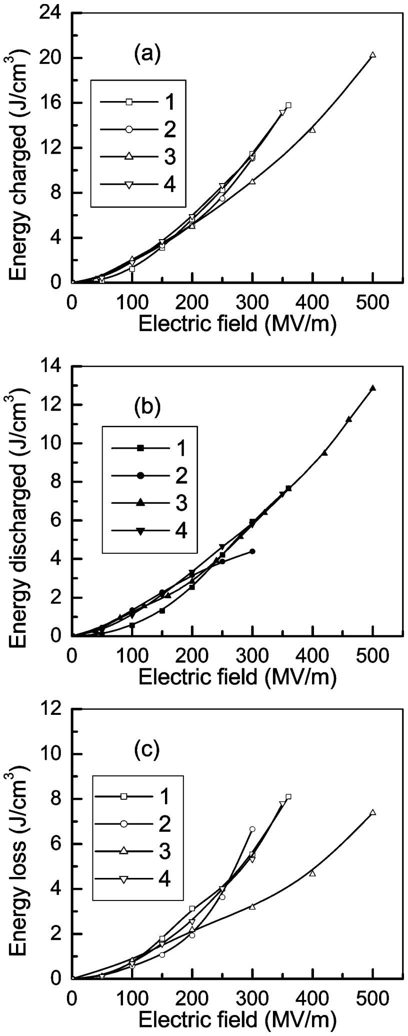

Figure 6. Comparison of (a) total energy charged during the charging cycle, (b) energy released during the discharge cycle (energy density), and (c) energy loss for the first set of the VDF/TrFE/CTFE terpolymers with (1) 92.2/0/7.8 (run A-2), (2) 80.7/11.6/7.7 (run C-10), (3) 65.6/26.7/7.7 (run C-6), and (4) 58.4/34.2/7.4 mol % (run C-3).

dipoles during the polarization−depolarization cycles, as well as polarization intensity due to the reduction of remnant polarization. However, increasing the CTFE content to near 10 mol %, the terpolymer loses some of its crystallinity. The increased amorphous phase broadens the hysteresis loop with an increase of energy loss.

Energy Density and Energy Loss. Figures 6 and 7 compare the total energy charged, energy discharged (energy density), and energy loss of the two sets of terpolymers in Figure 5, respectively. Figure 8 shows their energy storage efficiency by dividing the total energy discharged (energy density) over the total energy charged. As expected, the total energy charged, energy discharged, and energy loss increase with the increasing applied electric field. The higher breakdown electric field offers higher energy density. The VDF/TrFE (63.3/36.7 mol %) copolymer shows very low-energy density. However, it was somewhat surprising to see the terpolymers exhibiting similar energy charged and discharged slopes, especially in the low-electric field range (E < 150 MV/m). The significant breakout is at a higher field (E > 200 MV/m), in which the higher activation energy is needed for phase transitions and for orienting larger polar crystals.

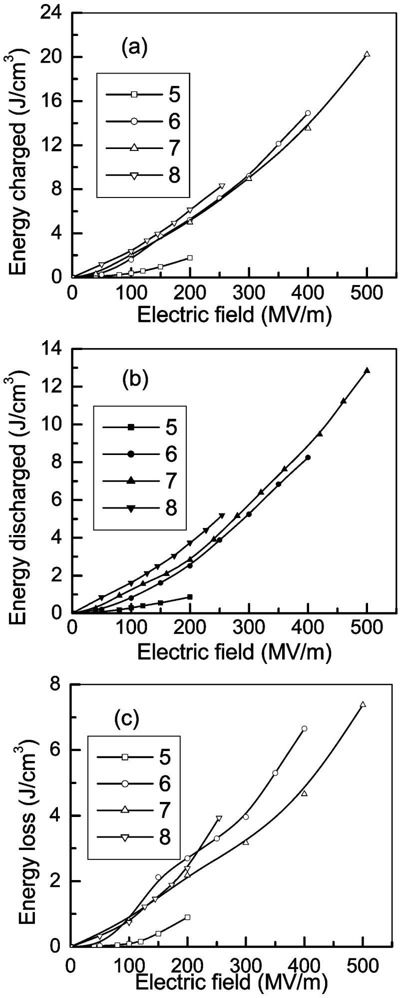

Figure 7. Comparison of (a) total energy charged during the charging cycle, (b) energy released during the discharge cycle (energy density), and (c) energy loss for the second set of the VDF/TrFE/CTFE terpolymers with (5) 63.3/36.7/0 (run B-3), (6) 67.327.2/5.5 (run C-5), (7) 65.626.7/7.7 (run C-6), and (8) 68.2/22.5/9.3 mol % (run C-7).

In Figure 6, when compared with the VDF/TrFE/CTFE (65.6/26.7/7.7) terpolymer (run C-6), both the poled VDF/CTFE (92.2/7.8 mol %) copolymer (run A-2) and VDF/TrFE/CTFE (80.7/11.6/7.7 mol %) terpolymer (run C-10) show higher energy charged in Figure 6a but almost the same or smaller energy discharged in Figure 6b, at above 200 MV/m. In other words, a significant higher energy loss (Figure 6c) is observed in the poled samples, and the energy storage efficiency is < 50% at the applied dc electric field > 300 MV/m (Figure 8a). On the other hand, the spontaneously poled VDF/TrFE/CTFE (65.6/26.7/7.7) sample shows a smooth increase of energy charged and energy released (about 13 J/cm^3 at 500 MV/m) and a stable energy storage efficiency (>60%) throughout a wide range of electric fields. However, the VDF/TrFE/CTFE (58.4/34.2/7.4) terpolymer (run C-3), with T_c below measurement temperature, shows an early dielectric saturation at about 200 MV/m and the maximum energy density of only about 4 J/cm^3. The energy loss also shapely increases above 200 MV/m, indicating that most of the energy charged is lost after 200 MV/m. The overall energy storage efficiency at breakdown (E = 300 MV/m) is only about 40% (Figure 8a). The paraelectric phases of this terpolymer fail to engage in the reversible polarization−depolarization cycle.

In Figure 7, all three terpolymers are spontaneously formed γ-phase crystals with the crystal size inversely proportional to the CTFE content. The charged and discharged energy during the polarization cycle follows the general trend. However, the

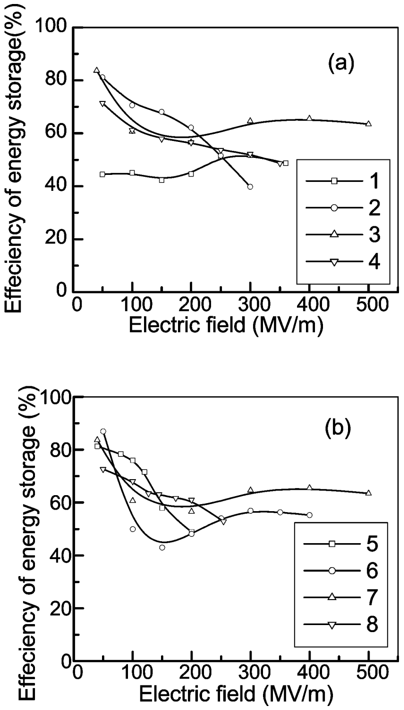

Figure 8. Comparison of energy storage efficiency of two sets of terpolymers under dc fields, (a) the first set of the VDF/TrFE/CTFE terpolymers containing (1) 92.2/0/7.8 (run A-2), (2) 80.7/11.6/7.7 (run C-10), (3) 65.6/26.7/7.7 (run C-6), and (4) 58.4/34.2/7.4 mol % (run C-3), (b) the second set of the VDF/TrFE/CTFE terpolymers containing (5) 63.3/36.7/0 (run B-3), (6) 67.327.2/5.5 (run C-5), (7) 65.626.7/7.7 (run C-6), and (8) 68.2/22.5/9.3 mol % (run C-7).

VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer (run C-6) seems again to be the most desirable material, having the highest breakdown strength, energy density, and energy storage efficiency. Both VDF/TrFE/CTFE terpolymers with slightly higher CTFE content (68.2/22.5/9.3 mol %, run C-7), resulting in an increase of amorphous phase, and slightly low-CTFE content (67.3/27.2/5.5 mol %, run C-5), resulting in a larger crystal size, show significantly low-breakdown strength and high-energy loss. Figure 8b clearly shows this VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) composition possessing the highest energy storage efficiency and breakdown electric field. As discussed, the key balancing act in the terpolymer composition is to tune its Curie temperature toward operation (near ambient) temperature, with small γ-crystalline domains and high crystallinity.

Conclusion

This paper systematically examines the structure−property relationship of PVDF-based polymers, containing TrFE units (controlling chain conformation) and CTFE units (tuning crystal structure), with the objective to understand their polarization−depolarization profiles under both dc and ac fields. The most desirable fluoropolymer composition seems to be the VDF/TrFE/CTFE (65.6/26.7/7.7 mol %) terpolymer with a high dielectric constant ($\epsilon \sim 65$), high-breakdown voltage (>500 MV/m), high-energy density (>13 J/cm^3), and low-energy loss (<40%). The polymer exhibits a relaxed ferroelectric behavior at the Curie transition close to operation temperature, which is the result of the TTTG chain conformation and small polar γ-phase crystalline domains with a high overall crystallinity. Compared with the current state-of-the-art capacitor technology, based on metallized BOPP film (<2 J/cm^3), the high dielectric fluoropolymer significantly increases the energy density but generates more energy loss (~40%). Both polymer systems are far from the ideal dielectric material for achieving both high-energy density and storage efficiency.

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Supporting Information Available: DSC curves and dielectric constant profiles (vs temperature) of PVDF homopolymer, VDF/TrFE and VDF/CTFE copolymers, and VDF/TrFE/CTFE terpolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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