

Electrical Storage in Poly(vinylidene fluoride) based Ferroelectric Polymers: Correlating Polymer Structure to Electrical Breakdown Strength

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The development of polymeric dielectric materials has generated considerable interest as a promising avenue for creating high-performance capacitors, gate dielectrics, memories, and power-storage devices.^{1–5} Dielectric polymers have many fundamental advantages over their inorganic counterparts, including high intrinsic electrical breakdown strength, light weight, ease of processing into large areas, and excellent reliability as a result of the graceful failure mechanism. For a linear dielectric material with a dielectric permittivity of ϵ_r , electrical energy density varies as $U_e = 1/2\epsilon_r\epsilon_0E^2$, where ϵ_0 is the vacuum permittivity ($\epsilon_0 = 8 \times 10^{-12}$ F/m) and E is an applied electric field. Therefore, both large permittivity and high electrical breakdown strength are required for a large energy storage capacity. Conventional polymeric dielectrics, such as biaxially oriented polypropylene (BOPP), generally display a low ϵ_r (e.g., ~ 2.2 for BOPP), thus severely limiting the energy density to much below 5 J/cm³.⁶ Superior ϵ_r has been observed in poly(vinylidene fluoride) (PVDF) based ferroelectric polymers, owing to the strong polarization originating from C–F bonds and the spontaneous orientation of dipoles in the crystalline phases.⁷ For instance, a terpolymer of vinylidene fluoride, chlorotrifluoroethylene (CTFE) and trifluoroethylene (TrFE), P(VDF-CTFE-TrFE), can exhibit an ϵ_r of 50 measured at 1 kHz and ambient temperature.^{8,9} These ferroelectric polymers with high dipole density and ϵ_r thereby offer great potential to achieve a very high electrical energy density. Indeed, an unparalleled energy density of over 17 J/cm³ with fast discharge time ($< 1 \mu\text{s}$) and low dielectric loss has recently been demonstrated in P(VDF-CTFE)s with an ϵ_r of 13.¹⁰ Despite the extensive interest in these ferroelectric polymers, their dielectric

Table 1. Structural Characteristics of the Prepared PVDF Based Ferroelectric Polymers

polymer	composition (mol %)			χ_c (%)	T_m (°C)	ϵ_r
	VDF	TrFE	CTFE			
1	73.6	0	26.4	7.2		14.1
2	73.6	3.9	22.5	14.4	37.8	16.4
3	73.6	9.2	17.2	17.1	72.5	24.1
4	73.6	11.9	14.5	18.0	86.7	24.0
5	73.6	18.3	8.1	24.2	121	14.7
6	73.6	19.3	7.1	28.6	127	14.2
7	73.6	26.4	0	35.4	163	10.4

breakdown behavior remains poorly understood.^{11–13} In this work, the structural dependence of dielectric strength for the ferroelectric polymers has been investigated. It is found by numerical calculations that an electromechanical breakdown agrees quantitatively with experimental characteristics of the breakdown field with polymer composition.

The synthetic route to the ferroelectric P(VDF-CTFE-TrFE) terpolymers involves copolymerization of VDF and CTFE followed by reductive dechlorination of CTFE (see Supporting Information).¹⁴ Different from the previously reported terpolymerization, this two-step approach leads to terpolymers with accurately controlled chemical compositions because of similar reactive ratios between VDF and CTFE (i.e., $r_{\text{VDF}} = 0.70$, $r_{\text{CTFE}} = 0.72$)¹⁵ and a quantitative dechlorination yield.¹⁶ The ability to tailor these polymers permits a systematic study of the influence of molecular composition on the dielectric breakdown field. Table 1 summarizes a series of the prepared P(VDF-CTFE-TrFE)s containing 73.6 mol % VDF and their structural parameters. The absolute weight-average molecular weight of the polymer, determined by gel permeation chromatography (GPC) equipped with light scattering detectors in DMF, is approximately 240 kDa with polydispersity of ~ 3.40 .

Wide-angle X-ray diffraction (WAXD) measurements were carried out to examine the evolution of the crystallinity of the polymers with chemical compositions. As shown in Table 1, the degree of crystallinity (χ_c) increases from 7.2% for polymer 1 to 35.4% for polymer 7. Consistent with the WAXD results, differential scanning calorimetry (DSC) studies indicate a continuous increase of the melting temperature (T_m) of the polymers with the decrease of CTFE content. The role of CTFE units as structural defects in the polymer chain was further clarified by Fourier transform infrared (FTIR) spectroscopy. The characteristic IR absorbance bands at 505, 614, and 1290 cm⁻¹ ascribed to *trans-gauche* (T_3GT_3G' and $TGTG'$) and all-*trans* ($T_{m>4}$) chain conformations, respectively, were used to calculate their relative fractions in the polymer.^{14,17} As presented in Figure

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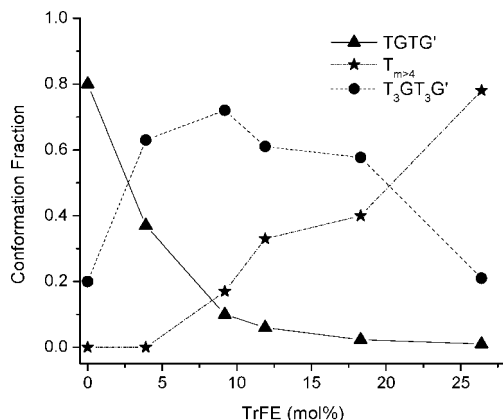


Figure 1. Fractions of TGTG', $T_{m>4}$, and T_3GT_3G' chain conformations in the PVDF based ferroelectric polymers.

1, the T_3GT_3G' and TGTG' conformations in the γ - and α -phases are steadily converted to the ordered all-*trans* conformation of the β -phase as more TrFE is incorporated into the polymer. The lengthened trans sequences in the polar β -phase increase the activation energy for dipole alignment and thus limit polarization responses, resulting in relatively low dielectric permittivities achieved in polymers 5–7 (see Table 1). On the other hand, polymers 3 and 4 exhibit the highest dielectric permittivity in this group of the polymers, thanks to the formation of smaller γ -crystals with T_3GT_3G' conformation that respond readily to the applied electric field. The reduction in dielectric permittivity for polymers 1 and 2 is attributed to a low amount of dipolar crystals from their low crystallinity.

An electrostatic pull-down method was used to measure the breakdown field, where a voltage ramp rate of 500 V/s was applied between a rounded electrode and the gold-coated polymer film.¹³ The electrical breakdown results were analyzed by a two-parameter Weibull distribution function:¹⁸ $P(E) = 1 - \exp[-(E/\alpha)^\beta]$, where $P(E)$ is the cumulative probability of failure occurring at the electric field $\leq E$.¹⁸ The scale parameter α reflects the $\sim 63\%$ probability for the sample to break down at the field α ; the shape parameter β evaluates the scatter of data. At least 25 data points were collected for each sample from which the α and β parameters were calculated. The α value correlates well with the amount of TrFE as summarized in Figure 2, where higher TrFE content corresponds to higher breakdown strength of the polymer. The β parameter also increases with the concentration of TrFE, indicating that the scatter of the breakdown values becomes smaller at higher TrFE contents. Since polymer 1 exhibits a very low modulus and largely varied breakdown strengths because of its amorphous nature, the results of polymer 1 are not included in Figure 2. The positive dependence of the dielectric strength on the TrFE concentration implies that the breakdown is mainly triggered by the electromechanical process. Electromechanical breakdown occurs when the stresses induced by the applied field exceeds

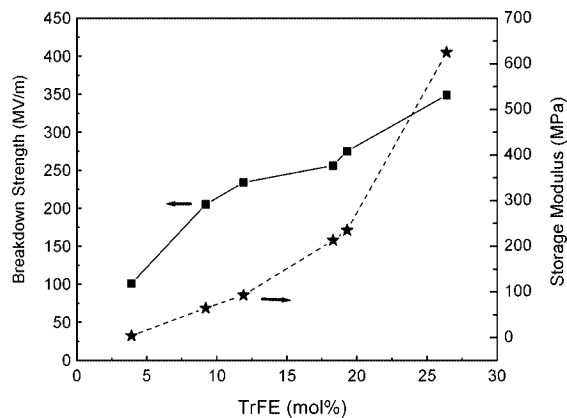


Figure 2. Breakdown strength and storage modulus of the polymers as a function of the TrFE concentration.

the yield stress of the polymers causing a rapid collapse of the electrodes inward and electrical discharge.¹⁹ As shown in Figure 2, the increase of TrFE content enhances the storage modulus of the polymers due to the increase of the crystallinity (see Table 1), which makes the polymer more resistant to the compressive force induced by the applied field and thus leads to a higher breakdown field. This is in sharp contrast to polyethylene based dielectric polymers where the dielectric strength increases with the decrease of crystallinity as a consequence of the electron avalanche breakdown mechanism.²⁰

Theoretical calculations have been performed to further verify the electromechanical breakdown mechanism operative in the ferroelectric polymers and to provide a quantitative assessment of the stress induced by the electric field. The electromechanical stress is generally composed of two components: $\sigma_{EM} = \sigma_{MW} + \sigma_E$, where σ_{EM} is the electromechanical stress, σ_{MW} is the Maxwell stress, and σ_E is the electrostrictive stress. The Maxwell stress arises from the Coulombic attraction of the electrodes carrying opposite charges. The electrostrictive stress defined here is the sum of all the electric-field-induced mechanical stresses in the material outside the Maxwell stress. The electrostrictive stress of P(VDF-TrFE) and P(VDF-TrFE-CTFE) polymers derives from conformation changes in the polymer chains under an electric field.^{7,21} These conformational changes can induce a crystal phase transformation that generates a compressive force along the longitudinal direction and can alter the c lattice dimension of the unit cell by up to $\sim 10\%$.

The breakdown strength of the polymers can be estimated when the total electromechanical stress equals the yield stress of the polymer. Table 2 lists the yield stresses (σ_y) of the polymers, which were determined using a linear force ramp to generate a stress versus strain curve where the yield stress was calculated from the intersection of the elastic and inelastic tangent lines. The Maxwell stress (σ_{MW}) can be calculated from the equation $\sigma_{MW} = \int q \, dE/A$, where q is charge, E is the electric field, and A is surface area. It should

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Table 2. Calculated and Experimental Breakdown Field (α), Yield Stress (σ_y), Electrostrictive Stress (σ_E), and Maxwell Stress (σ_{MW}) of the Polymers^a

polymer	α (exp.) (MV/m)	α (calc.) (MV/m)	σ_y (MPa)	σ_E (MPa)	σ_{MW} (MPa)
2	101 (± 3.14)	93.9	1.10		1.10
3	205 (± 6.65)	148	3.40		3.40
6	271 (± 5.22)	249	14.7	7.83	6.87
7	353 (± 2.41)	406	10.5	3.61	6.89

^a The parentheses indicate the 90% confidence interval of α .

be noted that many PVDF based ferroelectric polymers exhibit nonlinear polarization responses at high electric fields.¹⁰ Therefore, q was extrapolated from measurements of the electric displacement as a function of the electric field. For the Maxwell stress, a polynomial function was used to fit the polymers displaying linear dielectric behavior while a logarithmic fit was employed for the polymers exhibiting nonlinear dielectric behavior (see Supporting Information). The calculated Maxwell stresses of polymers **2**, **3**, **6**, and **7** are presented in Table 2. Since polymer **2** has a low crystallinity, it is anticipated that the electrostrictive contribution to the electromechanical stress will be minimal. Alternatively, the Maxwell stress is expected to play a dominative role because of its low mechanical modulus. This is exactly illustrated by the good agreement between the experimental result of polymer **2** and the breakdown strength calculated from the Maxwell stresses as shown in Table 2. As the TrFE content is increased to 9.2 mol % (polymer **3**), the Maxwell contribution alone underestimates the breakdown strength resulting in the least accuracy of all predictions. It is suspected that at this composition, the electrostrictive contribution begins to have a noticeable effect as the polymer becomes more crystalline and ferroelectrically active.

The electrostrictive response of the PVDF based ferroelectric polymers can be determined as $\sigma_{EM} = YQD^2$, where Y is the modulus, Q is the electrostrictive coefficient, and D is the electric displacement.²² Typically in the literature, this equation is referred to as the electrostrictive stress and includes both the Maxwell and the electrostrictive stress components.²³ To stay consistent with the definition in this paper, it will be called the electromechanical stress. The breakdown strength was calculated by equating the electromechanical stress to the yield stress and solving for the electric field in the above equation (see Supporting Information). Unfortunately, an estimate for the electrostrictive contribution for polymer **3** was not possible because of the lack of an electrostriction coefficient in the literature for that particular chemical composition. For polymers **6** and **7**, the calculated breakdown strengths of 249 and 406 MV/m

respectively match well to the measured values with an average error of $\sim 11\%$. It is interesting to note that polymers **6** and **7** have identical Maxwell stresses indicating that the electric displacements of the polymers are similar despite the different breakdown fields. However, as a result of different chain conformation contents, polymer **6** exhibits over twice the electrostrictive response as polymer **7** (Table 2). The small amount of CTFE in polymer **6** converts the normal ferroelectric into a relaxor ferroelectric via breaking up large ferroelectric domains into a variety of paraelectric and ferroelectric nanoscopic domains, where the nonpolar paraelectric phase consists of a mixture of *trans* and *gauche* bonds.²⁴ Under an electric field, the T_3GT_3G' conformation in polymer **6** transforms to polar ferroelectric domains with all-*trans* conformations which gives the relaxor its large electrostriction.²⁵ On the other hand, for polymer **7** with a much lower content of T_3GT_3G' conformation, that is, 21% versus 58% in polymer **6** (Figure 1), the prevalence of polar β phase with all-*trans* conformations limits its electrostrictive stress. Thus for relaxor ferroelectric polymers, the electrostrictive component produces a significant contribution to the electromechanical stress over normal ferroelectric polymers.

In conclusion, a series of PVDF based ferroelectric polymers were prepared for the first time for a systematic investigation of the correlation between the chemical structure and the dielectric breakdown strength. The observed positive dependence of breakdown strength on crystallinity and modulus suggests that the electromechanical breakdown mechanism is mainly responsible for electrical failure in these polymers. As also supported by theoretical calculations, the electromechanical stress is dominated by the Maxwell stress for the ferroelectric polymers with low crystallinity. For a ferroelectric relaxor, the electromechanical stress has contributions from both the Maxwell and the electrostrictive effects. The principle demonstrated in this work opens new opportunities for the development of high energy density polymers such as design of cross-linking networks or incorporation of molecular-scale inorganic components for improved electrical breakdown strengths. Efforts toward these directions are underway and will be reported in due course.

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Supporting Information Available: Experimental details for the synthesis and characterization (PDF). This material is available free of charge via the Internet at <http://pub.acs.org>.

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