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Enhanced Permittivity and Energy Density in Neat Poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) Terpolymer Films through Control of Morphology

O'Neil L. Smith,[†] Yunsang Kim,[‡] Mohanalingam Kathaperumal,[†] Matthew R. Gadinski,^{||} Ming-Jen Pan,[§] Qing Wang,^{||} and Joseph W. Perry^{*,†}

[†]School of Chemistry and Biochemistry, and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[‡]School of Materials Science and Engineering, and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

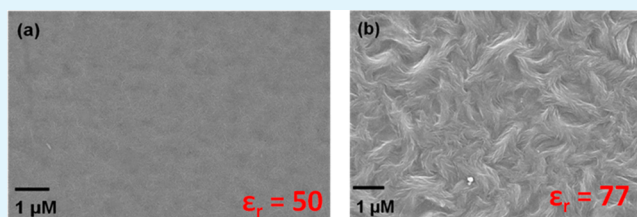
[§]Naval Research Laboratory, 4555 Overlook Avenue, Washington, D.C. 20375, United States

^{||}Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

Supporting Information

ABSTRACT: Polymer materials with large dielectric constants are desirable for the development of high energy density capacitors. We show that the dielectric properties of poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE)] can be improved by the use of processing conditions that favor formation of a highly crystalline morphology of the nonpolar α -phase. Through the use of spin coating, thermal treatment above the melting temperature, and quenching, we were able to attain a highly crystalline, α -phase rich morphology that has a quite large dielectric constant of 77 ± 10 at 1 kHz. The final morphology and phase composition of the terpolymer films depend strongly on the postprocessing thermal treatment and the quality of the solvent. Evaluation of the polarization behavior of the terpolymer films as a function of electric field reveal that the polymer exhibits a relaxor-ferroelectric behavior and has a substantial energy density of 9.7 J/cm^3 at fields of up to approximately $470 \text{ V}/\mu\text{m}$. Under millisecond pulsed charge–discharge measurements a 3-fold increase in energy density (27 J/cm^3) is obtained at high fields ($\sim 600 \text{ V}/\mu\text{m}$). Our study demonstrates that the processing conditions and morphology of fluorinated terpolymer films are controlling factors for achievement of high dielectric permittivity and energy density that are critical for high performance capacitors.

KEYWORDS: dielectric, terpolymer, capacitor, high permittivity, energy density



1. INTRODUCTION

The development of efficient, high-energy density dielectric materials for electrical energy storage is an enabling technology for the advancement of electronic devices and systems such as integrated circuits, field effect transistors, mobile devices, and hybrid electric vehicles.^{1–4} In this class of materials, polymeric systems are well recognized for their high breakdown strength ($>300 \text{ V}/\mu\text{m}$), low dielectric loss, and relatively fast charge/discharge speed.^{5–8} The stored energy density (U) in dielectric films is generally expressed as shown in eq 1:

$$U = \int E \, dD \quad (1)$$

where E is the applied electric field and D is the electric displacement. Therefore, in addition to having a high breakdown strength, a large electric displacement—which is obtained through high permittivity—is also desirable in order to maximize the storage capacity of dielectric materials.⁹

Unfortunately, most polymeric systems that are utilized in capacitor applications generally suffer from a low dielectric constant (<15) which, in turn, limits their achievable energy density. Biaxially oriented polypropylene (BOPP), for example, has remained the commercial state-of-the-art for numerous years because of its high breakdown strength ($\sim 730 \text{ V}/\mu\text{m}$); however, its low permittivity (~ 2.2 at 1 kHz) limits the energy density to about $1\text{--}3 \text{ J/cm}^3$.^{10,11} More recently, aromatic polythiourea and polyurea based polymers have been shown to exhibit energy densities as high as 22 J/cm^3 , as well as a very high breakdown field of $1000 \text{ V}/\mu\text{m}$.^{12–14}

Poly(vinylidene fluoride) (P(VDF)) based co- and terpolymers offer potential alternatives for achieving high energy density dielectric films owing to both their high permittivity

Received: April 1, 2014

Accepted: May 29, 2014

and dielectric strength.¹⁵ However, while these systems have substantial energy storage capacity, the P(VDF) homopolymer and various P(VDF) copolymers suffer from large polarization hysteresis, which precludes efficient extraction of the stored energy.⁹ One method of mitigating the large hysteresis is to prepare terpolymers that incorporate bulky monomeric groups into the main chain of P(VDF)-based polymers that serve as molecular defect sites and promote a reduction in the Curie transition temperature, thereby facilitating the paraelectric–ferroelectric phase transition¹⁶ and allowing high dielectric constants under ambient conditions. Such results have been obtained for terpolymers prepared by the incorporation of chlorotrifluoroethylene (CTFE) monomer units into the copolymer poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) thereby converting a ferroelectric system into one that is a relaxor ferroelectric, with relatively large permittivity and reduced hysteresis.^{17–20} Therefore, in addition to the high breakdown strength and large dielectric constant of P(VDF)-based terpolymers, their ferroelectric relaxor behavior makes them promising candidates for high-energy density capacitors.

In addition to the chemical composition of the polymeric backbone, the dielectric properties of P(VDF)-based polymers can be significantly influenced by their crystalline structure and morphology.²¹ These properties are highly dependent on the processing conditions used to prepare the films. Processing methods have been developed that allow for the controlled formation of various crystalline polymorphs and, consequently, the ability to tailor the microstructure of the polymers for various electroactive applications.^{22–25} Considerable experimental and theoretical work on P(VDF)-copolymers incorporating chlorotrifluoroethylene (CTFE) indicates that the non-polar α -phase is the more thermodynamically stable form, for CTFE content lower than 17%, with the polar β -phase being about 180 meV higher in energy.^{15,17–20} The conversion of α -phase to β -phase has been examined theoretically for P(VDF-CTFE), and a low barrier pathway involving an α -phase \rightarrow γ -phase transition (barrier height \sim 50 meV) followed by a γ -phase \rightarrow β -phase (barrier height \sim 100 meV) transition has been identified.^{26,27} These relatively low barriers facilitate the electric field induced conversion from α -phase \rightarrow β -phase that dominates the polarization response, yielding relaxor ferroelectric behavior. Accordingly, processing protocols that increase the crystalline α -phase and reduce the amorphous content could favorably impact the permittivity, the energy storage capacity, and the energy extraction efficiency.^{9,16,26–28}

In this paper, we report on the dielectric properties of a poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE)] terpolymer thin film with a highly crystalline, fibrillar, α -phase morphology as obtained through spin coating and a subsequent thermal treatment process. The terpolymer investigated herein has a composition of 78.8 mol % VDF, 7.2 mol % TrFE, and 14 mol % CTFE, which has been reported to have a permittivity of \sim 50 at 1 kHz.^{19,29} While this terpolymer system has typically been processed by drop casting, we show that an alternative processing method, i.e. spin coating of films followed by high-temperature thermal treatment (above the melting temperature, T_m) and then quenching from the melt under ambient conditions, allows for a marked enhancement in dielectric constant, as well as a very high energy density. Furthermore, we present a detailed study of the morphology and its impact on the dielectric properties that are relevant for

capacitor applications. A thorough investigation of the energy storage capacity via polarization–electric field (P–E) and pulsed charge–discharge (C–D) measurement on the films is also presented.

2. EXPERIMENTAL SECTION

2.1. Thin Film Processing. In the first processing method (**M1**), 1.5–2 mL of a 10 wt % terpolymer solution in ambient atmosphere equilibrated *N,N*-dimethylformamide (DMF) was filtered, cast onto a glass slide, and then dried at 72 °C in a vacuum oven for 2 h. The film was then cooled to room temperature prior to its removal from the glass substrate by a “lift-off” process with distilled water and then placed in a vacuum oven at 50 °C. After 2 h the films are subjected to further annealing at 65 °C, 14 °C below its melting temperature, for 5 h prior to electrode deposition. In the second method (**M2**), the terpolymer was dissolved in dry DMF and stirred at room temperature for at least 8 h. Thin films were then prepared from the polymer solution by spin-coating \sim 1.5 mL onto oxygen plasma (Plasma Etch, 2 min) treated aluminum bottom electrodes on glass substrates. The spin-coated films were then soft baked at 80 °C for \sim 10 min and then heated overnight under vacuum at 120 °C, followed by quenching at ambient temperature. In order to evaluate the dielectric properties of the polymer, parallel plate capacitors were fabricated by depositing aluminum top electrodes on the spun film.

2.2. Thin Film Characterization. The morphology of the films was characterized by both scanning electron (Zeiss Ultra 60) and atomic force microscopies (Agilent N9524B). Further characterization of the films was performed using Fourier transform infrared (FT-IR, PerkinElmer Spectrum 1000) spectra and X-ray diffraction (XRD, PANalytical, X'Pert PRO Alpha-1). Profilometry (Dektak 6M, Veeco) was used to determine the thickness of the films.

2.3. Device Fabrication and Characterization. Parallel plate capacitors of the terpolymer films were fabricated in order to evaluate their dielectric properties. For films prepared via the method **M1**, a 25 nm thick gold electrode was sputtered onto both sides of the terpolymer films (Denton Vacuum Desk IV sputter coater) and their dielectric properties were characterized on an HP LCR meter (HP 4284A). In the case of the films prepared using method **M2**, circular aluminum top electrodes (0.25 and 1.0 mm²) were deposited on the spin-coated films through a shadow mask by using a thermal evaporator (Kurt J. Lesker PVD75, rate = 3 Å s^{−1}). Automated dielectric characterization of the devices was performed using a LabVIEW software interface. Samples with an electrode area of 0.25 mm² were used to perform dielectric strength measurements through the use of a Keithley 248 power supply by ramping the applied voltage from 50 V_{DC} at a rate of 10 V s^{−1}, until catastrophic failure, as evidenced by a spiking of the current, from the device under test. An Agilent 4284 LCR meter was used to measure the frequency-dependent permittivity and dissipation factor over the range of 20 Hz to 1 MHz. Unipolar P–E measurements were conducted using a high voltage amplifier (Trek 610-D) in conjunction with a charge integrator circuit under unipolar sawtooth waveforms with a period of 0.01 s. The energy storage capacity of the thin films was measured at multiple electric field strengths using a C–D test circuit and making use of an electrode with an area of 1 mm².^{30,31}

3. RESULTS AND DISCUSSION

3.1. Morphological Characterization of the Thin Films.

The terpolymer films were imaged using scanning electron microscopy (SEM). Figure 1 presents the SEM top surface image of the films **A** and **B** that were prepared from the as-synthesized terpolymer using **M1** and **M2**, respectively.

The SEM images reveal a qualitative difference in the morphology of the two terpolymer films. The images show distinct crystalline and amorphous phases in both films, but the number density and apparent size of the crystalline domains observed in film **B** are much more pronounced. This suggests

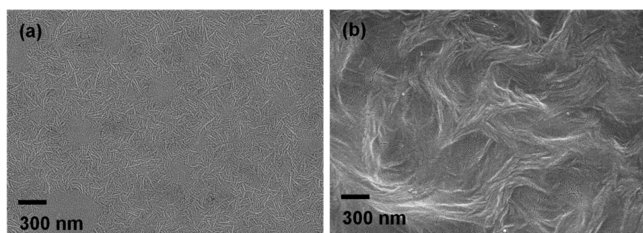


Figure 1. Top surface SEM image of neat P(VDF-TrFE-CTFE) films: (a) film A and (b) film B.

that thermal treatment of the terpolymer at 120 °C, well above its T_m of ~ 79 °C,¹⁹ and the subsequent nucleation and crystallization during the relatively slow quenching process are key to the formation of the dense, fibrillar crystalline morphology observed in film B. This difference in morphology can have significant effects on the dielectric properties of the films, as the character of the crystalline domains are known to be responsible for the high permittivity in P(VDF) based polymers.³² Additional larger area SEM images are provided in Figure S1. AFM analysis of the films provided the RMS surface roughness values of 1.5 and 3.6 nm for films A and B, respectively (Figure S2).

3.2. Analysis of the Phase Composition of the Thin Films.

Figure 2 shows the room temperature X-ray diffraction

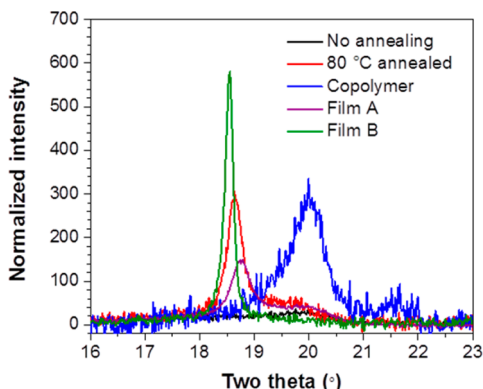


Figure 2. XRD (200, 110) reflections of terpolymer Films A and B. Films that represent intermediary steps in the M2 process (i.e., no annealing vs. annealing at 80 °C for 10 min) are also included. The spectrum of a copolymer p(VDF-TrFE) 70:30 mol % film is also shown. All the spectra were normalized for thickness.

(XRD) patterns of films A and B. An analysis of each sample was performed using a Gaussian peak fitting analysis with Origin software, and the results are presented in Table S1. Film B showed a single diffraction peak at approximately 18.5° (equivalent to a crystal interchain spacing of 4.75 Å), which is consistent with the angle of the reflection typically observed for the nonpolar α -phase in the terpolymer, perhaps along with a small amount of the polar γ -phase.^{16,33} The XRD of a copolymer poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] 70/30 mol % was included for comparison and was found to have a interchain crystal spacing of 4.45 Å.

This shows that the terpolymer has a larger interchain distance, which has been attributed to the incorporation of the bulky, chlorinated monomer into the polymeric backbone, due to chlorine having a greater van der Waals radius than fluorine.^{16,33} Film A shows a (020) diffraction peak at a 2θ of 18.8°, which we attribute to the overlap of the (100) and (020)

reflections of the α -phase. A shoulder observed at a 2θ value of 19.4° was assigned to overlapping α -phase (110) and β -phase (110) reflections. The higher angle diffraction appears in the same region where the ferroelectric β -phase of the P(VDF-TrFE) ($2\theta \sim 19.8^\circ$) is typically observed for copolymers with VDF content between 50 and 80 mol %.^{32,34} On this basis, we conclude that the M2 processing technique gives rise to a predominance of nonpolar α -phase domains, along with the amorphous phase, in the terpolymer, while M1 gives a mixture of polar and nonpolar domains, again with the amorphous phase. The dominance of the α -phase in the terpolymer is consistent with the thermodynamic stability of the α -phase in PVDF copolymers, such as p[VDF-CTFE], with CTFE volume fractions below 17%, as determined through theoretical calculations.²⁴

In order to track the evolution of crystal formation associated with M2, XRD data of films that represented intermediate steps in the M2 process were evaluated. The film that was not melt processed (i.e., spin coated and allowed to dry at room temperature) showed a small amount of the β -phase but was mostly amorphous in nature. This suggests that in the absence of annealing the polar phase seems to be the thermodynamically stable crystal phase in the terpolymer. Annealing at 80 °C for 10 min provided a film with overlapping α -peaks (110 and 020) at 18.9° and 18.6°, respectively. Subsequent annealing at 120 °C overnight gives a predominantly nonpolar (020) microstructure.^{16,33} This demonstrates that the high temperature treatment followed by quenching is highly effective in promoting high α -phase content and relaxor ferroelectric behavior in the terpolymer.

Assessment of the coherence lengths of the crystallites (L) of the various phases was determined via XRD using the Scherrer equation (eq 2)

$$L = 0.9\lambda/B \cos \theta \quad (2)$$

where λ is the X-ray wavelength, B is the full width at half-maximum in radians, and θ is the angular position of the diffraction peak.³⁵ The results of the Scherrer analysis are shown in Table S1. The size of crystallites in the nonpolar phase progressed from being nonexistent under room temperature drying conditions to 30.2 nm after high temperature treatment at 120 °C followed by quenching. In the polar phases of the differently annealed films, the interchain spacing of the films remains relatively constant regardless of thermal treatment while their coherence lengths show a small difference between the annealed and nonannealed samples. It is evident from these results that not only is the formation of the nonpolar phase promoted by quenching from high temperature but the size of the crystallites formed increases with the temperature of the thermal treatment.

FT-IR measurements were performed on films A and B in order to provide molecular structural information (Figure S4). The vibrational spectrum of film A shows three characteristic absorption bands at 505, 616, and 1290 cm^{-1} which are attributed to the CF_2 bending mode in the TTTG⁺TTTG⁻ (trans (T), gauche (G)) conformation of the γ -phase, the α -phase TG⁺TG⁻ conformation, and the CF_2 stretching vibration of the all-trans ($T_{m>4}$) β -phase, respectively.^{18,29} Film B shows a similar crystalline composition with the exception of a diminished γ -phase. For comparison, the FT-IR spectrum of P(VDF-TrFE) prepared using M2 is also presented. The copolymer film is comprised solely of a highly all-trans β -phase suggesting that this polar phase is the thermodynamically stable

conformation in the copolymer.^{16,34,36} Therefore, while the introduction of CTFE units into the copolymer backbone contributes to the destabilization of the polar phase it promotes the formation of the α -phase and the consequent ferroelectric relaxor behavior.

3.3. Evaluation of Dielectric Permittivity and Failure Statistics. The effect of the processing method on the dielectric constant and failure statistics of the films was investigated, and the results are presented in Table 1. Owing

Table 1. Dielectric Characteristics of Neat Terpolymer Films A and B Prepared Using the Two Methods

	film A [M1]	film B [M2]
thickness (μm)	20–40	3.9 ± 0.1
relative permittivity (at 1 kHz)	$\sim 50 \pm 5$	77 ± 10^a
dielectric strength ($\text{V}/\mu\text{m}$)	96 ± 40^b	261 ± 62^b
Weibull parameter (β)	2.9 ± 0.2^b	5.6 ± 0.2^b

^aThe error bars associated with the dielectric measurements reflect the standard deviation of the average values. ^bPropagation of error from Weibull analysis was used to determine the uncertainty in Weibull parameter (β) and dielectric strength.

to the statistical nature of dielectric breakdown, the failure analysis was performed on the films using Weibull statistics.^{37,38} In this approach the cumulative probability of failure (P_F) at an applied electric field (E) is given by eq 3.

$$P_F(E) = 1 - \exp[-((E - \gamma)/\alpha)^\beta] \quad (3)$$

where γ is the threshold electric field below which no breakdown occurs, α is the estimated value of E at which the cumulative probability is 63.2%, and β is the Weibull parameter which represents the scattering in the measured dielectric strength values.

As mentioned above, films A and B represent samples prepared from the pristine/as-synthesized terpolymer using M1 and M2, respectively. Dielectric spectroscopy measurements reveal that the film prepared using M2 has a higher permittivity than those prepared via M1. Film B has a rather high dielectric constant of 77 (at 1 kHz) which, to the best of our knowledge, is the highest relative permittivity value reported for a neat organic fluoropolymer material. The increase in dielectric constant for B relative to film A is believed to originate from the increase in the amount of crystalline α -phase domains, as indicated by the microstructure in the SEM images (Figure 1),

which are able to undergo substantial polarization in the presence of an electric field.³² As mentioned above, the mediation of the field-induced conversion of the α -phase to β -phase by the γ -phase in the polymer matrix facilitates a reduction in the activation barrier for the phase transition and, consequently, a more rapid reorientation of CF_2 groups, thereby affording high permittivity at room temperature.¹⁹ It is important to note that when film A is redissolved in dry DMF and processed into films via M2 (film C) the high permittivity observed in film B is reproduced (Table S2) thereby demonstrating the consistency of the processing methods. However, while films A and B exhibit marked differences in permittivity they both demonstrate relatively low dielectric loss ($\tan \delta < 0.04$) at 1 kHz.

The impact of solvent quality as well as polymer solution aging on the dielectric performance of the films was also examined, and the results are presented in Table S2. Films E and F represent samples prepared using atmosphere equilibrated and dry DMF, respectively. The results show a reduction in the permittivity, dielectric strength, and Weibull modulus of film E, relative to film B, although both films were prepared using M2 which indicates that the presence of moisture in the DMF is deleterious to the properties. While the permittivity and E_B of film F did not improve relative to film A under the same preparation protocol (M1), the Weibull modulus showed significant improvement in film F. Furthermore, if the solution used to prepare the film is allowed to age for a period of four months under ambient conditions prior to making films using M2 (film D) the dielectric properties are diminished relative to film B. Based on these findings it is evident that the use of anhydrous solvent is critical for obtaining high dielectric constant and dielectric strength terpolymer films with moderate Weibull moduli. Taken together, these results indicate that the details of the method used to prepare terpolymer films have a marked impact on the morphology, crystallinity, and consequent electrical performance of the dielectric material. Specifically in the case of the terpolymer, the dielectric properties can be maximized by making films from freshly prepared, dry DMF solutions using the M2 method reported here.

3.4. Energy Density Characterization. Polarization–electric field (P–E) measurements were performed on film B, and the results are shown in Figure 3. The unipolar P–E response of the film at fields up to $\sim 470 \text{ V}/\mu\text{m}$ are shown in Figure 3a; the loops show relatively narrow hysteresis, small

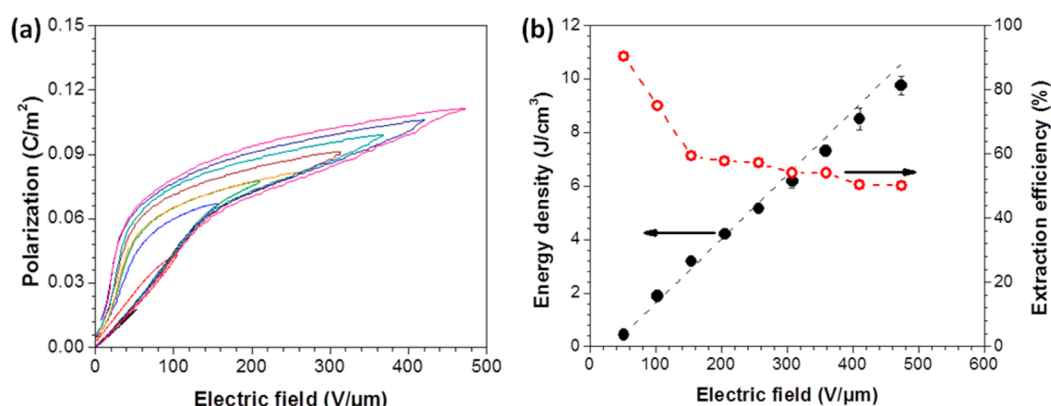


Figure 3. Unipolar P–E curves of film B prepared from the as synthesized terpolymer using M2 (a) and the corresponding recoverable energy density and extraction efficiency curves (b). Dashed lines serve as guides for the eye.

remnant polarization, and relaxor ferroelectric behavior, all of which are desirable properties for achieving efficient, high energy density storage materials. However, the gradual widening of the loops with increasing field indicates that some energy loss is being incurred from conduction and/or charge injection at high fields.^{39,40} Additionally, the P–E curves also show a reduction in the polarization response at ~ 150 V/ μm which is evidence of displacement saturation. Figure 3b shows the values of the discharged energy density and extraction efficiency as a function of the applied field as determined from the integration of the areas between the charge and discharge curves of the P–E loops and the ordinate.⁹

Unlike linear dielectrics, which show a quadratic energy density dependence with electric field, the terpolymer exhibits near-linear behavior as the field is increased. In addition, the extraction efficiency appears to taper off rapidly prior to the onset of dielectric saturation at ~ 150 V/ μm . For example, film B which gave a maximum extractable energy density of ~ 9.7 J/ cm^3 at ~ 470 V/ μm did so only with an extraction efficiency of about 50%. It is clear that the onset of early polarization saturation (i.e., saturation at a field that is much lower than the breakdown field strength) and conduction/leakage at high fields imposes a limit on the achievable energy density and the extraction efficiency.⁹ This serves to reinforce the notion that consideration must be given to extraction efficiency when assessing the discharged energy density for various capacitor applications. Therefore, it may be advantageous to develop high permittivity terpolymer systems in which the threshold for dielectric saturation is much closer to the breakdown field of the film. The impetus behind the synthesis of the terpolymer was the introduction of a bulky CTFE monomeric group into the main chain of P(VDF-TrFE) in order to reduce the size of the crystalline β -phase domains and simultaneously lower the energy barrier for ferroelectric–paraelectric phase transition giving rise to a high dielectric constant.³⁶ Furthermore, in order to delay the onset of early dielectric saturation the polymer system would have to be optimized such that it has a lower permittivity value that allows for the energy density to be maximized at higher field.⁹ It therefore stands to reason that a systematic study of the chemical composition of the bulky monomer as well as the crystallization behavior of the resulting terpolymer is needed to properly understand and control the relaxor ferroelectric behavior.

Key to the development of fluoropolymer energy storage materials are the design and processing of dielectrics that are capable of rapidly storing and nearly instantaneously delivering large amounts of energy in an efficient manner.

We investigated the energy density of the terpolymer films with charge–discharge (C–D) measurements to evaluate the performance of film B under pulsed conditions as shown in Figure 4. Film B shows a maximum extractable energy density of ~ 27 J/ cm^3 which is almost three times as high as that achieved under P–E conditions. It is also important to highlight the fact that, under pulsed conditions, fields up to ~ 604 V/ μm can be achieved prior to the occurrence of catastrophic failure, which is markedly higher than the fields reached under the longer time scale of breakdown testing. Since, both C–D and breakdown testing are performed until catastrophic failure, the superior performance of the terpolymer film under pulsed conditions is believed to be a result of the ability of the material to withstand electrical and mechanical stress developed in the

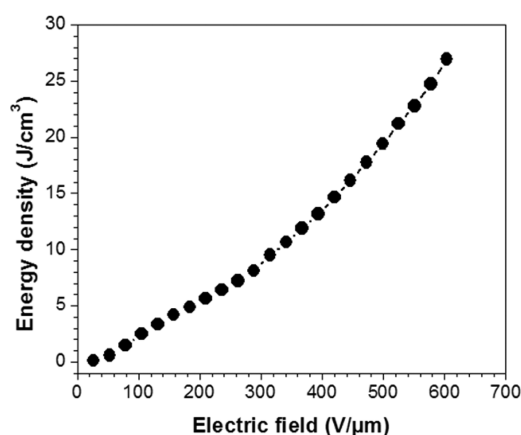


Figure 4. Discharged energy density of film B as determined from charge–discharge measurements. Standard deviation (1σ) in the measurement of the energy density was less than 0.5 J/ cm^3 .

dielectric during measurement, as well as the differences in the time scales of the techniques.

4. SUMMARY

We have developed a processing method that yields p(VDF-TrFE-CTFE) films, with a highly crystalline, fibrillar morphology dominated by the nonpolar α -phase, that leads to an enhanced dielectric constant of 77 ± 10 at 1 kHz, associated with the reversible field-induced phase transition between paraelectric and ferroelectric phases. Under P–E analysis, the highly crystalline α -phase terpolymer films obtained through the improved processing method show a sizable high-energy density (9.7 J/ cm^3) and moderate charge extraction efficiency at high fields (<470 V/ μm). Significantly, under millisecond pulsed charge–discharge measurements an almost 3-fold enhancement in the maximum energy density (27 J/ cm^3) was realized at a maximum electric field of >600 V/ μm . Taken together, these results demonstrate the importance of the processing conditions that increase the volume fraction of α -phase crystallites for high electrical energy storage and pulsed-power applications for this class of ferroelectric fluoropolymers.

■ ASSOCIATED CONTENT

Supporting Information

Scanning electron microscopy and atomic force microscopy images; tabulated XRD data; FT-IR spectra; and leakage current data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: joe.perry@gatech.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research (Grant No.: N000141110462, Capacitor Program) and the Air Force Office of Scientific Research (FA9550-10-1-0555, BioPAINTS MURI). The authors thank Prof. Kippelen for use of instruments in his lab. O’N.L.S. and Y.K. thank the Center for Organic Photonics and Electronics for COPE Fellowships.

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