Effects of Rigid Amorphous Fraction and Lamellar Crystal Orientation on Electrical Insulation of Poly(ethylene terephthalate) Films

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TOC Graphic

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Abstract

In response to the stringent requirements for future DC-link capacitors in electric vehicles (EVs), it is desirable to develop dielectric polymer films with high temperature tolerance (at least 105 °C) and low loss (dissipation factor, $tan\delta < 0.003$). Although the biaxially oriented poly(ethylene terephthalate) (BOPET) film has an alleged temperature rating of 120 °C, its dielectric performance in terms of breakdown strength and lifetime cannot satisfy the stringent requirements for power electronics in EVs. In this work, we carried out a structure-electrical insulation property relationship study to understand the working mechanism for various PET films, including a commercial BOPET film, an amorphous PET (AmPET) film, and two annealed PET films (AnPET, i.e., cold-crystallized from AmPET). Structural analyses revealed a uniform edgeon crystalline orientation in BOPET with the a^* axis in the film normal direction. Meanwhile, a high content of the rigid amorphous fraction (RAF) was identified for BOPET, which was resulted from biaxial stretching during processing. On the contrary, AnPET films had a random crystal orientation with lower RAF contents. From dielectric breakdown and lifetime studies, the high crystallinity AnPET film exhibited better electrical insulation than BOPET, and AmPET had the worst electrical insulation. Electrical conductivity results revealed that the high RAF content in BOPET led to high breakdown strength and long lifetime only at low temperatures (<100 °C). Meanwhile, PET crystals were more insulating than the amorphous phase, whether mobile, rigid or glassy. In particular, the flat-on lamellae in the AnPET film were more effective than the edgeon lamellae in BOPET to block the conduction of charge carriers (electrons and impurity ions). This understanding will help us design high-temperature semicrystalline polymer films for DClink capacitors in EVs.

Introduction

A direct current (DC)-link capacitor is an important passive component of power electronics in electric vehicles (EVs), which connects the DC/DC converter or battery and the DC/alternating current (AC) inverter for powerful electric drive.¹ Compared to ceramic^{2, 3} and electrolytic capacitors,⁴ polymer film capacitors have advantages of high ripple current, high voltage, low loss, and self-healing capability,⁵⁻⁷ and are proven to be the most suitable technology for high voltage, high temperature, and high ripple current power electronics used in EVs.^{1, 8} Among many polymer film capacitors, biaxially oriented polypropylene (BOPP) film capacitors are the state-of-the-art technology.^{5, 6, 9, 10} The thinnest BOPP film is about 2.5 µm thick without sacrificing any dielectric performance in terms of breakdown strength and lifetime.^{1,9} Thinner polymer films increase the capacitance density at the capacitor level and save material costs for However, BOPP film capacitors have a low temperature rating of only 85 °C, capacitors. significantly lower than the 140 °C ambient temperature in the insulated gate bipolar transistor- or SiC-based inverter unit. As a result, a 60-70 °C water cooling system must be used to keep the BOPP film capacitors below 85 °C.¹ This is largely attributed to the 30-50% voltage derating because of the deteriorated breakdown strength and lifetime of the BOPP film. In addition, BOPP has a low dielectric constant and thus the film-level energy density is low.

In response to the stringent requirements for DC-link capacitors in EVs, it is desirable to develop a high temperature dielectric film that possesses good dielectric properties as BOPP (i.e., low dielectric loss, high breakdown strength, and long lifetime). Note that the film thickness should be comparable to that (2-3 μ m) of the state-of-the-art BOPP film in order to keep a high capacitance density for low material costs. In the past decade, many research efforts have been carried out to search for next generation polymer dielectrics.¹¹⁻¹⁸ However, most of them focus

on increasing dielectric constant and energy density for polymer or polymer nanocomposite films. One should be cautious about pursuing high polarization, because more polarization mechanisms (e.g., orientational, interfacial, and space charge polarizations) cause higher dielectric losses.¹² In practical capacitor applications, when the dissipation factor (tan δ) is above 0.003, polymer film capacitors will suffer from high heat generation during operation.⁵ Therefore, pursuing low dielectric loss while enhancing high temperature tolerance should be the first priority for DC-link capacitors in EVs.

Among various high temperature capacitor films, such as poly(phenylene sulfide) (PPS),^{19,} ²⁰ polycarbonates (PC), and poly(ether imide) (PEI),²¹ poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) are the most promising, because they can also be readily processed into high quality thin films down to 1 μm using biaxial orientation via the tenter-line processing.²² Their dielectric constant is about 3.3-3.5; therefore, the energy density is about 1.5 times that of BOPP. Meanwhile, the temperature ratings are 120 °C for biaxially oriented PET (BOPET)⁵ and 150 °C for biaxially oriented PEN (i.e., BOPEN).²³ Despite good dielectric performance at low temperatures (<80 °C), BOPET films have been practically proven not suitable for DC-link capacitors in EVs, because they exhibit a higher electric conduction and a lower breakdown strength/lifetime than BOPP films at high temperatures. The fundamental understanding for this observation is still lacking.

In this study, the structure-electrical insulation property relationship was studied for various PET films, including a commercial BOPET film, a melt-extruded amorphous PET (AmPET) film, and two cold-crystallized PET films (i.e., AmPET annealed at 120 and 190 °C, denoted as AnPET-120 and AnPET-190, respectively). From both structural and thermal analyses, crystallinity, content of rigid amorphous fraction (RAF),²⁴⁻²⁶ and crystalline lamellar orientation

were determined for these PET films. Correlating to these structural parameters, dielectric breakdown strength and lifetime were investigated for different PET films. Effects of RAF and crystal orientation were discussed in order to understand the primary reason for the unsatisfied dielectric performance of BOPET, especially at elevated temperatures. This knowledge will help us to develop new low loss BOPEN films for even higher temperature rating up to $150 \,^{\circ}C.^{23, 27}$

Experimental Section

Materials and Sample Preparation. The BOPET film (6.0 μ m) was provided by SBE, Inc. (Barre, VT). PET resin was purchased from Eastman Chemical Co. (Eastar 6763, Kingsport, TN), and was dried under vacuum at 80 °C for 2 d prior to melt extrusion. The amorphous PET (AmPET) film was melt-cast at 260 °C with a film thickness of ca. 10 μ m. The AnPET films were prepared by annealing the AmPET above the glass transition temperature (T_g) for cold crystallization. Two temperatures, above (i.e. 190 °C) and below (i.e. 120 °C) the peak coldcrystallization temperature (i.e., 145 °C), were chosen to obtain randomly oriented PET crystals. The annealing time was set as 2 h to complete the cold crystallization at both temperatures (see Figure S1 and discussion in the Supporting Information). This result was consistent with those reported before.^{28, 29}

Characterization Methods and Instrumentation. ¹H solid-state nuclear magnetic resonance (ssNMR) echo (90- τ -90- τ) experiment was conducted using a Bruker AVANCE III 300 MHz instrument equipped with a 4 mm double resonance probe. The ¹H resonance frequency is 300.1 MHz. The ¹H 90° pulse was 2.3 µs and the echo delay time (τ) was set to 7 µs (or 200 µs) to record all the proton signals.

Conventional and temperature-modulated differential scanning calorimetry (DSC and

TMDSC) experiments were performed on a TA Q2000 DSC (TA Instruments, New Castle, DE) under a nitrogen flow at 50 mL/min. For conventional DSC, the scanning rate was 10 °C/min. For TMDSC, the protocol with a heating rate of 2 °C/min and a modulation amplitude of 0.32 °C for every 60 s was chosen. This protocol has been reported to show high sensitivity and resolution,³⁰⁻³² and thus is suitable for studying microstructure evolution in semicrystalline polymers.

Two-dimensional (2D) small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements were conducted at the beamline BL16B1 of the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). The monochromatic X-ray beam operated at a wavelength of 0.124 nm with a beam size of 300×500 µm², and the sample-to-detector distances for WAXD and SAXS experiments were 131 and 1866 mm, respectively. The 2D SAXS and WAXD images were collected with an X-ray charge-coupled device (CCD) detector (Model SX165, resolution of 2048×2048 pixels, Rayonix Co. Ltd., Evanston, IL).

Breakdown strength of PET films was measured using a home-made fixture. Aluminum electrodes of 50 nm thickness and 4.57 mm² area were thermally deposited on both sides of the film. High voltage was supplied by a Quadtech Guardian 20 kV HiPot tester (Marlborough, MA), and was ramped at a speed of 500 V/s until dielectric breakdown. All breakdown tests were carried out in silicone oil to avoid surface corona discharge. At least forty repetitions were measured for each sample for perform the Weibull statistical analysis.

Broadband dielectric spectroscopy (BDS) measurements were performed on a Novocontrol Concept 80 broadband dielectric spectrometer with temperature control (Montabaur, Germany). The applied voltage was $1.0 V_{rms}$ (i.e., root-mean-square AC voltage). Temperature scans were performed from -100 to 180 °C at a heating rate of 2 °C/min with frequency ranging from 1 Hz to 1 MHz. Frequency scans were performed with frequency from 10^{-3} Hz to 10 MHz under a constant temperature. 20 nm gold (10 mm diameter) was evaporated on both sides of the PET films as electrodes with an area of 78.5 mm².

Low-field (<120 MV/m) leakage current measurements were performed using a Novocontrol Concept 80 broadband dielectric spectrometer equipped with a Keithley 6517B electrometer. Immediately after the application of a DC voltage, the leakage current was recorded for 30 min at each temperature. The steady-state current was used to calculate the bulk conductivity: $\sigma = J/E$, where J is the current density and E is the applied electric field. To avoid the interference of discharge currents and to minimize ionic conduction, the leakage current experiments were conducted with DC voltage from low to high and temperature from high to low. 50 nm thick aluminum (10 mm diameter) was evaporated on both sides of the film sample. High-field (up to 600 MV/m) leakage current was measured by a Premiere II ferroelectric tester (Radiant Technologies, Inc., Albuquerque, NM) equipped with a Trek 10/10B-HS high voltage amplifier (0-10 kV AC). Tests were performed in silicone oil at different temperatures. Aluminum electrodes with 50 nm thickness and 5.15 mm² area were coated on both sides of the film. A period of 21 s was used as both the soak and measurement time to lower the transient current and avoid breakdown during tests.

Lifetime measurement was carried out using a self-built apparatus. A schematic representation of the electric circuit is shown in Scheme S1. High DC voltage was supplied using a Matsusada AMT-20B10-B high voltage amplifier. A thin layer of gold (ca. 5 nm) was evaporated onto both sides of the film with an overlapping area of 78.5 mm². It was important to keep the gold electrode thin (i.e., semi-transparent to light) in order to achieve self-healing.^{1, 7, 33} The film sample was immersed in silicone oil to avoid surface corona discharge.

Temperature was controlled using an Arex-6 Conn. Pro System (Chemglass, Vineland, NJ). A National Instruments card (NI USB-6002, Austin, TX), which was in parallel with a 4 k Ω resistor, was used to record the breakdown event as a function of time using LabVIEW. Sample capacitance was measured before and after each lifetime test. Capacitance change as a function of time was estimated by assuming each breakdown caused the same decrease in capacitance for the sample.



Figure 1. Baseline normalized solid state ¹H NMR at different temperatures: (A) 100 °C, (B) 120 °C, and (C) 140 °C. The echo delay time (τ) was set to 7 µs. After peak-fitting, the f_{RAF} , f_{MAF} , and f_{cryst} are shown in the plot (C).

Results and Discussion

Determination of RAF Content in Various PET Films. For semi-rigid crystalline polymers, the three-phase model is commonly used to describe the microstructure, i.e., the crystalline phase, the mobile amorphous fraction (MAF) and the RAF between the crystalline phase and the MAF.^{24, 25, 29} Especially, large-scale plastic deformation during mechanical stretching can lead to oriented amorphous chains stemming out from the oriented crystals.²⁵ ssNMR spin-diffusion experiments have been used to provide information about microdomains with different chain mobilities in heterogeneous polymers.^{34, 35} In this study, ¹H ssNMR was used to demonstrate the existence of RAF in various PET films. The baseline-normalized ¹H NMR

spectra at different temperatures are shown in Figure S2 (T < 100 °C) and Figure 1 (T \ge 100 °C). Below 70 °C (Figure S2), a very broad ¹H peak was observed, because all samples were below their T_g. At 90 °C (Figure S2), AmPET exhibited a narrower ¹H peak, indicating enhanced chain mobility above its T_g at 76 °C. In order to observe distinct differences in molecular mobility for the three components, the test should be conducted above the dynamic T_g at the time scale of the ssNMR experiment.³⁶

When the temperature increased to above 100 °C, chain mobility in the AnPET and BOPET films started to enhance. Especially for the temperature above 120 °C, the AnPET showed a sharp resonance peak compared to BOPET (Figure 1), indicative of the existence of microdomains with a higher chain mobility. Deconvolution of the ssNMR spectra at 140 °C was performed to obtain contents of three components (f_{cryst} , f_{RAF} , and f_{MAF}); see Figure S3. As shown in Figure 1C, BOPET had a significantly higher f_{RAF} and thus a lower f_{MAF} than AnPET-120 and AnPET-190 at 140 °C. Meanwhile, the full-width at half maximum (FWHM) for RAF in BOPET was much larger than that in AnPET, i.e., 14.2 kHz for BOPET vs. 10.9 kHz for AnPET-190 and 11.9 kHz for AnPET-120, indicating that the RAF in BOPET had a lower chain mobility than that in AnPET. Note that ssNMR cannot accurately determine the content of three components, because the peak shape also depended on the echo delay time (e.g., 7 µs for Figure 1). It was observed that at a longer echo delay time of 200 µs, signals from the rigid and semi-rigid components would be completely screened out, as shown in Figure S4. Below, we used TMDSC and WAXD to determine the crystallinity (x_c) . Then, we used BDS to determine the MAF content. After subtraction, the RAF content could be determined. Note that this method can be more versatile, because it does not depend on the known heat capacity values and can be applied to polymers that are not listed in the ATHAS data bank.³⁷



Figure 2. (A) Conventional DSC first-heating curves for different PET films at a heating rate of 10 °C/min. (B) TMDSC first-heating curves with a modulation period of 60 s and an amplitude of 0.32 °C. The heating rate was 2 °C/min.

Although conventional DSC was performed for various PET films (Figure 2A), the crystallinity (x_c) was difficult to be accurately determined due to the influence of cold crystallization and/or crystal perfection during the normal heating speed at 10 °C/min.²⁴ Since TMDSC can separate reversible processes from irreversible processes under certain appropriate conditions, it was used to reveal the microstructure and determine the initial crystallinity for various PET films (see Figure 2B and Figures S5A-C). The characterization results are summarized in Table 1. For AmPET, Tg was determined by conventional DSC to be 76 °C, consistent with the result for purely amorphous PET.^{30, 38, 39} Meanwhile, its amorphous nature for AmPET was also confirmed by the WAXD result later. Based on the TMDSC results, the Tg values for BOPET, AnPET-120, and AnPET-190 were found to be 99, 85, and 81 °C, respectively (see Figure S5D). The x_c was calculated from the sum of melting and crystallization processes observed in the reversing and non-reversing curves, as shown in Figure S6.⁴⁰ Here, $\Delta H_f^0 =$ $140.2 \text{ J/g}.^{37}$ The related results are shown in Table 1, i.e., 42% for BOPET, 21% for AnPET-120,

and 33% for AnPET-190. These results are consistent with those reported for BOPET⁴¹ and coldcrystallized PET.²⁹

The T_g and x_c values obtained by other methods (i.e., BDS for T_g and WAXD for x_c) are also listed in Table 1. Although the absolute values of T_g and x_c varied for different measurements, the trends appeared to be similar. That is, BOPET had the highest crystallinity as well as the highest RAF. Another interesting phenomenon was that the trend of T_g was different from that of x_c in the annealed samples, i.e., the x_c in AnPET-190 was higher than that in AnPET-120. However, AnPET-120 exhibited a higher T_g, suggesting a somewhat higher RAF content. This is consistent with previous reports that low temperature cold-crystallized polymers had a higher content of RAF.^{29,42}



Figure 3. Temperature-scan BDS results of $(A,C,E,G) \varepsilon_r'$ and $(B,D,F,H) \varepsilon_r''$ for various PET films: (A,B) BOPET, (C,D) AnPET-120, (E,F) AnPET-190, and (G,H) AmPET.

sample	$x_{\rm c}$ (%)	x_{c} (%)	$T_{g}(^{\circ}C)$	T_g (°C)	x_{RAF} (%)	x_{RAF} (%)
	(TMDSC)	$(XRD)^{a}$	(TMDSC)	(BDS at 1 Hz)	$(NMR)^{c}$	(TMDSC-BDS) ^d
AmPET	0	0	76 ^b	81	-	-
AnPET-120	21	14	85	90	26	29
AnPET-190	33	35	81	84	19	16
BOPET	42	36	99	100	31	34

Table 1. T_g , x_c , and x_{RAF} Determined by Different Methods.

^{*a*} Calculated using the 1D WAXD profiles integrated from 2D WAXD patterns. Note that the crystallinity calculated from the oriented WAXD pattern of BOPET may not reflect the true crystallinity due to crystal orientation.

^b AmPET T_g is calculated from conventional DSC.

^c Taken as the f_{RAF} in the deconvoluted ¹H ssNMR spectrum at 140 °C (see Figure S3).

^d Calculated using the percentage of total amorphous phase from TMDSC minus the percentage of MAF from BDS.

For a semi-rigid polymer with polar groups in the main chain such as PET, the MAF contributes to the dielectric constant change during glass transition, whereas RAF should not. Figure 3 shows temperature-scan BDS results for BOPET, AnPET-120, AnPET-190, and AmPET. The dynamic T_g determined by the relaxation peak in the ε_r " curves at 1 Hz was 100, 90, 84, and 81 °C, respectively. These values were slightly higher than those determined by DSC, but the trend was similar. The dielectric constant increment ($\Delta\varepsilon_r$ ') values during the glass transition at 1 Hz are also shown in Figure 3. The $\Delta\varepsilon_r$ ' for AmPET was 2.11. If this value was taken as 100% amorphous, then the MAF contents in AnPET-120, AnPET-190, and BOPET were calculated to be 50%, 51%, and 24%, respectively. Using the non-crystalline contents from TMDSC (i.e., 75% for AnPET-120, 68% for AnPET-190, and 59% for BOPET), the RAF contents were calculated to be 29%, 16%, and 34% for AnPET-120, AnPET-190, and BOPET, respectively.

It has been reported that the x_{RAF} was determined by quasi-isothermal TMDSC to be around 40% for cold-crystallized PET at 117 °C,²⁹ significantly higher than 29% determined by the TMDSC-BDS method. It is imperative for us to compare these two experimental methods and understand the different x_{RAF} values. Note that the x_{RAF} determined by quasi-isothermal TMDSC is right at the T_g for the sample studied, whereas BDS needs to heat above the T_g range to obtain x_{MAF} . In Figure 3, for example, we need to heat to 120 °C to determine x_{MAF} . As such, the x_{RAF} determined by the TMDSC-BDS method should be around 120 °C, which is higher than the T_g values for all the PET films (i.e., 80-100 °C). It has been reported that significant devitrification happens for RAF around the T_g range for various semicrystalline polymers, including PET, poly(butylene terephthalate) (PBT), and isotactic polystyrene (iPS).⁴³⁻⁴⁵ For example, the x_{RAF} is ca. 42% for a melt-crystallized PET at 80 °C, and it decreases to 18% at 120 °C.⁴³ Beyond the T_g range, the decrease in x_{RAF} becomes gradual and eventually RAF disappears above a certain temperature (below the T_m, e.g., 210 °C for PET^{43, 45}). Therefore, significant devitrification of RAF around the T_g range should explain why the x_{RAF} determined by TMDSC-BDS is lower than that determined by quasi-isothermal TMDSC. Since we are interested in the high temperature insulation property (i.e., above 100 °C), the x_{RAF} determined by TMDSC-BDS should be more relevant.

For the commercial BOPET film, $x_{RAF} = 0.34$, which is slightly higher than that reported in the literature for BOPET with a 3.5×3.5 draw ratio ($x_{RAF} \sim 0.31$).⁴¹ We consider that it is likely that the draw ratio for the commercial BOPET is higher than 3.5×3.5, and more RAF is formed during the tenter-line biaxial stretching process.²²



Figure 4. 2D WAXD patterns for BOPET [(A) flat-on and (B) edge-on], (C) AnPET-120, and (D) AnPET-190 at room temperature. (E) Corresponding 1D WAXD profiles for different PET films.

Lamellar Crystal Orientation in Different PET Films. Lamellar crystal structures in these PET films were characterized by SAXS and WAXD. SAXS results are shown in Figure S7. Since lamellar scattering concentrated on the horizontal direction when the X-ray was flat-on to the film (Figure S7A), PET crystals oriented vertically in the BOPET film (see the right panel of Scheme 1). For AnPET-120 and AnPET-190, random lamellar orientation was observed (Figure S7B,C and see the left panel of Scheme 1). The weaker SAXS peak intensities for BOPET and AnPET-120 indicated poorer lamellar stacking than that in AnPET-190. From the SAXS peaks in Figure S7D, the long periods for BOPET, AnPET-120, and AnPET-190 were 13.6, 11.2, and 15.4 nm, respectively. Using the TMDSC crystallinities, crystalline lamellar thicknesses were calculated to be 5.53, 2.80, and 4.90 nm for BOPET, AnPET-120, and AnPET-190, respectively.

PET crystal orientation was further characterized by 2D WAXD, and results are shown in Figure 4. For BOPET, the flat-on WAXD pattern showed isotropic reflections, indicating a more

or less random orientation with respect to the film normal direction (ND; see Figure 4A). This suggests that the biaxial stretching along the machine (MD) and the transverse directions (TD) should be similar. From the edge-on WAXD pattern, the (100) reflection (i.e., a^*) was observed in the vertical direction, whereas the (010) reflection (i.e., b^*) tilted in the quadrant direction (Figure 4B). Therefore, the WAXD pattern should be a (100)-uniaxial pattern with the *c*- and *b*-axes oriented in the film (see the right panel of Scheme 1). In other words, the lamellar crystals oriented edge-on in the BOPET film. For AnPET samples, random crystal orientation was observed (Figures 4C,D; see the left panel of Scheme 1).

From the WAXD patterns for BOPET (Figures 4A,B), we can see that the film was not ultradrawn mechanically; therefore, no mesophase, which was reported for ultradrawn PET fibers,⁴⁶, should be present. In addition, when PET was uniaxially drawn below the T_g , a precursor mesophase was observed before cold crystallization, as evidenced by the smectic-like ordering on the meridian.⁴⁷. However, when stretched above the T_g , no such mesophase could be seen.^{48, 49} Since all tenter-line BOPET films are processed above the T_g ,²² no such precursor mesophase should exist for the BOPET film. Therefore, we do not need to consider the influence of mesophase on the RAF in this study.



Scheme 1. Schematic of crystal orientation in the AnPET (including both AnPET-120 and AnPET-190) and the BOPET films.

The crystallite size (d_{hkl}) along each axis was estimated using the Scherrer equation after peak-fitting (see Figure S8), and results are shown in Table 2. It is seen that the d_{100} and d_{001} were smaller than the d_{010} for BOPET. The crystallite sizes (d_{100} and d_{010}) of BOPET were smaller than those of AnPET-190 regardless of its random orientation. Due to poor cold crystallization in AnPET-120, all crystallite sizes were the smallest because of limited crystal growth. Meanwhile, the crystallinity determined by WAXD (see Figure S8D) was not very accurate due to weak and broad WAXD reflections from the poor crystals.

 Table 2.
 Calculated Crystallite Size along Each Axis using Scherrer Equation.^a

		0	0	
Samples	d_{100}	d_{010}	d_{001} b	$l_{\rm c}$ (SAXS)
	(nm)	(nm)	(nm)	(nm)
BOPET (flat-on)	5.15	6.57	5.48	5.53
BOPET (edge-on)	3.88	6.84	5.99	-
AnPET-190	5.73	7.04	6.30	4.90
AnPET-120	4.25	4.19	3.73	2.80

^{*a*} The crystallite size (d_{hkl}) is calculated using Scherrer equation: $d_{hkl} = \frac{K\lambda}{\beta cos \theta_{hkl}}$, where K = 1.0, λ is the X-ray wavelength, β is the full width at half maximum, and θ_{hkl} is the half scattering angle for the (hkl) reflection.

^b Method proposed by Hisao et al.:⁵⁰ $D_{001} = D_{0\overline{1}1} \cos \alpha_1$, where α_1 is the angle between (001) and (011) planes, which is calculated to be 27°.



Figure 5. (A) Weibull characteristic $E_b(\alpha)$ and (B) slope (β) for different PET films as a function of temperature. Lines are used to guide the eyes. The BDS T_g at 1 Hz was marked with dotted lines. The Weibull plots are shown in Figure S9.

Dielectric Breakdown and Lifetime of Various PET Films. Given the understanding of crystalline structures in these PET films, dielectric insulation properties including breakdown strength (E_b) and lifetime analyses were carried out.⁵¹ For Weibull analysis of breakdown strength, at least 40 individual samples with a parallel plate capacitor geometry and an electrode area of 5.15 mm² were tested for each data point. Experimental data were analyzed using twoparameter Weibull statistics (Figure S9). The characteristic Weibull strength (α) or E_b at 63.2% failure probability and the Weibull slope (β) as a function of temperature are plotted in Figures 5A and B, respectively. At room temperature (i.e., below T_g), E_b values of different samples were similar. When temperature increased to 50 °C, the E_b for AmPET and AnPET films showed certain increases. This was attributed to the decreased brittleness of AmPET and AnPET when increasing the temperature close to their T_g. Note that at room temperature, both AmPET and AnPET films were brittle, and crazing failure under the high Maxwell pressure made the E_b low. When temperature further increased, especially above the T_g of each PET film, the E_b exhibited an obvious decrease, primarily owing to enhanced segmental motion of polymer chains to facilitate transport of charge carriers. The decrease in E_b was the most significant for AmPET (up to 100 °C). Note that the AmPET would not cold crystallize in a short time under 100 °C. Therefore, amorphous PET was the most conductive for charge carriers.

After AmPET crystallized (i.e., AnPET-120 and AnPET-190), E_b significantly increased, suggesting that crystals were more insulating than amorphous PET regardless of the random crystal orientation. Between 50 °C and T_g around 100 °C, the AnPET films had even higher E_b than BOPET. Above 100 °C, AnPET-190 and BOPET exhibited the highest E_b . Besides high crystallinities (33% for AnPET-190 and 42% for BOPET; see Table 1), the reasons for their high breakdown strength might be somewhat different. AnPET-190 had a random crystal orientation. Some lamellae must be oriented flat-on in the film (see the left panel in Scheme 1), and they served as effective blocks for the conduction of charge carriers (e.g., injected electrons). For BOPET, all lamellar crystals were edge-on in the film (see the right panel in Scheme 1), and the blocking effect from these edge-on crystals should be limited. However, the high RAF content in BOPET should be responsible for reducing the chain mobility and thus charge carrier conductivity.

Similarly, the Weibull slopes also exhibited certain temperature dependence and were related to the T_g of PET films (Figure 5B). The Weibull slope for BOPET was the highest among all samples for T < 100 °C, primarily owing to the uniform film thickness from biaxial film processing. In addition to the uniform film thickness, surface roughness can also influence dielectric breakdown, as reported recently.⁵²



Figure 6. Normalized capacitance $(C_p/C_{p,0})$ as a function of time for the AmPET film during lifetime tests at 50 °C. The applied DC fields ranged from 300 to 450 MV/m.

Note that the Weibull breakdown study only analyzed the first breakdown strength for each sample, and the first breakdown could be related to extrinsic defects during the film processing. To reflect the intrinsic insulation property, it would be better to study the lifetime of dielectric films with repeated breakdowns.⁵¹ Different from our previous reports, ^{53, 54} where the dielectric lifetime tests were performed in air, the film sample was immersed in paraffin oil to avoid corona discharge. In such a way, we observed that each breakdown only generated a small pinhole, rather than large and connected breakdown holes due to the plasma-enhanced breakdowns in air.^{53,} When holding at a certain DC electric field, initial breakdown events should have eliminated the extrinsic defects, and later breakdowns should more or less reflect the intrinsic insulation property of the film. Example breakdown histograms for BOPET, AmPET, AnPET-120, and AnPET-190 films under a constant DC field are shown in Figure S10. By assuming that each breakdown event cleared out the same amount of metal electrode, the capacitance decrease during the lifetime test could be obtained and reflected by the normalized Cp/Cp,0 (Cp and Cp,0 are capacitance at time t and 0 s, respectively). Typical lifetime results for the AmPET film at 50 °C are shown in Figure 6. For 300 MV/m, the AmPET film survived 40000 s without significant decreased in capacitance. When the electric field increased to 350 and 400 MV/m, the lifetime at 5% capacitance loss ($t_{95\%}$) was around 900 s. Finally, for 450 MV/m, the $t_{95\%}$ drastically decreased to 88 s. At the end of lifetime test, the normalized capacitance decreased to as low as 25%.



Figure 7. Normalized capacitance $(C_p/C_{p,0})$ as a function of time for (A,D,G) BOPET, (B,E,H) AnPET-120, and (C,F,I) AnPET-190 films during lifetime tests at: (A,B,C) 50 °C, (D,E,F) 100 °C, and (G,H,I) 120 °C, respectively. The applied DC electric fields are indicated in each plot.

Using this new test method, the lifetime was studied for BOPET, AnPET-120, and AnPET-190 films at 50, 100, and 120 °C, respectively (Figure 7). At 50 °C, the t_{95%} of BOPET at 400 MV/m was 7214 s (Figure 7A), significantly higher than that (896 s) of AmPET (Figure 6). Therefore, BOPET was more insulating than AmPET. This could be attributed to both high crystallinity and high RAF content in BOPET. However, it was less insulating than AnPET-120 ($t_{95\%} = 17574$ s; see Figure 7B) and AnPET-190 ($t_{95\%} = 14456$ s; see Figure 7C) at 400 MV/m. In addition, the final $C_p/C_{p,0}$ was only 25% for BOPET at 400 MV/m, much lower than the final

capacitance of 90% for AnPET-120 and 91% for AnPET-190. The poorer insulation for BOPET than AnPET could be attributed to the exclusive edge-on crystal orientation from biaxial orientation, which was less effective in blocking injected hot electrons from the metal electrode. When the temperature increased to 100 °C (Figure 7D) and 120 °C (Figure 7G), the insulation of BOPET further dropped and it could not survive 400 MV/m. Even at a reduced field of 350 MV/m, the t_{95%} was rather low with massive breakdowns after the initial breakdown event.

On the contrary, AnPET-120 was somewhat more insulating than BOPET at 100 °C. For example, the final $C_p/C_{p,0}$ was 69% for AnPET-120, higher than that of 26% for BOPET at 350 MV/m. AnPET-190 was more insulating than AnPET-120 at 100 °C, because its $t_{95\%}$ at 400 MV/m (737 s) was higher than that of AnPET-120 (236 s). When the temperature increased to 120 °C, similar insulation trend was observed. Namely, AnPET-190 was more insulating than AnPET-120 and BOPET. Intriguingly, at 120 °C BOPET was more insulating than AnPET-120 at 300 MV/m. This could be again attributed to the more uniform film thickness of commercial BOPET than AnPET-120, which was extruded using our single-screw extruder. From this lifetime study, the better dielectric lifetime of AnPET-190 than BOPET at high electric fields and high temperatures could be attributed to the randomly oriented PET crystals in AnPET-190, among which some should orient flat-on to block the conduction of injected space charges. From this lifetime study, we conclude that the effect of RAF on reduction of space charge conductivity should be less important than crystal orientation for the electrical insulation property.



Figure 8. Frequency-scan BDS results of ε_r " for various PET films at different temperatures: (A) 75 °C, (B) 100 °C, (C) 125 °C, and (D) 150 °C.

To prove our hypothesis of flat-on crystals blocking charge transport and RAF reducing charge mobility, low-field BDS study was used to study the impurity ionic conduction in various PET films. Figure 8 shows frequency-scan BDS results of ε_r " for various PET films at 75-150 °C. The corresponding ε_r ' results are shown in Figure S11. At 75 °C, α (i.e., T_g) and β (i.e., sub-T_g) relaxation peaks were observed at low and high frequencies, respectively. No impurity ion conduction peak was observed. At 100 °C, impurity ion conduction peaks showed up at low frequencies with AmPET being the most conductive and BOPET being the least conductive. At 125 and 150 °C, BOPET was still the least conductive for impurity ions. This was primarily

attributed to the reduced chain mobility of the high RAF content in BOPET and thus reduced ion mobility/conduction.



Figure 9. Electronic conductivity as a function of applied electric field at different temperatures: (A) 60 °C, (B) 80 °C, and (C) 100 °C. The leakage current was measured by Novocontrol Concept 80 with a Keithley 6517B electrometer (the maximum DC voltage is 1000 V). The measurement time was 30 min.

To study electronic conductivity, leakage current tests were carried out by holding these PET films at a constant voltage for a long enough time (e.g., 30 min).⁵⁵ Because of the voltage limit of 1000 V for the Keithley 6517B power supply, we could not reach high electric fields above 100 MV/m for AmPET and AnPET films. Figure 9 shows the conductivity as a function of electric field for various PET films at 60-100 °C. Figure S12 shows the electronic conductivity as a function of temperature for these films. Obviously, AmPET had the highest conductivity, especially around its T_g (Figure 9B). At a low temperature such as 60 °C and low electric fields, BOPET had the lowest electronic conductivity. At high temperatures (>80 °C) and high electric fields, AnPET-190 should have the lowest electronic conductivity if extrapolated to high fields (>90 MV/m; see Figure 9C).



Figure 10. High-field conductivity as a function of applied electric field at different temperatures: (A) 50 °C; (B) 80 °C; (C) 100 °C and (D) 120 °C. The leakage current was measured using the Radiant ferroelectric tester. Both the soak time and the measurement time were 21 s.

Measurements of electronic leakage current under high electric fields (i.e., holding at >200 MV/m for >30 min) have been performed for BOPP films.¹⁰ However, it is difficult for PET films because of their higher conductivity and thus low breakdown strength/lifetime. To measure leakage current at high fields, we used the Radiant ferroelectric tester with the leakage current function, where the soak time and the measurement time were 21 s, respectively. Because of the short measurement time, the measured leakage current could have a significant contribution from ionic contribution, especially at high temperatures. Therefore, the measured conductivity should

be the overall conductivity, rather than pure electronic conductivity. The results are shown in Figure 10. When the temperature was below 80 °C, AmPET had the highest overall conductivity. This is the reason why AmPET exhibit the lowest breakdown strength and shortest lifetime. Above 80 °C, AnPET-190 exhibited the lowest overall conductivity. This explained why AnPET-190 had the longest lifetime. Meanwhile, BOPET had a lower overall conductivity than AnPET-120 for the electric field below 350 MV/m. This explained why BOPET had a better life than AnPET-120 (see Figures 7G and H).

From this study, we understand that RAF is the major working mechanism for BOPET to maintain reasonably high breakdown strength and lifetime for temperatures below 100 °C. This is why the temperature rating for Mylar film capacitors is 120 °C. However, BOPET does not have the highest breakdown strength and lifetime, especially at high temperatures (>50 °C) and under high DC fields (>300 MV/m). This is because of its edge-on lamellar crystals from biaxial orientation during processing. Better breakdown and lifetime can be achieved if the PET lamellar crystals could orient flat-on in the film, because flat-on crystals are more insulating and can prevent the conduction of space charges and impurity ions.⁵⁶ However, the flat-on crystal orientation is not compatible with the biaxial stretching processing. Note, biaxial orientation is the most effective way to achieve uniform thickness and decrease/eliminate extrinsic defects for polymer films,²² which is important for quality control in film-manufacturing. It is still challenging to further improve breakdown strength and lifetime for PET films.

Conclusions

In this study, effects of RAF and crystal orientation on dielectric breakdown and lifetime were studied for various PET films: melt-extruded AmPET, cold-crystallized AnPET with low (AnPET-120) and high (AnPET-190) crystallinities, and commercial BOPET. From ¹H ssNMR, TMDSC, and XRD results, the crystallinities are:

AmPET: 0%, AnPET-120: 21%, AnPET-190: 33%, and BOPET: 42%.

On the basis of these crystallinity results, the RAF contents in these PET films are determined by temperature-scan BDS:

AmPET: 0%, AnPET-120: 29%, AnPET-190: 16%, and BOPET: 34%.

In addition, 2D WAXD showed that BOPET exhibit an edge-on crystal orientation with the reciprocal *a** normal to the film. AnPET had a random crystal orientation with certain crystalline lamellae flat-on in the film. Frequency-scan BDS and leakage current conductivity studies suggested that the electrical insulation property decreased in the order of crystals > RAF > MAF. Indeed, AnPET-190 had the best dielectric lifetime performance, as revealed by dielectric breakdown and lifetime tests. This could be attributed to the presence of certain flat-on crystals and relatively high crystallinity in AnPET-190. BOPET had better dielectric lifetime than AnPET-120 because of its higher crystallinity, although the edge-on lamellar crystals were less effective in blocking conduction of injected hot electrons. The major working mechanism for BOPET was the high content of RAF as a result of biaxial orientation during the manufacturing process. Finally, AmPET exhibited the lowest breakdown strength and the shortest lifetime.

On the basis of this study, electrical insulation can be further enhanced by achieving flaton crystals for PET films. However, this is not compatible with the biaxial stretching processing of high quality polymer films. Research effort is needed to tackle this difficulty. For example, confined crystallization of PET can induce flat-on crystals in multilayer films.⁵⁷ In the future, we plan to study PET-based multilayer films to achieve better electrical insulation.

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Notes

The authors declare no competing financial interest.

Acknowledgments

L.Z. acknowledges partial financial support of the dielectric measurements by National Science Foundation, Division of Materials Research (DMR), Polymers Program (DMR-1708990). Y.L. acknowledges partial financial support from the National Natural Science Foundation of China (51803138) and the Fundamental Research Funds for the Central Universities (Grant 2018SCU12005). We acknowledge the Beamline BL16B of SSRF, Shanghai, China, for synchrotron SAXS and WAXD measurements. **Supporting Information.** The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxxx.

Cold crystallization kinetics at 120 and 190 °C for AnPET-210 and AnPET-190 studied by conventional DSC, schematic of lifetime measurement circuit, ¹H ssNMR spectra at temperatures <100 °C, peak deconvolution for the ¹H ssNMR spectra at 140 °C and at different echo delay times, TMDSC curves and calculation of crystallinity for BOPET, AnPET-120, and AnPET-190, SAXS results for various PET films, peak deconvolution for WAXD results, Weibull breakdown analysis at different temperatures, example histograms of breakdown events during lifetime tests, frequency-scan BDS results of ε_r for various PET films at different temperatures, and temperature dependent electronic conductivity under different electric fields.

References

- Li, Z.; Chen, X.; Zhang, C.; Baer, E.; Langhe, D.; Ponting, M.; Brubaker, M.; Hosking, T.; Li, R.; Fukuto, M.; Zhu, L. High Dielectric Constant Polycarbonate/Nylon Multilayer Films Capacitors with Self-Healing Capability. *ACS Appl. Polym. Mater.* 2019, *1*, 867-875.
- 2. Setter, N.; Colla, E., *Ferroelectric Ceramics: Tutorial Reviews, Theory, Processing, and Applications*; Birkhäuser: Basel, 1993.
- 3. Li, J.; Li, F.; Xu, Z.; Zhang, S. Multilayer Lead-Free Ceramic Capacitors with Ultrahigh Energy Density and Efficiency. *Adv. Mater.* **2018**, *30*, 1802155.
- 4. Nishino, A. Capacitors: Operating Principles, Current Market and Technical Trends. *J. Power Sources* **1996**, *60*, 137-147.
- Sarjeant, W. J.; Zirnheld, J.; MacDougall, F. W. Capacitors. *IEEE Trans. Plasm. Sci.* 1998, 26, 1368-1392.

- Sarjeant, W. J.; Clelland, I. W.; Price, R. A. Capacitive Components for Power Electronics. Proc. IEEE. 2001, 89, 846-855.
- Mayoux, C. Degradation of Insulating Materials under Electrical Stress. *IEEE Trans. Dielectr. Electr. Insul.* 2000, 7, 590-601.
- Montanari, D.; Saarinen, K.; Scagliarini, F.; Zeidler, D.; Niskala, M.; Nender, C. Film Capacitors for Automotive and Industrial Applications. *Proceedings of CARTS U.S.A. 2009*; Jacksonville, FL, March 30-April 2, 2009.
- 9. Ho, J.; Jow, T. R. *Characterization of High Temperature Polymer Thin Films for Power Conditioning Capacitors*; Army Research Laboratory: Adelphi, MD, 2009.
- Ho, J.; Jow, T. R. High Field Conduction in Biaxially Oriented Polypropylene at Elevated Temperature. *IEEE Trans. Dielectr. Electr. Insul.* 2012, 19, 990-995.
- Zhu, L.; Wang, Q. Novel Ferroelectric Polymers for High Energy Density and Low Loss Dielectrics. *Macromolecules* 2012, 45, 2937-2954.
- Zhu, L. Exploring Strategies for High Dielectric Constant and Low Loss Polymer Dielectrics.
 J. Phys. Chem. Lett. 2014, 5, 3677-3687.
- Baer, E.; Zhu, L. 50th Anniversary Perspective: Dielectric Phenomena in Polymers and Multilayered Dielectric Films. *Macromolecules* 2017, 50, 2239-2256.
- Chen, Q.; Shen, Y.; Zhang, S.; Zhang, Q. M. Polymer-based Dielectrics with High Energy Storage Density. *Annu. Rev. Mater. Res.* 2015, 45, 433-458.
- Prateek; Thakur, V. K.; Gupta, R. K. Recent Progress on Ferroelectric Polymer-based Nanocomposites for High Energy Density Capacitors: Synthesis, Dielectric Properties, and Future Aspects. *Chem. Rev.* 2016, *116*, 4260-4317.
- 16. Soulestin, T.; Ladmiral, V.; Dos Santos, F. D.; Ameduri, B. Vinylidene Fluoride- and

Trifluoroethylene-Containing Fluorinated Electroactive Copolymers. How Does Chemistry Impact Properties? *Prog. Polym. Sci.* **2017**, *72*, 16-60.

- Li, Q.; Yao, F.-Z.; Liu, Y.; Zhang, G. Z.; Wang, H.; Wang, Q. High-Temperature Dielectric Materials for Electrical Energy Storage. *Ann. Rev. Mater. Res.* 2018, 48, 219-243.
- Bonardd, S.; Moreno-Serna, V.; Kortaberria, G.; Diaz, D. D.; Leiva, A.; Saldias, C. Dipolar Glass Polymers Containing Polarizable Groups as Dielectric Materials for Energy Storage Applications. A Minireview. *Polymers* 2019, *11*, 317
- Huo, P.; Cebe, P. Dielectric-Relaxation of Poly(Phenylene Sulfide) Containing a Fraction of Rigid Amorphous Phase. J. Polym. Sci., Part B: Polym. Phys. 1992, 30, 239-250.
- Ho, J.; Jow, T. R. High Field Conduction in Heat Resistant Polymers at Elevated Temperature for Metallized Film Capacitors. 2012 IEEE Int. Power Modulator High Voltage Conf. (IPMHVC), 399-402, June 2012.
- Tan, D.; Zhang, L.; Chen, Q.; Irwin, P. High-Temperature Capacitor Polymer Films. J. Electron. Mater. 2014, 43, 4569-4575.
- DeMeuse, M. T. Biaxial Stretching of Film Principles and Applications; Woodhead Pub.: Oxford, 2011.
- 23. Schosseler, L., A New Commercial High Temperature Capacitor Dielectric for Power Applications. *Bodo's Power Systems* **2016**, April 50-51.
- 24. Wunderlich, B. Reversible Crystallization and the Rigid-Amorphous Phase in Semicrystalline Macromolecules. *Prog. Polym. Sci.* **2003**, *28*, 383-450.
- 25. Mandelkern, L. The Structure of Crystalline Polymers. Acc. Chem. Res. 1990, 23, 380-386.
- Chen, W.; Wunderlich, B. Nanophase Separation of Small and Large Molecules. *Macromol. Chem. Phys.* 1999, 200, 283-311.

- Miranda, D. F.; Zhang, S. H.; Runt, J. Controlling Crystal Microstructure To Minimize Loss in Polymer Dielectrics. *Macromolecules* 2017, *50*, 8083-8096.
- Zhao, J.; Dong, W.; Li, C.; Guo, M.; Fan, Q. Study of the Dual Amorphous Phases in Semicrystalline Poly(ethylene terephthalate) using the Heat Capacity Increment at the Glass Transition. *Macromolecules* 2003, *36*, 2176-2178.
- Androsch, R.; Wunderlich, B. The Link Between Rigid Amorphous Fraction and Crystal Perfection in Cold-Crystallized Poly(ethylene terephthalate). *Polymer* 2005, 46, 12556-12566.
- 30. Hamonic, F.; Miri, V.; Saiter, A.; Dargent, E. Rigid Amorphous Fraction versus Oriented Amorphous Fraction in Uniaxially Drawn Polyesters. *Eur. Polym. J.* **2014**, *58*, 233-244.
- Esposito, A.; Delpouve, N.; Causin, V.; Dhotel, A.; Delbreilh, L.; Dargent, E. From a Three-Phase Model to a Continuous Description of Molecular Mobility in Semicrystalline Poly(hydroxybutyrate-*co*-hydroxyvalerate). *Macromolecules* 2016, 49, 4850-4861.
- 32. Wang, Z.-G.; Hsiao, B. S.; Sauer, B. B.; Kampert, W. G. The Nature of Secondary Crystallization in Poly(ethylene terephthalate). *Polymer* **1999**, *40*, 4615-4627.
- 33. Reed, C. W.; Cichanowski, S. W. The Fundamentals of Aging in HV Polymer-Film Capacitors. *IEEE Trans. Dielectr. Electr. Insul.* **1994**, *1*, 904-922.
- 34. Hedesiu, C.; Demco, D. E.; Kleppinger, R.; Vanden Poel, G.; Gijsbers, W.; Blumich, B.; Remerie, K.; Litvinov, V. M. Effect of Temperature and Annealing on the Phase Composition, Molecular Mobility, and the Thickness of Domains in Isotactic Polypropylene Studied by Proton Solid-State NMR, SAXS, and DSC. *Macromolecules* 2007, 40, 3977-3989.
- Gabrielse, W.; Gaur, H. A.; Feyen, F. C.; Veeman, W. S. ¹³C Solid-State NMR Study of Differently Processed Poly(ethylene terephthalate) Yarns. *Macromolecules* 1994, 27, 5811-

5820.

- Hedesiu, C.; Demco, D. E.; Kleppinger, R.; Buda, A. A.; Blumich, B.; Remerie, K.; Litvinov,
 V. M. The Effect of Temperature and Annealing on the Phase Composition, Molecular Mobility and the Thickness of Domains in High-Density Polyethylene. *Polymer* 2007, 48, 763-777.
- 37. Wunderlich, B., Thermal Analysis of Polymeric Materials; Springer: Berlin, 2005.
- Alves, N. M.; Mano, J. F.; Balaguer, E.; Duenas, J. M. M.; Ribelles, J. L. G. Glass Transition and Structural Relaxation in Semi-crystalline Poly(ethylene terephthalate): A DSC Study. *Polymer* 2002, 43, 4111-4122.
- Hamonic, F.; Prevosto, D.; Dargent, E.; Saiter, A. Contribution of Chain Alignment and Crystallization in the Evolution of Cooperativity in Drawn Polymers. *Polymer* 2014, 55, 2882-2889.
- 40. Thomas, L. C. Modulated DSC Paper #6: Measurement of Initial Crystallinity in Semicrystalline Polymers. TA Instruments, 2005.
- Okazaki, I.; Wunderlich, B. Modulated Differential Scanning Calorimetry in the Glass Transition Region. 5. Activation Energies and Relaxation Times of Poly(ethylene terephthalate)s. J. Polym. Sci., Part B: Polym. Phys. 1996, 34, 2941-2952.
- Kolesov, I.; Androsch, R. The Rigid Amorphous Fraction of Cold-Crystallized Polyamide 6.
 Polymer 2012, 53, 4770-4777.
- 43. Righetti, M. C.; Laus, M.; Di Lorenzo, M. L. Temperature Dependence of the Rigid Amorphous Fraction in Poly(ethylene terephthalate). *Eur. Polym. J.* **2014**, *58*, 60-68.
- 44. Righetti, M. C.; Di Lorenzo, M. L. Rigid Amorphous Fraction and Multiple Melting Behavior in Poly(butylene terephthalate) and Isotactic Polystyrene. *J. Therm. Anal. Calorim.*

2016, *126*, 521-530.

- 45. Chen, H.; Cebe, P. Vitrification and Devitrification of Rigid Amorphous Fraction of PET during Quasi-Isothermal Cooling and Heating. *Macromolecules* **2009**, *42*, 288-292.
- Fu, Y. G.; Annis, B.; Boller, A.; Jin, Y. M.; Wunderlich, B. Analysis of Structure and Properties of Poly(Ethylene Terephthalate) Fibers. *J. Polym. Sci., Part B: Polym. Phys.* 1994, 32, 2289-2306.
- Ran, S.; Wang, Z.; Burger, C.; Chu, B.; Hsiao, B. S. Mesophase as the Precursor for Strain-Induced Crystallization in Amorphous Poly(ethylene terephthalate) Film. *Macromolecules* 2002, 35, 10102-10107.
- Kawakami, D.; Hsiao, B. S.; Burger, C.; Ran, S.; Avila-Orta, C.; Sics, I.; Kikutani, T.; Jacob,
 K. I.; Chu, B. Deformation-Induced Phase Transition and Superstructure Formation in Poly(ethylene terephthalate). *Macromolecules* 2005, *38*, 91-103.
- Zhang, Q.; Zhang, R.; Meng, L.; Lin, Y.; Chen, X.; Li, X.; Zhang, W.; Li, L. Biaxial Stretch-Induced Crystallization of Poly(ethylene terephthalate) above Glass Transition Temperature: The Necessary of Chain Mobility. *Polymer* 2016, *101*, 15-23.
- Wang, Z.-G.; Hsiao, B. S.; Fu, B. X.; Liu, L.; Yeh, F.; Sauer, B. B.; Chang, H.; Schultz, J. M. Correct Determination of Crystal Lamellar Thickness in Semicrystalline Poly(ethylene terephthalate) by Small-Angle X-ray Scattering. *Polymer* 2000, *41*, 1791-1797.
- Dissado, L. A.; Fothergill, J. C. *Electrical Degradation and Breakdown in Polymers*; P. Peregrinus: London, 1992.
- 52. Tan, D. Q. Differentiation of Roughness and Surface Defect Impact on Dielectric Strength of Polymeric Thin Films. *IET Nanodielectrics* **2020**, *3*, 28-31.
- 53. Zhou, Z.; Mackey, M.; Carr, J.; Zhu, L.; Flandin, L.; Baer, E. Multilayered

Polycarbonate/Poly(vinylidene fluoride-*co*-hexafluoropropylene) for High Energy Density Capacitors with Enhanced Lifetime. *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 993-1003.

- 54. Tseng, J.-K.; Tang, S.; Zhou, Z.; Mackey, M.; Carr, J. M.; Mu, R.; Flandin, L.; Schuele, D.
 E.; Baer, E.; Zhu, L. Interfacial Polarization and Layer Thickness Effect on Electrical Insulation in Multilayered Polysulfone/Poly(vinylidene fluoride) Films. *Polymer* 2014, 55, 8-14.
- 55. Yang, L.; Ho, J.; Allahyarov, E.; Mu, R.; Zhu, L. Semicrystalline Structure Dielectric Property Relationship and Electrical Conduction in a Biaxially Oriented Poly(vinylidene fluoride) Film under High Electric Fields and High Temperatures. ACS Appl. Mater. Interfaces 2015, 7, 19894-19905.
- Huang, H.; Chen, X.; Li, R.; Fukuto, M.; Schuele, D. E.; Ponting, M.; Langhe, D.; Baer, E.; Zhu, L. Flat-on Secondary Crystals as Effective Blocks To Reduce Ionic Conduction Loss in Polysulfone/Poly(vinylidene fluoride) Multilayer Dielectric Films. *Macromolecules* 2018, *51*, 5019-5026.
- 57. Flores, A.; Arribas, C.; Fauth, F.; Khariwala, D.; Hiltner, A.; Baer, E.; Balta-Calleja, F. J.; Ania, F. Finite Size Effects in multilayered Polymer Systems: Development of PET Lamellae under Physical Confinement. *Polymer* 2010, *51*, 4530-4539.