Conduction Mechanisms and Structure–Property Relationships in High Energy Density Aromatic Polythiourea Dielectric Films

Quinn Burlingame, Shan Wu,* Minren Lin, and Q. M. Zhang

Aromatic polythiourea (ArPTU) is an amorphous, polar, glass-phase dielectric polymer which features extremely high dielectric breakdown strength (>1.1 GV/m), low loss at high electric fields (10% at 1.1 GV/m), and a high maximum electrical energy density (>24 J/cm³). This work presents a study of the structure–property relationships and electrical conduction in ArPTU, and offers a phenomenological explanation for the experimentally observed high-field loss characteristics which facilitate the excellent energy storage properties.

1. Introduction

Electrical energy storage devices are among the most important components in modern electronics, and are growing rapidly in conjunction with alternative energy sources such as wind and solar. Batteries, fuel cells, supercapacitors, electrochemical capacitors, and parallel plate capacitors are all energy storage devices which make unique tradeoffs between high energy density, the ability to rapidly discharge energy, and tolerance to high voltage. Parallel plate capacitors are capable of discharging energy most rapidly, but lag far behind the high energy densities found in batteries and fuel cells.[1,2]

To enhance the energy density of capacitors, a significant amount of work has been done recently to improve existing organic dielectrics and synthesize new materials with advantageous energy storage characteristics.[1–8] Several distinct approaches have emerged; high dielectric constant (high-k) polymer nanocomposites, pure high-k polymers; lower dielectric constant insulating polymers with low loss; and high breakdown polymers with low high-field loss. To approach higher energy densities, polymer nanocomposites and pure high-k materials attempt to take advantage of the linear permittivity dependence in the maximum energy density equation:

$$U_e = \frac{1}{2}\varepsilon_r \varepsilon_o E_{\max}^2 \qquad (1)$$

where ε_r is the dielectric constant, ε_o is the permittivity of free space (8.85 × 10^{-12} F/m), and $E_{\max}$ is the highest applied electric field which the material can sustain. Unfortunately, these high permittivity materials are usually accompanied by high losses, which make them inefficient for energy storage and can cause thermally induced dielectric breakdown at lower fields.[2] Low loss, lower permittivity dielectrics such as polypropylene have been commercially successful because they are very efficient at low fields, but fail to produce high energy densities.[9,10] The most effective way to enhance the maximum electric energy density is to increase the breakdown strength of the material. High breakdown strength dielectrics take advantage of the square dependence of energy density on electric field, but are even more sensitive to loss, since loss is accentuated at high electric fields.[6,9]

Aromatic polythiourea (ArPTU), which is the focus of this work, is a material which is designed for high electric field operation, high-field loss minimization, and thus high energy density. The ArPTU polymer chain, which can be seen in **Figure 1**(a), contains dipolar thiourea monomers ($H_4N_2C = S$) encapsulated in aromatic rings which provide environmental protection and thermal stability.[10] The ArPTU molecules with the best high-field dielectric properties have a high molecular weight (typically several 1,000),[10] which has been shown to reduce conductivity. While high molecular weight is electrically advantageous, it also results in a lower solubility than low molecular weight ArPTU chains. ArPTU is synthesized as a white or yellowish powder, which can be dissolved at low concentrations (typically 1% by weight) in polar solvents. Previous films of ArPTU were cast from dimethylformamide (DMF), which is a highly polar solvent, but film quality and electrode interfaces were often problematic. Films in this study were cast from a similar solvent, N,N-dimethylacetimide (DMAc), which is also polar, but features a higher boiling point. The higher boiling point solvent evaporates more slowly and uniformly during film casting, leaving behind higher quality surfaces and uniform thicknesses for superior electrode interfaces.

Once cast, ArPTU films exhibit many properties which are excellent for high-field current limitation, high breakdown strength, and high energy density. ArPTU films are glass-phase at room temperature which limits chain motion and ferroelectric loss, as well as amorphous—which reduces the conductivity

Q. Burlingame, S. Wu, Dr. M. Lin, Prof. Q. M. Zhang
The Department of Electrical Engineering
& The Materials Research Institute
The Pennsylvania State University
University Park, PA, 16802, USA
E-mail: szw148@psu.edu

FULL PAPER
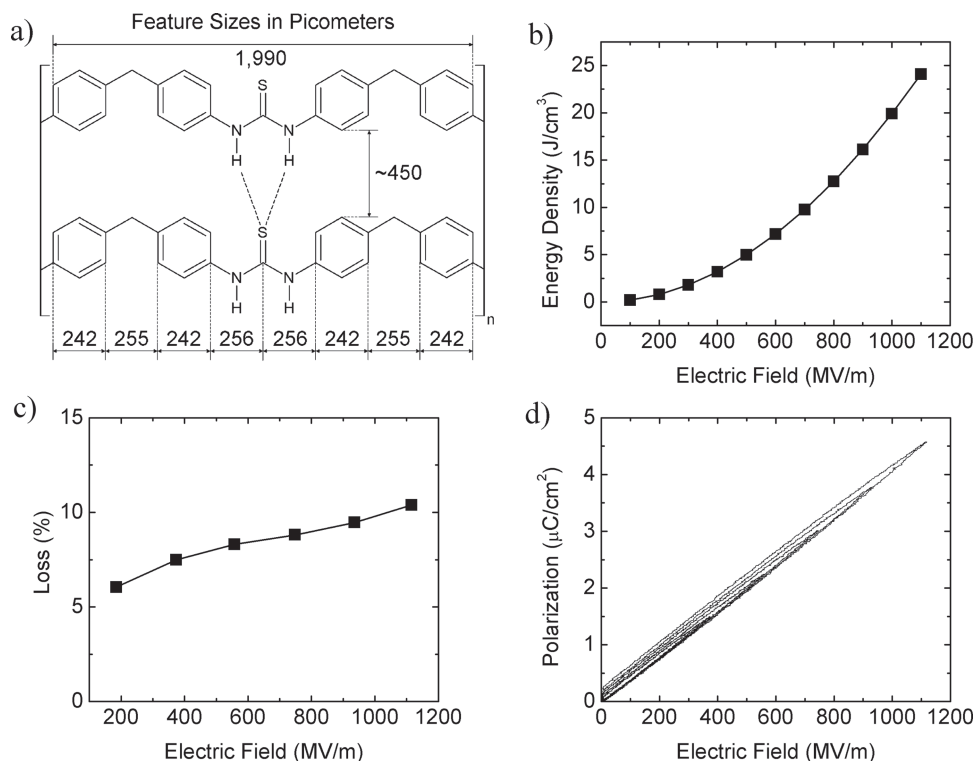
Figure 1. a) Feature sizes of two parallel ArPTU molecules with weak intermolecular coupling between the sulfur and hydrogen atoms of adjacent thiourea monomers; b) Energy density of ArPTU vs. electric field; c) Loss of ArPTU vs. electric field; d) Polarization vs. electric field loops

and eliminates band conduction. ArPTU has a high dipole moment (4.89 Debye)[11] thiourea monomer to scatter carriers and drive up the dielectric constant and energy density, and has only short range ordering and dipole interaction to avoid remnant polarization and hysteresis loss.[1,2,10,12] These material properties result in a static dielectric constant of 4.5,[10] an extremely high dielectric breakdown strength (>1.1 GV/m), a slow linear growth in loss up to very high applied fields (~10% at 1.1 GV/m), and a maximum electrical energy density in excess of 24 J/cm^3.

2. Results and Discussion

The energy density (Figure 1(b)) and electrical efficiency (Figure 1(c)) are two of the most important metrics for evaluating energy storage dielectrics. The high energy density in ArPTU results from the high breakdown strength, and the dielectric constant as shown in Equation 1. ArPTU has a dielectric constant of 4.5, which is higher than many polymeric insulators such as polypropylene (ε_r = 2.2), polyester (ε_r = 3.3), and aromatic polyurea (ε_r = 4.2).[6,9,13] Increasing dielectric constant results in a linear increase in the energy density, which means that in ideal (lossless) systems, the ratio of energy densities between any two materials will scale as the ratio of the dielectric constants at any electric field. The maximum sustainable electric field provides an exponential increase in energy density, which can also be seen in Equation 1. The DMAc casted ArPTU films in this study display a discharged energy density of >24 J/cm^3, which is higher than previous DMF casted ArPTU films,[10] an order of magnitude higher than typical BaTiO$_3$ polymer nanocomposites, and only slightly lower than high-k PVDF copolymers (~30 J/cm^3) which have significantly higher losses and lower breakdown strengths.[7]

Efficiency is extremely important for practical capacitor devices, but will also be a limiting factor for high breakdown strength, because loss will induce thermal breakdown before intrinsic breakdown occurs. The efficiency can be calculated from the polarization vs. electric field loops (Figure 1(d)) by integrating the area under the charging and discharging portions of the curve and taking their ratio. Efficiency is the amount of electrical energy the material discharges divided by the amount of energy that is charged into the material. The loss (Figure 1(c)) is 1 minus the efficiency.

The low-field loss (< 1% at 40 Hz-1 MHz) in ArPTU is higher than many nonpolar, insulating materials, such as polypropylene, but increases very slowly with electric field. Compared with other dielectric materials, the high-field loss is very low (~10% at 1.1 GV/m), and is likely responsible for the extremely high breakdown strength in ArPTU. No other polymer dielectrics achieve such high breakdown strengths, because they rapidly drop in efficiency at high voltages.[7,9] The breakdown strength in ArPTU is most closely approached by aromatic polyurea, which has an identical structure except for its dipolar monomer. Aromatic polyurea features a urea monomer (H$_4$N$_2$C = O) in place of the thiourea monomer in the ArPTU structure, which gives it a lowered dielectric constant of 4.2, and a maximum recorded breakdown strength of 800 MV/m.[9] Polyester

Materials
Views
www.MaterialsViews.com

ADVANCED
ENERGY
MATERIALS
www.advenergymat.de

FULL PAPER
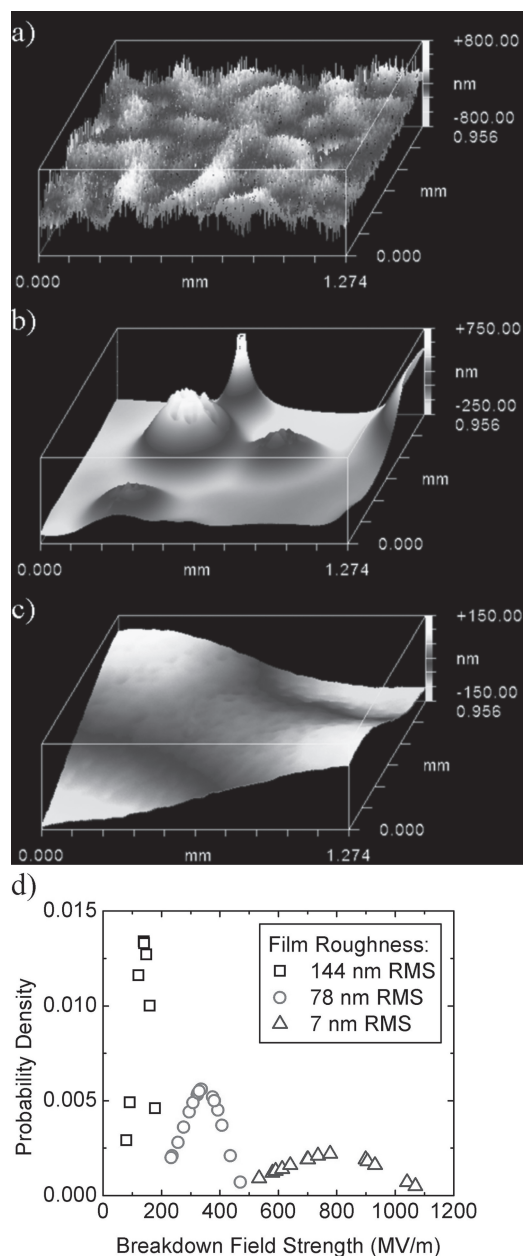
Figure 2. Optical profilometry surface profiles of ArPTU with a) 144 nm RMS roughness; b) 78 nm RMS roughness; c) 7 nm RMS roughness; d) Weibull distribution of breakdown field strengths of the ArPTU films in Figures 1(a-c)

(570 MV/m), polycarbonate (530 MV/m), polypropylene (650 MV/m), and polyimide (300 MV/m) all break down at substantially lower voltages, because despite the lower loss at low fields, their efficiencies decrease more rapidly with field than the efficiency in ArPTU.

To realize dielectric films with low loss, and high breakdown strength, it is known that the film morphology is extremely important.[14,15] Optical profilometry results (**Figures 2**(a–c)) and subsequent electrical characterizations (Figure 2(d)) show that films with less defects were found to have higher breakdown voltages. Figure 2(a) contains optical profilometer data from a

very low quality ArPTU thin film casted from a DMF solution. The RMS surface roughness of the scanned area (1.22 mm²) in this film was 144 nm, and the minima and maxima are separated by 1.6 μm, which is more than 50% of the total film thickness (~2.5 μm). Figure 2(b) and Figure 2(c) profile films with fewer defects casted from DMAc, which feature RMS roughness values of 78 nm and 7 nm respectively. Most importantly, the magnitude of the vertical features decreases as the film quality increases, as shown by the z-axes in Figures 2(a–c). Avoidance of deep valleys is essential for high dielectric strength, since the sputtered electrode metal will penetrate into the defect areas and reduce the effective dielectric thickness. The film in Figure 2(c) appears to bow from corner to corner, which is due to aberration in the optics of the profilometer.[16] The film quality correlates with the Weibull distributions of the breakdown test results, which are shown in Figure 2(d), indicating a strong link between film surface uniformity and breakdown strength.

The solvent type is an important factor in determining film quality, and resultant electrical performance. To dissolve the high molecular weight, polar polymer chains, polar solvents are required. DMF was previously the standard polar solvent for ArPTU casting, but due to high film surface roughness and high defect densities,[10] new solvents were needed. The high quality films in Figure 2 and the films throughout this work were casted using DMAc as the solvent. Although both DMF (C_3H_7NO) and DMAc (C_4H_9NO) are polar solvents, DMAc is slightly less polar (3.7 Debye to 3.86 Debye), and has a higher boiling point (165 °C to 152 °C). Both of these factors are favorable for high quality films, since the solvent with higher boiling point will exit the film more slowly, and the solvent with lower polarity will interact less with the polar thiourea units in the polymer chains. Controlling the drying speed to a slow and uniform rate improves the film quality, which makes the solvent and thermal processing sequence very important.[14,15]

High breakdown voltage in polymers is almost always inversely related to conductivity, since more conductive materials are at risk of accumulating current at high fields and suffering thermal breakdown.[1,2,13,17] To limit high-field conduction, an amorphous film structure is preferred to increase the charge scattering, break up the formation of large polarization domains, and eliminate band conduction. At high electric fields, amorphous scattering is even more important since it prevents coherent ballistic transport which can be possible over large distances in crystalline materials.

To examine the structure of ArPTU, an x-ray diffraction (XRD) measurement was carried out. The measurement, shown in **Figure 3**(a), shows a very broad diffraction peak, which is indicative of an amorphous material. The peak centers around $2\theta = 19°$, which corresponds to a spacing of 450 pm. Since this is much larger than the chemical structure of the thiourea unit and the aromatic rings, this broad diffraction peak is due to spacing between polymer chains which has a Gaussian distribution. Figure 1(a) is a schematic of two parallel ArPTU chains, with their approximate sizes and spacing shown. Due to the electronegativity of the sulfur in the thiourea unit, there may be some weak coupling between the ArPTU chains as shown in Figure 1(a). The 4.5 angstrom spacing in ArPTU is also consistent with pi-pi stack spacing in other materials with aromatic rings.

ADVANCED
ENERGY
MATERIALS
www.advenergymat.de

Materials
Views
www.MaterialsViews.com

FULL PAPER
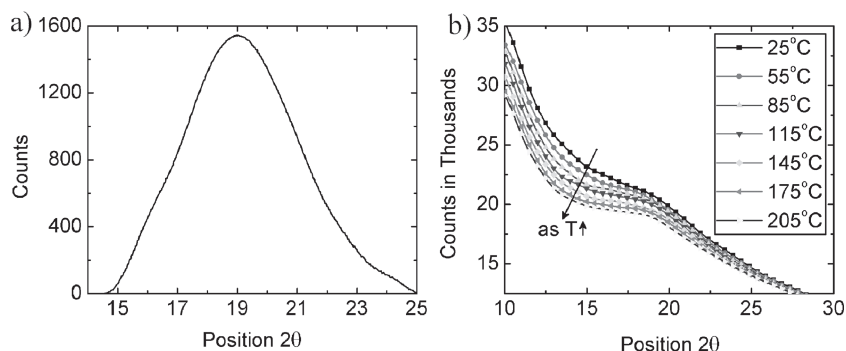
Figure 3. a) Background normalized, room temperature x-ray diffraction peak of ArPTU; b) X-ray diffraction of ArPTU at varied temperature from 25 °C to 205 °C

A temperature dependent XRD measurement was also carried out (Figure 3(b)) to study the change in crystallinity at high temperatures. To ensure that the annealing during casting would not change the amorphous structure, temperatures from 25 °C to 205 °C were studied. As the temperature increases, a small increase in diffraction intensity relative to the background was observed. Additionally, the $2\theta = 19°$ peak narrows slightly, which indicates that there is an increase in crystallographic ordering with temperature. Once returned to room temperature, the diffraction peak returns to near the original value, indicating that the thermally induced order is not permanent. The thermosetting temperature and cross-linking temperature must be higher than 205 °C, which means that the film preparation thermal treatments (up to 140 °C) will not crystallize or significantly cross-link the amorphous structure in ArPTU.

Different from most semi-crystalline polymers, which can be treated as wide band gap semiconductors with a HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), trap-limited hopping conduction was found to dominate in amorphous ArPTU.[18–20] The exponential nature of the current voltage relationship shown in **Figure 4** is indicative of solid state hopping conduction, where
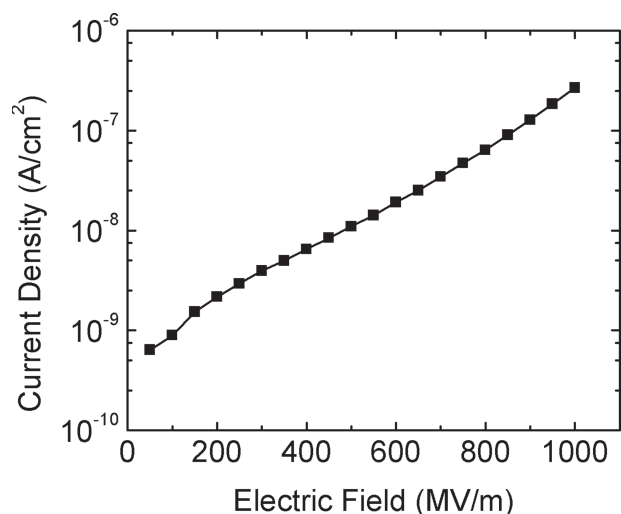
localized carriers jump between resonant energy states in the direction of the electric field.[21,22] Hopping conduction is typical in disordered organic materials, and features substantially lower mobilities than band conducting crystalline materials which improves the conduction loss. In amorphous materials, electron and ionic hopping can be modeled by the equation:

$$J = 2qn\lambda\nu * \exp(-U/kT) * \sinh(\lambda q\, E/2kT)$$
(2)

where q is the charge of the carriers, n is the carrier concentration, λ is the ionic/electronic hop distance, ν is the escape frequency, U is the barrier height of trap sites, k is Boltzmann's constant, T is the temperature, and E is the electric field.[21,23] During measurement, when voltage is first applied, there are high transient charging currents which are observed. After several seconds, a steady state current emerges in ArPTU, which is due primarily to electronic conduction. Since ions cannot be injected from the contacts, ionic conduction may be a portion of the transient current, but is not significant at steady state. For purposes of measurement, a 20 second current stabilization delay was introduced at each voltage to ensure that only the electronic contribution is being measured.

Equation 2 contains dependencies on trapping levels, temperature, hopping distance, and escape frequency, but can be simplified into a quasi-steady-state current density equation with lumped parameters:

$$J = J_o \sinh(\alpha E)$$
(3)

where J_o and α are constants related to charge concentration, electron jump distance, and the barrier height of trap sites; and E is the electric field in MV/m.[21–23] Applying the exponential data fitting in equation 3 to the data in Figure 4, J_o is 6×10^{-10} A/cm^2 and α is 6 cm/V. J_o, which depends on trap depth, temperature, and carrier density can be viewed as the low-field current. The value in ArPTU (6×10^{-10} A/cm^2) is reasonably high, particularly compared to low-loss insulating polymers such as polypropylene. As a point of reference, J_o in semicrystalline polypropylene is typically between 2×10^{-14} A/cm^2 and 3×10^{-13} A/cm^2 depending on the crystallinity.[23] This extremely low low-field current explains why there is virtually no conduction loss in polypropylene at low voltages,[6] and the higher starting current in ArPTU explains the higher measured loss (>5% at 100 MV/m).

The second parameter, α, is related to hop distance and temperature, and determines how fast the current density increases with electric field. The value measured in ArPTU (6 cm/V) is almost three times lower than a typical value in polypropylene (>16.6 cm/V),[23] which is consistent with the loss behavior. At high-fields, the current density in ArPTU remains low (~0.2 µA/cm^2 at 1 GV/m) and results in a low loss (10% at 1 GV/m). In PVDF and PVDF based co/terpolymers, polyimide, polycarbonate, polyester, polyethylene-naphlate, polyethylene-sulfate, and polypropylene, electrical breakdown occurs at much lower voltages (<650 MV/m)[6] which is a result of rapidly growing current densities and resultant high-field losses.

Figure 4. Current density vs. applied field of ArPTU

3. Conclusion

The improved ArPTU thin films shown in this work are polymeric dielectrics with extremely high breakdown voltages (>1.1 GV/m), high electric energy densities (>24 J/cm^3), and low losses at high field (~10% at 1.1 GV/m). The conduction in ArPTU is consistent with an electronic hopping model, and features a very slowly increasing current density. When compared with previous studies of ArPTU, and other organic dielectrics like aromatic polyurea, polyester, polycarbonate, polyimide, polypropylene, and PVDF, the high voltage energy storage characteristics of ArPTU films casted from a DMAc solution are superior. The higher boiling point of DMAc solvent, compared with DMF, leaves behind smoother films and better electrode interfaces. The amorphous glass-phase structure, high dipole moment, and slowly growing current in the material make it a nearly ideal high-field dielectric, and if the processing can be refined and scaled up, ArPTU should have great potential for future high voltage dielectric and energy storage applications.

4. Experimental Section

ArPTU in this study was synthesized using microwave assisted polycondensation of 4,4'-diphenylmethanediamine (MDA) and thiourea in n-methyl-2-pyrrolidone (NMP) with p-tolunesulfonic acid as a catalyst.[24] The solution was microwave irradiated at 200 Watts for 7 minutes, followed by a 400 Watt irradiation lasting 8 minutes. Molecular weight of the aromatic polythiourea in this study was obtained by gel permeation chromatography (GPC) calibrated with standard polystyrenes. The molecular weight could be controlled in the range of 2000–12000 g/mol by changing the microwave power and the reaction time.[10] Because high molecular weight can lead to a low solubility, which is important for the thin film fabrication, the polythiourea sample used here had a MW (weight average molecular weight) of 4000 g/mol and a polydispersity index (PDI) of <1.1. This produces aromatic polythiourea as a fine white yellowish powder, which is soluble in N,N-dimethylacetamide (DMAc). The solution of ArPTU in DMAc was prepared on a hot/stirring plate with a stirring bar at elevated temperature. The ArPTU films with thicknesses ranging from 1–2.5 μm were prepared by casting the ArPTU solution onto 0.5″ × 0.5″ silicon substrates pre-coated with 40 nm of aluminium or platinum. After casting, films were dried in a vacuum oven for 4 hours at room temperature, cured overnight at 110 °C, and annealed for 12 hours at 140 °C. In order to characterize the electrical properties of the films, several dozen 1 mm diameter gold contacts were sputtered onto each sample. The high voltage breakdown and polarization measurements were carried out with a modified Sawyer-Tower Circuit, employing a Trek Model 30/20 +/– 30 kV High Voltage Amplifier System and an HP 4140B pA meter/DC Voltage Source. The current density vs. voltage measurement was done on a Cascade Microtech Probe Station with an HP 4140B pA meter/DC voltage source and a Model BOP 1000M Kepko Bipolar Operational Power Supply/Amplifier.

The optical profilometry data was obtained on a Zygo New View 7300. The x-ray diffraction measurement was carried out at on a PANalytical XPert Pro MPD theta-theta diffractometer. The energy density was calculated from polarization vs. electric field measurements by integrating the discharge curve with respect to polarization. The loss was calculated by taking one minus the discharged energy over the charged energy.

[1] H. S. Nalwa, *Ferroelectric Polymers: Chemistry, Physics, and Applications*, Marcel Dekker Inc., New York **1995**, 353–392.

[2] H. S. Nalwa, *Handbook of Low and High Dielectric Constant Materials and Their Applications*, Academic Press, San Diego **1999**, 138–211 & 289–317.

[3] A. Lovinger, *Science* **1983**, *220*, 1115.

[4] Y. Cao, P. C. Irwin, K. Younsi, *IEEE Trans. Dielectr. Electr. Insul.* **2004**, *11*, 797.

[5] W. J. Sarjeant, J. Zirnheld, F. MacDougall, *IEEE Trans. Plasma Sci.* **1998**, *26*, 1368.

[6] M. Rabuffi, G. Picci, *IEEE Trans. Dielectr. Electr. Insul.* **2002**, *30*, 1939.

[7] B. Chu, X. Zhou, K. Ren, B. Neese, M. Lin, Q. Wang, F. Bauer, Q. M. Zhang, *Science* **2006**, *313*, 334.

[8] P. Kin, N. Doss, J. Tillotson, P. Hotchkiss, M. Pan, S. Marger, J. Li, J. Calame, J. Perry, *ACS Nano* **2009**, *3*, 2581.

[9] Y. Wong, X. Zhou, M. Lin, Q. M. Zhang, *Appl. Phys. Lett.* **2009**, *94*, 202905.

[10] S. Wu, W. Li, M. Lin, Q. Burlingame, Q. Chen, A. Payzant, K. Xiao, Q. M. Zhang, *Adv. Mater.* **2013**, *25*, 1734.

[11] W. D. Kumler, G. Fohlen, *J. Am. Chem. Soc.* **1942**, *64*, 1944.

[12] M. Ieda, *IEEE Trans. Electr. Insul.* **1980**, *EI-15*, 206.

[13] A. Facchetti, M. Yoon, T. Marks, *Adv. Mater.* **2005**, *17*, 1705.

[14] I. Galperin, W. White, *IEEE Trans. Electr. Insul.* **1985**, *EI-20*, 55.

[15] I. L. Hosier, A. S. Vaughan, S. G. Swingler, *J. Mater. Sci.* **1997**, *32*, 4523.

[16] P. DeGroot, *Appl. Opt.* **2009**, *48*, 6788.

[17] J. Claude, Y. Lu, Q. Wang, *Appl. Phys. Lett.* **2007**, *91*, 212904.

[18] M. Ieda, M. Nagao, M. Hikita, *IEEE Trans. Dielectr. Electr. Insul.* **1994**, *1*, 934.

[19] S. M. Sze, K. K. Ng, *Physics of Semiconductor Devices*, John Wiley & Sons Inc., Hoboken **2007**.

[20] N. Mott, E. Davis, *Electronic Processes in Non-Crystalline Materials* 2nd edition, Oxford University Press, New York **1979**.

[21] K. C. Kao, *Dielectric Phenomena in Solids*, Elsevier Academic Press, San Diego, **2004**, 381–569.

[22] V. Ambegaokar, B. I. Halperin, J. S. Langer, *Phys. Rev. B* **1971**, *48*, 2612.

[23] K. Ikezaki, T. Kaneko, T. Sakakibara, *Jpn. J. Appl. Phys.* **1980**, *20*, 609.

[24] D. Bogdal, P. Penczek, J Pielichowski, A. Prociak, *Adv. Polym. Sci.* **2003**, *163*, 193.