Supporting Information

High Energy Density and High Efficiency All-Organic Polymers with Enhanced Dipolar Polarization

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Experimental Procedures

General Characterization
Fourier Transform Infrared (FTIR) spectra were collected on film samples using a Nicolet Magna 560 FTIR spectrometer with 32 scans and are reported in wavenumbers (cm^{-1}) from 400 to 4000 cm^{-1}. Thermogravimetric Analysis (TGA) was performed using a TA Instrument's TGA Q500 with a heating rate of 10°C per minute from 25°C to 600°C under nitrogen atmosphere. Differential Scanning Calorimetry (DSC) was performed on a TA Instrument's DSC Q20 with a first heating cycle rate of 30°C per minute, a cooling cycle of 30°C min^{-1} followed by a second heating cycle of 10°C per minute. Solution ^{1}H NMR (400 MHz and 300MHz) was performed using a Bruker AVANCE III 400 and AVANCE 300 high resolution digital NMR spectrometer with acetic acid-*d4*. Chemical shifts are reported in parts per million (ppm, δ) versus the chemical shift of the residual acetic acid peak being labeled at 2.04 ppm. Splitting patterns are reported as singlet (s), doublet (d), triplet (t), multiplet (m), etc. The sample thickness was determined using a thickness gauge (Model LE1000-2, Measure It All) as the average of five measurements. The thickness of the five measurement points varied by no more than 10%. The instrument has a guaranteed absolute accuracy of 0.2 μm.

Electrical Characterization
Broadband Dielectric spectra were measured using Solartron 1260 impedance analyzer and Agilent 4284A precision inductance, capacitance, and resistance (LCR) meter. The measurement covered a frequency range of 0.01 Hz-1 MHz and a temperature range from -130ºC to 120ºC. The data were acquired under a nearly isothermal condition after reaching the set temperature for 30 minutes, with a temperature step of 10ºC. High-field polarization behavior under different voltage was characterized by a modified Sawyer-Tower polarization loop tester, employing a Trek Model 10/40 10 kV high voltage amplifier. The applied voltage was a 100 Hz positive half sinusoidal wave for unipolar polarization/depolarization characterization.

Materials Synthesis and Film Processing

Synthesis of PDTC-HK511 and thin film processing

The polymer in the polythiourea family is a combination of para-phenylene diisothiocyanate (PDTC) and jeffamine HK511, named PDTC-HK511. To a dry 50 mL 3-neck flask, 0.96g (5 mmol) of para-phenylene diisothiocyanate, 1.10g (5 mmol) of Jeffamine HK511 and 20 mL NMP solvents were added under inert atmosphere with stirring. After 6h at room temperature, the reaction mixture was poured into methanol with fiber-like precipitation, followed by washing with methanol, and dried at 50℃ under vacuum overnight. White fiber-like solid was obtained with 87 % yield (1.80g).

The weight-average molecular weight (Mw) of PDTC-HK511 determined by Gel permeation chromatography (GPC) was 48,720 g/mol and the number-average molecular weight (Mn) was 26,830 g/mol measured against a monodisperse PMMA standard, indicating a polydispersity index (PDI) of 1.66.

FTIR: vmax/cm^{-1} 3230, 3040, 2973, 1510, 1310, 1230, 1103, 1038.

^{1}H NMR δH (400 MHz; DMSO-d6) 1.06-1.13 (7 H, m, Me), 3.52-3.56 (12 H, m, CH$_2$), 4.49 (2 H, m, CH), 7.36 (4 H, s, benzene), 7.52 (2 H, s, NH), and 9.44 (2 H, s, NH). Chain end: 1.27 (0.0641 H, s, NH$_2$).

Thin film processing: Free standing films were made using a 10 wt% dimethylacetamide (DMAc) solution that was filtered through a 0.45 μm syringe filter and placed on a glass substrate using a film coater. More specifically, the film was cast on a borosilicate glass plate with an Erichsen CoatMaster Film Applicator using a 500um blade gap at 70°C. The temperature was then raised to 80°C and allowed to dry for 6 hours before ultimately being dried in a vacuum oven at 100°C for 12 hours to drive off any remaining solvent. Figure S1a shows a film of PDTC-HK511 after it had been removed from the glass substrate measuring roughly 6 inches by 6 inches.

Synthesis of TDI-EDR148 and thin film processing
The polymer in the polyurea family is made with toluene-2, 4-diisocyanate (TDI) and jeffamine EDR148, named TDI-EDR148. The polyurea TDI-EDR148 was synthesized by an addition polymerization of two monomers, toluene-2, 4-diisocyanate (TDI) and an etheramine produced by Huntsman Corporation known as Jeffamine EDR-148. The monomers were added in equal molar quantities to a round bottom flask with DMAc as a solvent. The solution was stirred under an inert argon atmosphere at 60°C for 6 hours. The polymer was precipitated in a stirred

methanol solution and vacuum dried at 50°C. Mw by GPC for TDI-EDR148 was roughly 99,000 g/mol and Mn was 68,000 g/mol, indicating a PDI of 1.45.

FTIR (cm-1): 3305, 3119, 2917, 2869, 1633, 1558, 1243, 1136, 886, 815, 677, 517, 453

^{1}H NMR δH (500 MHz; DMSO-d6) : 2.03-2.18 (3H, m, CH3), 3.19-3.31 (4H, m, CH2), 3.42-3.53 (4 H, m, CH2), 3.2-3.53-3.65 (4 H, m, CH2), 6.02-6.16(1 H, s, CH), 6.60-6.77 (1 H, m, NH) ,6.89-7.02 (1 H,dd, CH),7.70-7.19(1H, m,CH), 7.60-7.96 (2 H, m, NH), and 8.30-8.53 (1 H, s, NH).

Thin film processing: TDI-EDR148 was dissolved in dimethylformamide (DMF) to a 10% concentration by weight and filtered through a 0.45 m poly(tetrafluoroethylene) PTFE syringe filter. The ideal conditions were determined to be by blade casting with an Erichsen CoatMaster film applicator using a blade height of 380 μm traveling at 10 mm/s on a glass substrate and a drying temperature of 70°C for 6 hours. A film roughly 6 inches by 6 inches square was produced on the glass substrate which was then cut down to remove the edges that were not uniform. The reduced film was then placed in a Teflon frame and dried under vacuum in an oven at 110°C for 24 hours to ensure complete removal of the solvent. The resulting films were 4 x 4-inches, free standing, 10 – 12 μm thick, and transparent (Figure S1b)

Synthesis of BTDA-HK25 and thin film processing

The polymer from the polyimide family is a copolymer of two polyimides. BTDA-HK511 is made with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and jeffamine HK511. BTDA-HDA is made with hexane-1,6-diamine (HDA). BTDA-HK25 is a copolymer of BTDA-HK511 and BTDA-HDA, where the molar ratio of BTDA-HK511 is 25%.

BTDA-HK511 and BTDA-HDA were identified and studied previously where BTDA-HK511 was found to exhibit a high dielectric constant. However, it was also found that BTDA-HK511 had a low T_g of 78°C, which is considered too low for polymer capacitor. On the other hand, while BTDA-HDA has a dielectric constant lower than BTDA-HK511, it possesses a much higher T_g of 150°C. Different compositions of the copolymer were studied in detail and BTDA-HK25 was selected to represent designed polyimides with the most optimal overall properties.

The two diamines were mixed together in DMAc before being added to the stirred dianhydride solution under nitrogen. The premixed diamines were added slowly to the dianhydride dissolved in DMAc to account for any differences in reactivity between the primary amine of the HDA and the secondary amine of the HK511, and to try and ensure as random of a copolymer as possible was formed. The reaction was then left to stir for 24 hours at 40°C to ensure complete polyamic acid formation. The polyamic acid solution was used to produce a thin film and thermally imidized after drying. The polyimide was insoluble in NMR solvents

FTIR (cm-1): 2935, 2861, 1772, 1702, 1668, 1440, 1391, 1293, 1246, 1155, 1094, 987, 919, 861, 725, 620, 545, 471

Thin film processing: Free standing films were cast from a 5% by weight solution of copolyimide in DMAc passed through a 0.45 μm syringe filter. An ideal condition was found to be using an Erichsen CoatMaster film applicator with a blade height of 380 μm traveling at 10 mm/s on a glass substrate. Then the film was dried on the glass substrate at 40°C for 24 hours. A film roughly 6 inches by 6 inches square was produced on the glass substrate which was then dried in a vacuum oven at increasing temperatures up to 100°C for 24 hours to ensure complete removal of the solvent. After the solvent was removed from the film, the glass plate was placed in a furnace at 100°C and increased 50°C every hour until 250°C where the film remained for 1 hour to ensure complete imidization of the polyamic acid film. The film was then placed in a bath of distilled water for up to 48 hours to aid in removal from the glass plate with the assistance of a razor blade. The copolyimide film was then cut down to remove the edges that were not uniform, and the reduced film was then placed in a Teflon frame and dried under vacuum in an oven at 110°C for 24 hours to ensure complete removal of water. A free-standing film was ultimately produced that had a thickness of 10-12 μm as shown in Figure S1c.
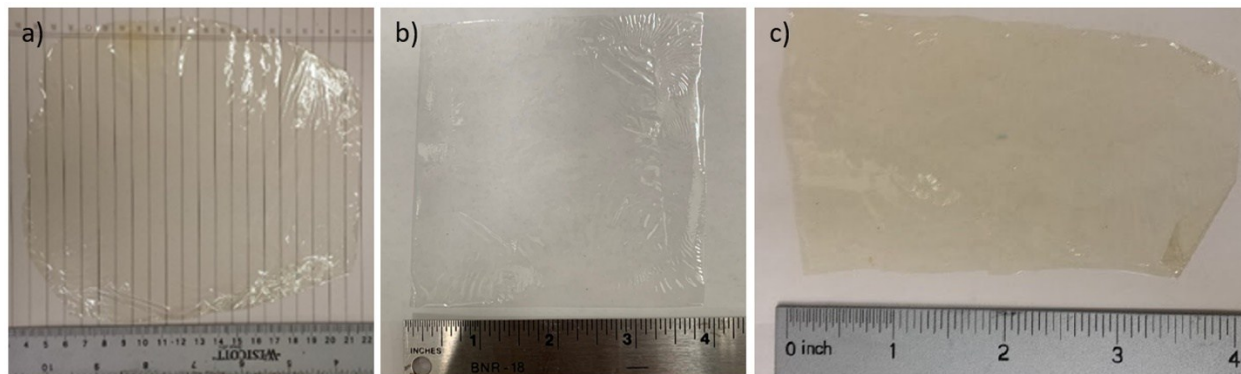
Figure S1. Images of free-standing films of a) PDTC-HK511, b) TDI-EDR148 and c) BTDA-HK25

Fourier Transform Infrared Spectroscopy

The spectra of PDTC-HK511 are shown in Figure S2a and plotted in absorbance verse wavenumber (cm^{-1}). Characteristic N-H stretching peak is evident at 3230 cm^{-1}. The major peak at 1510 cm^{-1} is a result from a N-H bending, which is known to be general to polythioureas. A second key band in thiourea films is evident at 1103 cm^{-1} and is due to the stretching of C=S of the thiocarbonyl.[1,2]

The spectra of TDI-EDR148 are shown in Figure S2b. The peaks at 1510 cm^{-1} (CO–N–H amide II) and 3230 cm^{-1} (N–H) indicated the formation of the urea functional group.[3] The amine peak at 3500 to 3200 cm^{-1} showed that the monomer subunit was fully polymerized, because a primary amine of EDR148 would show two peaks, whereas the single peak here was indicative of a secondary amine.

The spectra of BTDA-HK25 are shown in Figure S2c. The presence of the imide functionality is evident by the strong imide (-C=O) band at 1772 (asymmetric) and 1702 (symmetric) cm^{-1}.[4,5]
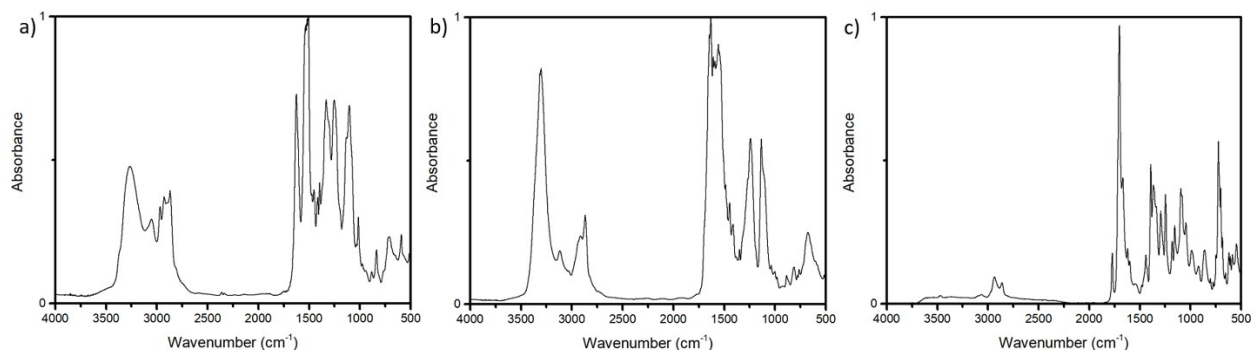

Figure S2. FTIR spectra of a) PDTC-HK511, b) TDI-EDR148 and c) BTDA-HK25

Thermal Properties

Thermal properties characterized by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are summarized in Figure S3 and S4 and TableS1.
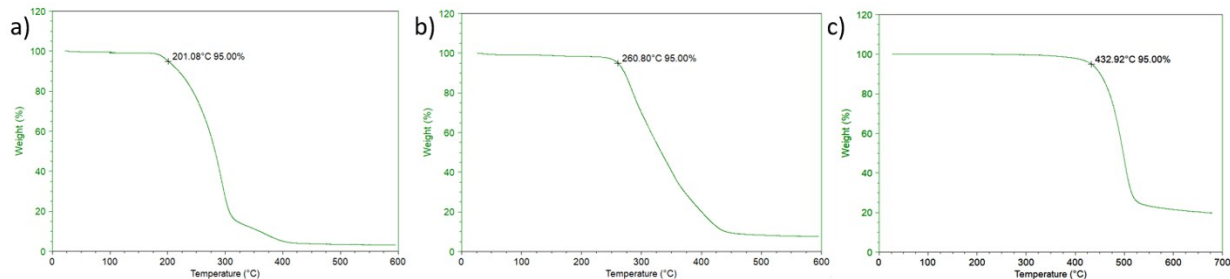
Figure S3. Thermal Gravimetric Analysis of a) PDTC-HK511, b) TDI-EDR148 and c) BTDA-HK25
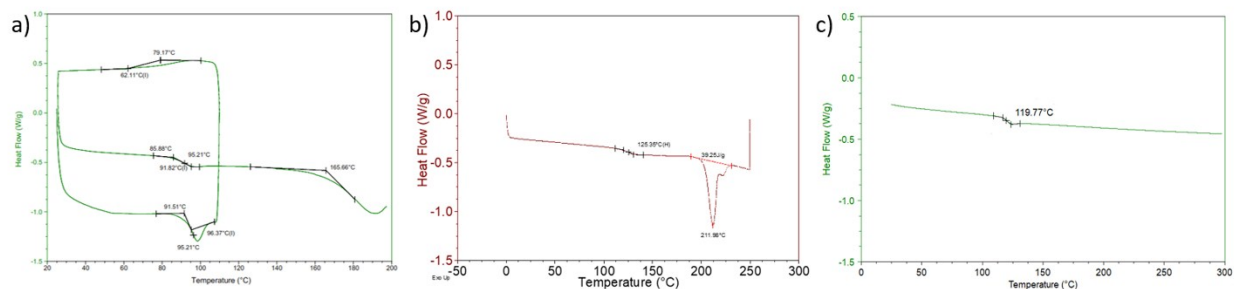

Figure S4. Differential Scanning Calorimetry of a) PDTC-HK511, b) TDI-EDR148 and c) BTDA-HK25

Table S1. Thermal Properties of three designed polymers

	T_g	$T_m^{[b]}$	$T_d^{[c]}$
PDTC-HK511	92	-	201
TDI-EDR148	125	212	261
BTDA-HK25	120	-	433

[a] Melting Temperature. [b] Degradation temperature

Optical Band Gap Measurement

Optical band gaps (E_g) were determined for thin films by scanning the UV−visible spectrum from 800 to 200 nm and measuring the wavelength of interband absorption onset, λ_{onset}, using Planck's equation: $E_g = (hc)/\lambda_{onset}$, where, h is the Planck's constant (4.136 x 10^{-15} eV·s), c is the speed of light in vacuum (2.998 x 10^{17} nm/s).

For PDTC-HK511, the onset is 315 nm correlating to a band gap of 3.9 eV. For TDI-EDR148, the onset is 353 nm correlating to a band gap of 3.5 eV. For BTDA-HK25, the onset is 308nm correlating to a band gap of 4.0 eV.

Dielectric properties

Dielectric constant and loss factor for three designed polymers under room temperature.
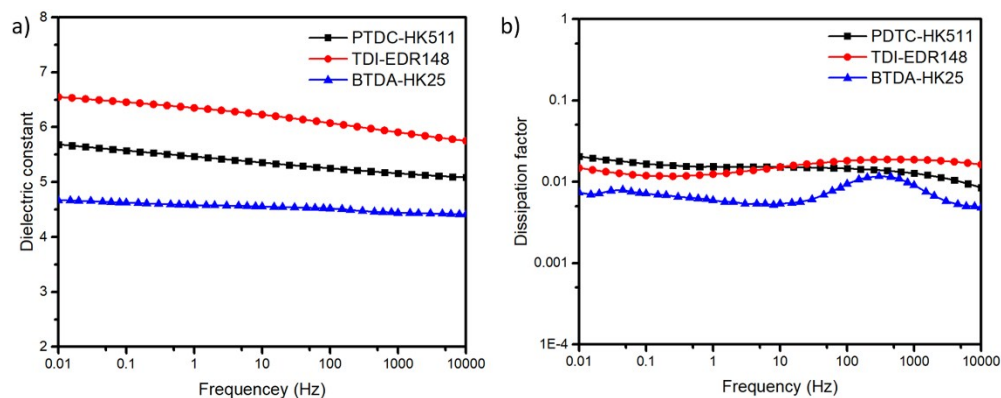
Figure S5. Dielectric properties of three designed polymers. a) dielectric constant versus frequency, b) loss factor versus frequency.

Calculation of dielectric constant from individual polarization process

The refractive indexes of polymers were taken by an ellipsometry at a wavelength of 589 nm, which is the sodium d line. The electronic dielectric constant is the square of the refractive index and thus can be obtained. Since the atomic polarization is caused by the IR modes in chemical bonds, they are expected to be active at any temperature above 0 K. However, the orientational polarization should decrease as the temperature is lowered as temperature moves below their solid-state energy barrier. At -130°C, dipolar polarization is "frozen" and only the electronic and atomic polarizations contribute to the dielectric constant. By subtracting the electronic portion from the lowest measured dielectric constant, the atomic dielectric constant can be obtained. Finally, the measured lowest dielectric constant can be subtracted from the dielectric constant at room temperature to calculate the portion of the dielectric constant from the dipolar polarization.

For PDTC-HK511, the dielectric constant at -130°C was 4.04. The refractive index was measured to be 1.64, which was converted to an $\varepsilon_{electronic}$ of 2.69. Subtracting 2.69 from 4.04 gave a ε_{atomic} of 1.35. By taking the room temperature dielectric constant of 5.8 and subtracting the $\varepsilon_{electronic+atomic}$ of 3.89, the $\varepsilon_{dipolar}$ is calculated to be 1.76.

For TDI-EDR148, the dielectric constant at -130°C was 4.76. The refractive index was measured to be 1.61, which was converted to an $\varepsilon_{electronic}$ of 2.58. Subtracting 2.58 from 4.76 gave a ε_{atomic} of 2.18. By taking the room temperature dielectric constant of 6.60 and subtracting the $\varepsilon_{electronic+atomic}$ of 3.89, the $\varepsilon_{dipolar}$ is calculated to be 1.84.

For BTDA-HK25, the dielectric constant at -130°C was 3.26. The refractive index was measured to be 1.64, which was converted to an $\varepsilon_{electronic}$ of 2.69. Subtracting 2.69 from 3.26 gave a ε_{atomic} of 0.57. By taking the room temperature dielectric constant of 4.77 and subtracting the $\varepsilon_{electronic+atomic}$ of 3.26, the $\varepsilon_{dipolar}$ is calculated to be 1.51.

Reference

1 C. Rao, R. Venkataraghavan, *Spectrochim. Acta,* 1962*,* **18,** 541.
2 P. W. Loscutoff, H.-B.-R. Lee, S. F. Bent, *Chem. Mater.,* 2010*,* **22**, 5563.
3 C. Wu, J. Wang, P. Chang, H. Cheng, Y. Yu, Z. Wu, D. Dong, F. Zhao, *PCCP,* 2012*,* **14**, 464.
4 Y. Watanabe, Y. Sakai, Y. Shibasaki, S. Ando, M. Ueda, Y. Oishi, K. Mori, *Macromolecules,* 2002*,* **35**, 2277.
5 Q. Zhang, K. Naito, Y. Tanaka, Y. Kagawa, *Macromolecules,* 2008*,* **41**, 536.