# CHEMISTRY OF MATERIALS

# Converting an Electrical Insulator into a Dielectric Capacitor: End-Capping Polystyrene with Oligoaniline

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**ABSTRACT:** We report a simple and low-cost strategy to enhance the dielectric permittivity of polystyrene by up to an order of magnitude via incorporating an oligoaniline trimer moiety at the end of the polymer chains. The oligoaniline-capped polystyrene was prepared by a copper-catalyzed click reaction between azide-capped polystyrene and an alkyne-containing aniline trimer, which was doped by different acids. By controlling molecular weight of polystyrene, the end-capped polymers can be induced to form nanoscale oligoaniline-rich domains embedded in an insulating matrix. Under an external electric field, this led to an increase in dielectric polarizability while maintaining a low dielectric loss. At frequencies as high as 0.1 MHz, the dielectric permittivity and dielectric loss (tan  $\delta$ ) were ~22.8 and ~0.02, respectively. This strategy may open a new avenue to increasing the dielectric permittivity of many other commodity polymers while maintaining relatively low dielectric loss.



**KEYWORDS:** dielectric polymers, energy storage, oligoaniline, nanodomain, polystyrene

# INTRODUCTION

Dielectric polymer film-based capacitors have shown promise in applications including portable electronic devices, hybrid electric vehicles, pulse power devices, and energy storage because of their light weight, low cost, and excellent processability.<sup>1–13</sup> Particularly, pulse power devices require accumulating much energy over a relatively long period of time and releasing it very quickly, thus increasing the available instantaneous power.<sup>14–24</sup>

Insulating commodity polymers play an important role in dielectric capacitors since most have very high dielectric breakdown strength, high volume availability, and low cost. Among various dielectric polymers, biaxially oriented polypropylene (BOPP) is the industrial standard polymer for fabrication of capacitors because of its high breakdown strength (>700 MVm<sup>-1</sup>) and low dielectric loss (tan  $\delta \sim 0.0002$  at 1 kHz). However, BOPP has a low dielectric permittivity ( $\varepsilon_r = 2.2$ ), ultimately leading to low energy densities (ca. 1–1.2 J/cm<sup>3</sup>).<sup>25,26</sup> Similarly, many other commodity dielectric polymers including polystyrene, polyethylene, polyvinyl chloride, and polycarbonate have high breakdown strength (~ 450–850 MV/m) and low dielectric permittivity ( $\varepsilon_r \sim 2.0-5.0$  at 1kHz).<sup>14,15</sup>

There is a crucial need to develop dielectric polymers with high dielectric permittivity while maintaining low dielectric loss. Poly(vinylidene fluoride) (PVDF) and its polymer derivatives have shown great promise since they have both high dielectric breakdown strength (500–700 MVm<sup>-1</sup>) and moderate permittivity ( $\varepsilon_r = 10-20$  at 1.0 kHz).<sup>26–33</sup> Recent studies have focused on modifying the chemical structure of PVDF with bulky

fluorinated comonomers to prepare random fluorinated copolymers such as poly((vinylidene fluoride)-*r*-(chlorotri-fluoroethylene)) (P(VDF-CTFE)).<sup>26,28,29,33–37</sup> Though these random copolymers are capable of high breakdown strength, fast energy discharge rates, and relatively low dielectric loss (e.g., tan  $\delta \sim 0.02$  at 1 kHz), their dielectric permittivity drops sharply at high frequency.<sup>34</sup>

Recently, a class of "molecular composites" has been developed, in which a conductive  $\pi$ -conjugated macromolecule is directly attached to the polymer backbone.<sup>19,38–43</sup> Delocalization of electrons across the  $\pi$ -network can produce high interfacial polarization upon charge displacement, ultimately resulting in large dielectric responses. The Wang group was the first to attach oligoaniline octamer moieties to the ends of a ferroelectric polymer.<sup>41</sup> This resulted in a "dumbbell-shaped" copolymer containing terminal oligoaniline units. The addition of 10 wt % oligoaniline units increased the dielectric permittivity from 12 to 85 at 1 kHz. However, the addition of more than 10 wt % aniline resulted in significant increases in dielectric loss, presumably because of electron conduction across the film. Stoyanov et al. prepared a block copolymer in which one domain was complexed with polyaniline.<sup>39</sup> While there were improvements in permittivity (from 2 to 8 at 1 kHz and from 2 to 7 at 1 MHz) between 1.0 and 1.8 wt % polyaniline, additions of above

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2.0 wt % polyaniline resulted in abrupt increases in conductivity. At this point complexation of the polyaniline with the polymer backbone was exhausted, and likely resulted in continuous conductive pathways across the film. Cui. et al. prepared a poly(ethylene oxide)-polyoligoaniline alternating copolymer that contained oligoaniline repeat units in the polymer main chain.<sup>40</sup> The copolymer films showed high dielectric permittivity ( $\varepsilon_r \sim 70$  at 1 MHz), but also exhibited extremely high dielectric loss (tan  $\delta = 2.72$ ).

Clearly, chemically integrating the conductive domain into the polymer chain inhibits aggregation, thus reducing dielectric loss. However, the loading content of the conductive domain remains limited, since increases in the  $\pi$ -conjugated fraction eventually result in conductivity abruptly increasing to high levels. To address this issue, we have recently taken a new approach to developing dielectric materials by creating interfacially dominated polymeric materials based on nanophase-separated block copolymers.<sup>44</sup> While the minor block forms nanodomains with high dielectric polarizability, the majority matrix block insulates the conductive domains to avoid percolation and minimize interdomain conduction. Under an external electric field, electronic conduction induces nanodipoles along the phase boundary because of space charge accumulation at the domain interfaces. Specifically, we prepared a series of diblock copolymers in which the major fraction was an insulating poly(methyl acrylate) block while the minor fraction had a side chain containing a sulfonic acid moiety, which was complexed with an oligoaniline trimer through supramolecular interactions. We observed both enhanced dielectric properties ( $\varepsilon_r = 11$  at 1 MHz) and decreased dielectric loss (tan  $\delta$  = 0.5 at 1 MHz) for the oligoaniline-complexed diblock copolymer compared to the uncomplexed diblock copolymer ( $\varepsilon_r = 5$  at 1 MHz and tan  $\delta = 2.7$ at 1 MHz). However, this approach was limited, as the sulfonic acid on the side chain of the block copolymer was the only possible dopant for oligoaniline.

In this paper, we report a new, simple, and low cost approach that could be generalized to enhance dielectric permittivity of many commodity polymers, which has not yet been considered for high performance dielectric capacitor materials. This approach is based on capping the ends of polystyrene chains with oligoaniline through a click reaction between azideterminated polystyrene and an alkyne-containing aniline trimer. The oligoaniline is then doped with various acids, including large organic acids such as dodecylbenzenesulfonic acid (DBSA) and camphorsulfonic acid (CSA). Because of the chemical incompatibility, it is expected that highly polar oligoaniline will self-assemble into nanoscale domains (i.e., a few nm) dispersed in a nonpolar polystyrene matrix (Scheme 1). Such highly polarizable nanodomains would make a positive contribution toward increasing the overall dielectric permittivity. Indeed, we observed that a small fraction of oligoaniline increased the dielectric permittivity of polystyrene by up to an order of magnitude while the dielectric loss remained low.

#### EXPERIMENTAL SECTION

**Materials.** All reagents were purchased from Alfa Aesar and Aldrich and used as received unless otherwise noted. Styrene was distilled before use. Hydroxy-terminated oligoaniline trimer (OANI–OH) was prepared according to a reported procedure.<sup>44</sup> Difunctional bromineand azide-terminated polystyrene was prepared according to a procedure previously reported.<sup>45</sup>

**Characterization.** <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. Gel permeation

Scheme 1. Oligoaniline End-Functionalized Polystyrene and Its Contribution to Increasing Dielectric Permittivity



chromatography (GPC) was performed at 50 °C on a Varian system equipped with a Varian 356-LC refractive index detector and a Prostar 210 pump. The columns were STYRAGEL HR1, HR2 (300 × 7.5 mm) from Waters. HPLC grade dimethylformamide (DMF) with 0.01 wt % LiBr was used as eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration. Mass spectrometry was carried out on a Waters Micromass Q-Tof mass spectrometer, with a positive ion electrospray as the ionization source. UV-vis spectroscopy was carried out on a Shimadzu UV-2450 spectrophotometer, scanning monochromatic light in the range of 190-900 nm. A quartz cuvette with a path length of 10.00 mm was used, and the solvent was DMF. FTIR spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer equipped with a Universal ATR sampling accessory. Thermal transitions of the polymers were measured by differential scanning calorimetry (DSC) using a TA Instruments Q2000 in a temperature range from -70 to 150 °C at heating and cooling rates of 5 °C/min under constant nitrogen flow at a rate of 50 mL/min. Samples (between 3 and 8 mg) were placed in aluminum hermetic pans and sealed. The data were collected on the second heating run.

Small-Angle X-ray Scattering (SAXS) data were acquired on a Bruker-AXS Nanostar-U instrument equipped as follows: copper rotating anode X-ray source (wavelength,  $\lambda = 0.154$  nm, 6 KW supply 0.1  $\times$  1 mm filaments) operated at 50 KV, 24 mA; Montel focusing optic; collimating assembly of 3 pinholes: (1) 750  $\mu$ M, (2) 400  $\mu$ M, and (3) 1000  $\mu$ M, spacing (1-to-2) 925 mm, (2-to-3) 485 mm; extended sample chamber with x-y stage (where the beam is the z axis), secondary beam path 1050–1060 mm; beam path between focusing optic and detector under vacuum (<0.1 mBar); 2-dimensional detector: Hi-star, multiwire proportional chamber, 1024 × 1024 pixels; control software: Bruker SAXS v. 4.1.36; detector flood-field and spatial calibrations use <sup>55</sup>Fe source; sample-to-detector distance calibrated using silver behenate. Bulk film samples were placed in a hole of copper spacer (1 mm thick) and then sandwiched between two sheets of Kapton films. The samples were then placed in the evacuated sample chamber at room temperature with a typical exposure time of 20 min. Data were integrated over the full circle of azimuthal angle values in the 2D SAXS scattering images with an

Scheme 2. Synthesis and Doping of Oligoaniline-Functionalized Polystyrene



increment of 0.01 degree in 2 $\theta$ . Finally, the intensity I(q) was plotted against  $q = 4\pi/\lambda \sin(\theta/2)$ .

Films for dielectric characterization were prepared by dissolving polymer samples in toluene (67 mg/mL) and casting in heavy-gauge aluminum pans. The solvent was removed by evaporation at 65 °C under slightly reduced pressure (635 mmHg absolute) for 24 h, producing films with uniform thickness without solvent bubbles, cracks, or other defects. Film thicknesses were measured at multiple positions with a micrometer; measured thicknesses ranged from 2 to 25  $\mu$ m. Strips of aluminum pan bearing copolymer films were cut using scissors; the aluminum pan served as the bottom electrode for dielectric measurements. Circular gold electrodes (area 1.13 cm<sup>2</sup>) were deposited on the films' top surfaces by sputter coating in an argon atmosphere through a shadow mask.

The films' complex impedance using an impedance analyzer (Agilent model 4192A LF).<sup>46–48</sup> Measurements were carried out at low applied voltage (typically 10 mV) and varying frequency (typically  $10^2$  to  $1.2 \times 10^7$  Hz) for 3–5 specimens of each sample to ensure reproducibility. A parallel RC circuit model expected to describe a "leaky" capacitor was used to determine the real and complex parts of the relative permittivity and the loss tangent from measured values of impedance magnitude and phase angle.

Polarization measurements at higher applied voltages were carried out using a Premier II ferroelectric polarization tester (Radiant, Inc.) using the same film specimens prepared for impedance testing. Films made from pure polystyrene (Aldrich, 192,000 g/mol) were also characterized. Polarization data (D vs E) were acquired for applied voltages ranging from 1 to 199 V and cycle frequencies of 100 Hz and 1 kHz. The maximum applied field strength ranged from 15 to 300 kV/ cm, depending on film thickness and the sample conductivity. Stored energy density  $\hat{W} = \int E \, dD$  was determined by numerical integration of the *D*-*E* data.

Synthesis of Oligoaniline-Alkyne (OANI-Alkyne, 2). 5-Hexvnoic acid chloride was prepared by heating 5-hexynoic acid (8.0 mL, 73 mmol) in thionyl chloride (8 mL, 110 mmol). After refluxing for 12 h, the product was collected by vacuum distillation. Hydroxy-terminated oligoaniline trimer (9.42 g, 34.1 mmol) was dissolved in 30 mL of dry tetrahydrofuran (THF), and the flask was purged with nitrogen. Triethylamine (7.1 mL, 51 mmol) was added, and the solution was cooled to 0 °C. A solution of 5-hexynoic acid chloride (5.48 g, 37.5 mmol) in 10 mL of dry THF was added over 30 min. After stirring at room temperature overnight, the reaction mixture was filtered and concentrated to dryness. The solids were dissolved in dichloromethane and extracted with water twice. The aqueous layers were combined and extracted with dichloromethane three times. The organic layers were combined and stirred over anhydrous sodium sulfate. The solution was filtered, and the filtrate was concentrated to dryness. The resulting solids were stirred in refluxing hexanes overnight. The red/brown liquid was filtered, leaving a dark purple solid. The product was collected, vacuumdried, and analyzed by NMR, FT-IR, and mass spectrometry. Yield: 10.2 g, 81.0%. <sup>1</sup>H NMR (2, DMSO-d<sub>6</sub>, δ): 7.92 (s, 1H, Ph-NH-Ph-NH-), 7.88 (s, 1H, Ph-NH-Ph-NH), 6.65–7.19 (m, 13H, Ph), 2.84 (t, 1H, C= CH), 2.61 (t, 2H, OC(O)CH<sub>2</sub>), 2.25 (td, 2H, CH<sub>2</sub>C≡CH), 1.78 (quin, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (2, DMSO-d<sub>6</sub>,  $\delta$ ): 172.21 (C=O), 145.28, 143.12, 142.79, 136.95, 129.54, 122.70, 120.16, 120.07, 118.79, 115.96, and 115.52 ( $C_q$  of Ph), 84.08 (CH<sub>2</sub>C $\equiv$ CH), 72.39 (CH<sub>2</sub>C $\equiv$ 

CH), 32.79 (C=OCH<sub>2</sub>), 23.85 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 17.58 (CH<sub>2</sub>CH<sub>2</sub>C). FTIR (cm<sup>-1</sup>): 3388, 3294, 3052, 2965, 2916, 1736, 1600, 1511, 1380, 1310, 1225, 1197, 1167, 1144, 861, 817, 749, 692. MS (EI), m/z calcd for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: 370.17; found: 370.

Synthesis of Oligoaniline-Terminated PS (OANI-PS-OANI, 5). Oligoaniline groups were added onto the end of the PS polymer chains through a click reaction with oligoaniline-alkyne (2) and the terminal azide groups from polymer 4. Cu(I)Br (0.1 equiv) was charged into a round-bottom flask and purged with nitrogen for 30 min. OANI-alkyne (2, 2 equiv), N<sub>3</sub>-PS-N<sub>3</sub>  $(4, 1 \text{ equiv N}_3)$ , and PMDETA (0.15 equiv) were added to a pear shaped flask, dissolved in THF, and bubbled with nitrogen for 30 min. The mixture in the pear shaped flask was transferred to the round-bottom flask and stirred at room temperature overnight. The reaction mixture was concentrated to dryness, dissolved in dichloromethane, and extracted with water three times. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated. The solution was then precipitated into methanol two times. The solid product was collected by filtration and vacuum-dried overnight. Products 5a and 5b were analyzed by <sup>1</sup>H NMR and FTIR. <sup>1</sup>H NMR (3a, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 6.2–7.2 (br, Ph), 3.28 (br, OC(O)CH<sub>2</sub>), 3.16, (br,  $N_{triazole}CH(Ph)CH_2$ ), 2.61 (br,  $CH_2CC_{triazole}$ ), 2.46 (br, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.1–2.4 (br, CH<sub>2</sub>CHPh). FTIR (cm<sup>-1</sup>): 3391, 3027, 2923, 2849, 1732, 1659, 1601, 1495, 1451, 1023, 906, 756, 697

**Doping of OANI-PS-OANI with HCI (6), DDBS (7), and CSA (8).** Fractions (0.2 g) of polymers **5a** and **5b** were dissolved in dry DMF (3 mL) and passed through microfilters (pore size  $0.2 \mu$ m). HCl, DBSA, or CSA (50 equiv per OANI group) was added to the polymer solutions. Ammonium persulfate (50 equiv per OANI group) was also added to each solution. The solutions were then stirred at 70 °C for 48 h. Once cooled, dichloromethane (40 mL) was added, and the mixture was extracted with deionized water three times. The organic layer was stirred over anhydrous sodium sulfate, filtered, and concentrated to dryness. A small sample of each doped polymer was taken for analysis by UV–vis spectroscopy. The remainder of the sample was dissolved in toluene (3 mL).

#### RESULTS AND DISCUSSION

Synthesis of Oligoaniline-Terminated PS. Oligoanilineterminated polystyrene (OANI-PS-OANI, 5) was prepared as outlined in Scheme 2. To add an alkyne-group onto the termini of the oligoaniline moiety, 5-hexynoic acid was refluxed in oxalyl chloride, effectively converting the acid group to an acid chloride. The resulting 5-hexynoic acid chloride was then reacted with the hydroxy-ended oligoaniline trimer (1) under basic conditions to give an alkyne-terminated oligoaniline trimer (OANI-alkyne, 2). The purity of 2 was confirmed by NMR, FTIR, and mass spectrometry. Besides the appearance of the alkyl chain protons from the addition of the hexynoic acid group in the proton NMR between 1.78 and 2.84 ppm, we also observed the disappearance of the hydroxide proton from compound 1 at 8.91 ppm and a shift of the amine protons from 7.65 ppm and 7.48 ppm for compound 1 to 7.92 ppm and 7.88 ppm for compound 2 (Figure 1). FTIR analysis showed the appearance of sharp bands at 3388 and 1736  $\text{cm}^{-1}$  for compound 2, correlating to an alkyne group and an ester group, respectively. These results from proton NMR and FTIR, along with mass spectrometry, confirmed that product 2 was successfully prepared through the halide displacement reaction.

Polystyrene was prepared by atom transfer radical polymerization (ATRP) using a difunctional initiator so that both ends of the PS would contain bromine atoms.<sup>45,49</sup> Specifically, dimethyl 2,6-dibromoheptanedioate was used as the difunctional initiator, and the molar ratio of [initiator]:[Cu(I)Br]:[PMDETA] was 1:1:1.1. Both high (**3a**) and low (**3b**) molecular weight PS homopolymers were prepared by adjusting the feed ratio of monomer to initiator. Both polymerizations were stopped below



Figure 1. <sup>1</sup>H NMR spectra of hydroxy-terminated (1) and alkyneterminated (2) oligoaniline.

60% monomer conversion to limit coupling termination reactions and to ensure that all polymer chain ends contained a bromine atom. Both difunctional PS polymers had low polydispersity indices (PDI < 1.1). The final molecular weight could be accurately determined by GPC analysis, as the system was calibrated using PS standards. The final molecular weight and PDI are shown in Table 1. The terminal bromine groups on difunctional PS homopolymers **3a** and **3b** obtained by ATRP were converted to azide groups by reaction with sodium azide.<sup>45</sup> The transformation from bromide to azide end groups was confirmed using FTIR, as a sharp band appeared at 2094 cm<sup>-1</sup>, which is typical for an azide stretching mode.

To prepare the oligoaniline-terminated PS, a click reaction was performed on the azide-terminated PS (4a and 4b) with the oligoaniline-alkyne (2) using copper(I) bromide and PMDETA in THF. The excess oligoaniline-alkyne and residual copper bromide were removed by extraction with water followed by precipitating into a large excess of methanol two times. The disappearance of the alkyne stretch at 3294 cm<sup>-1</sup> and the azide band at 2094 cm<sup>-1</sup>, the appearance of a band at 1504 cm<sup>-1</sup>, which is typical of a triazole group, and the appearance of a small, broad peak at 3391 cm<sup>-1</sup> from the amine groups of the oligoaniline confirmed the addition of the oligoaniline onto the PS chain end (Figure 2).

Doping with Acids. The oxidation states of the oligoaniline trimer were previously investigated by UV-vis spectroscopy.<sup>44,50–54</sup> Briefly, when oligoaniline is in the fully reduced form, only one absorption peak at 310 nm is observed in a solution of DMF. When an oxidant (e.g., ammonium persulfate) and an acid dopant are added, the oxidized oligoaniline displays a peak around 570 nm due to the charge transfer from the benzenoid ring to the quinoid ring. Additionally, the peak that was at 310 nm shifts to 301 nm. As these peaks are very prominent, UV-vis was again used to confirm the oxidation and complexation of oligoaniline when doping with acids. Polymers 5a and 5b were doped with HCl (6a and 6b), dodecylbenzenesulfonic acid (DBSA, 7a and 7b), and camphorsulfonic acid (CSA, 8a and 8b), as summarized in Table 2. An excess of acid as well as ammonium persulfate were added to the polymer solution (5a and 5b) and stirred at 70 °C for 48 h to ensure that all oligoaniline moieties were oxidized and doped with the corresponding acid. Removal of excess acids is crucial, as it has been previously shown that any free acid can result in increased dielectric loss in final dielectric materials because of ionic conduction.<sup>44</sup> To ensure that all excess free acids and remaining ammonium persulfate were removed, the polymer solutions were dissolved in dichloromethane and extracted with deionized water three times. The organic layer was

| entry | polymer                           | [monomer]:[initiator] | $M_{\rm n}$ , g/mol (NMR) <sup>a</sup> | $M_{\rm n'}  { m g/mol}  ({ m GPC})^b$ | PDI (GPC) |
|-------|-----------------------------------|-----------------------|----------------------------------------|----------------------------------------|-----------|
| 3a    | Br-PS-Br                          | 480:1                 | 29,000                                 | 29,800                                 | 1.05      |
| 3b    | Br-PS-Br                          | 98:1                  | 6,200                                  | 6,300                                  | 1.04      |
| 4a    | N <sub>3</sub> -PS-N <sub>3</sub> |                       |                                        | 29,800                                 | 1.06      |
| 4b    | N <sub>3</sub> -PS-N <sub>3</sub> |                       |                                        | 6,300                                  | 1.08      |

<sup>a</sup>Calculated by <sup>1</sup>H NMR using monomer conversion. <sup>b</sup>Calculated by GPC calibrated by polystyrene standards.



Figure 2. FTIR overlay for oligoaniline-alkyne (OANI-alkyne, 2), bromide- (3b), azide- (4b), and oligoaniline- (5b) end functionalized polystyrene.

then dried over sodium sulfate, filtered, and vacuum-dried. Small samples of the final doped polymers (6a-8b) were analyzed by UV-vis. As an example of confirmation of the doping process, the UV-vis spectra for the lower molecular weight doped polymers 5b, 6b, 7b, and 8b are shown in Figure 3. Polymers 5a, 6a, 7a, and 8a exhibited similar UV-vis spectra, as listed in Table 2. The oxidation and doping process was clearly observed with the shift of the  $\pi - \pi^*$  peak from 310 nm to around 300 nm, as well as the appearance of peaks around 390 and 525 nm.

Dielectric Properties. The dielectric properties of oligoaniline-capped PS (OANI-PS-OANI), undoped and doped with various acids, were characterized using impedance spectroscopy and polarization testing. Impedance measurements yield the relative permittivity as a function of frequency (Figure 4) for polymers 3a-8b. The higher molecular weight (~30,000 g/mol) Br-terminated polystyrene 3a has a relative permittivity of about 2.7, nearly independent of frequency. Upon converting the endgroup from Br to OANI units, the relative permittivity for polymer 5a increases to a value of about 3.5, again constant across the  $10^3 - 10^6$  Hz frequency range. Polymer **6a**, in which the OANI units are doped with HCl, shows a slight increase in relative permittivity ( $\varepsilon_r = 3.9-4.1$  between  $10^3-10^6$  Hz) compared to polymer 5a. In the same frequency range, the permittivity of polymer 7a (OANI-PS-OANI doped with DBSA)

increases to values between 6 and 9; polymer 8a, (OANI-PS-OANI doped with CSA) shows greater enhancement of permittivity with values in the 8.8-12 range.

Lower molecular weight oligoaniline-capped PS polymers show similar trends but larger enhancement in permittivity. The lower molecular weight (~6,000 g/mol) Br-terminated polystyrene 3b has a nearly constant permittivity of about 4.3. Undoped polymer 5b has permittivity value of about 3.6. HCldoped polymer 6b has permittivity values around 8; DBSA doped polymer 7b had permittivity between 13.3 and 20; and CSA doped polymer 8b had permittivity values between 22.6 and 24.2 across the range of  $10^3 - 10^6$  Hz. The permittivity of polymer 8b is nearly 1 order of magnitude higher than that of polystyrene homopolymer, indicating the significant impact of the oligoaniline chain end when doped by the large organic acid, CSA. The greater enhancement in permittivity for the lower molecular weight OANI-PS-OANI polymers can be attributed to their higher fraction of aniline. The weight percents of the oligoaniline/acid complex relative to the total molecular weight of the polymers are summarized in Table 2.

As shown in Figure 5, the loss tangents for all polymers, including the acid doped polymers, remain below 0.6 across the range 10<sup>3</sup>-10<sup>6</sup> Hz. For CSA-doped polymers 8a and 8b with highest permittivity, the dielectric loss at frequency 0.1 MHz was

| Table | 2. | Pre | paration | of | Oxidized | and D | oved ( | )lig | roaniline | -Ended | PS         |
|-------|----|-----|----------|----|----------|-------|--------|------|-----------|--------|------------|
|       |    |     |          | ~  | ·        |       | •••••  |      |           |        | - <b>u</b> |

| entry | polymer | oxidant          | dopant | absorbance peaks $(nm)^a$ | wt % OANI/acid <sup>b</sup> |
|-------|---------|------------------|--------|---------------------------|-----------------------------|
| 5a    | 5a      | none             | none   | 310                       | 1.81%                       |
| 5b    | 5b      | none             | none   | 310                       | 7.94%                       |
| 6a    | 5a      | $(NH_4)_2S_2O_8$ | HCl    | 300, 395, 524             | 1.93%                       |
| 6b    | 5b      | $(NH_4)_2S_2O_8$ | HCl    | 300, 395, 524             | 8.41%                       |
| 7a    | 5a      | $(NH_4)_2S_2O_8$ | DBSA   | 298, 385, 520             | 2.84%                       |
| 7b    | 5b      | $(NH_4)_2S_2O_8$ | DBSA   | 298, 385, 520             | 12.02%                      |
| 8a    | 5a      | $(NH_4)_2S_2O_8$ | CSA    | 299, 383, 529             | 2.56%                       |
| 8b    | 5b      | $(NH_4)_2S_2O_8$ | CSA    | 299, 383, 529             | 10.91%                      |

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<sup>a</sup>Values from UV-vis. <sup>b</sup>Calculated assuming complete doping of oligoaniline.

7b 0.8 8b 0.6 0.4 02 0.0 500 600 700 200 300 400 800 9<u>0</u>0 Wavelength (nm) Figure 3. UV/vis spectra for polymers 5b-8b.



1.0

Absorbance (AU)

5h

6b



Figure 4. Relative permittivity versus frequency for polymers (A) 3a–8a and (B) 3b–8b.



Figure 5. Loss tangent (dielectric loss) versus frequency for (A) polymers 3a-8a and (B) polymers 3b-8b.

only 0.05 and 0.02, respectively. This was substantially lower than other oligoaniline-containing ferroelectric copolymers as previously reported.  $^{39-41}$ 

Past experimental and theoretical studies have shown that bulky organic acids can have a large effect on the conductivity in polyaniline and oligoaniline films.<sup>55,56</sup> A recent study utilizing density functional theory (DFT) found that organic acid CSA has much stronger interactions with the nitrogen atoms of oligoaniline than HCl, resulting in more stable complexes.<sup>57</sup> This suggests that organic acids produce more charge transfer between the dopant and the oligoaniline complex, allowing for greater electron transfer, and ultimately enhanced conductivity. As shown in Figure 6, polymers 7a, 7b, 8a, and 8b, which contain



Figure 6. Conductivity versus frequency for (A) polymers 3a-8a and (B) polymers 3b-8b.

oligoaniline units doped by large organic acids (DBSA and CSA), display much higher levels of electrical conductivity than HCl-doped polymers **6a** and **6b**. Specifically polymers **7a**, **7b**, **8a**, and **8b** display conductivities 2 orders of magnitude greater than **6a**,**b** at low frequencies ( $10^3$  Hz), and an order of magnitude greater at high frequencies ( $10^6$  Hz). These higher levels of conductivity directly correlate to higher levels of permittivity across the range of  $10^3-10^6$  Hz (Figure 4).

In addition, DBSA- and CSA-doped polymers 7a, 7b, 8a, and 8b display relative permittivity that decreases noticeably with increasing frequency. Bulky DBSA and CSA anions complexed with oligoaniline create relatively large dipoles that may undergo orientational polarization and contribute to the permittivity, especially at low frequencies. Orientational polarization might be responsible for the energy dissipation observed at low frequencies for polymers 7a, 7b, 8a, and 8b (Figure 5). Orientational polarization relaxes at higher frequencies (>10<sup>4</sup> Hz), where the enhanced dielectric responses likely result

primarily from electronic polarization. Again, organic acids DBSA and CSA facilitate greater charge separation and local space charge buildup at the interface between conducting and insulating segments. These results are consistent with previous work which utilized large organic acids to dope polyaniline and oligoaniline-containing polymers to prepare highly conductive aniline-based films.<sup>41,58</sup>

Figure 7 shows results from polarization testing at low to moderate voltages (1-199 V), in contrast to the impedance results obtained at very low applied voltage (typically 10 mV). As expected, the polarization curves for PS homopolymer are nearly linear with low hysteresis. In contrast, all acid-doped OANI-capped PS polymers show significantly enhanced dielectric polarization compared to PS homopolymer, as evidenced by the slopes of the *D-E* curves in Figure7. This shows that acid-doped OANI-capped PS polymers have much higher energy storage capacity than PS homopolymer.

Figure 8 shows the stored energy density of acid-doped OANIcapped PS relative to that of pure PS measured at the same electric field polarization. The higher molecular weight polymers (**6a**, **7a**, **8a**), containing 2–3% OANI (Table 2), have stored energy densities that are 4–8 times higher than that of the PS homopolymer. For lower molecular weight polymers (**7b**, **8b**), doped with DBSA or CSA and having 11–12% OANI, the relative energy densities increase further, to 10–12 times higher than that of PS. However, the relative energy density of polymer **6b** (HCl-doped, 8.41% OANI) decreases relative to that of polymer **6a**, although it is still more than twice as large as the energy density stored in PS homopolymer at the same applied field strength. This trend can be seen in Figure 7A, in which the *D-E* curve for polymer **6b** has a smaller slope than that of polymer **6a**.

The *D-E* curves in Figure 7 also show that all acid-doped OANI-capped PS polymers manifest more nonlinearity and hysteresis than PS homopolymer. In general, the energy loss percentage (not shown here) increases with OANI content and maximum applied electric field, and decreases with increasing polarization cycle frequency.

The significant enhancement of the permittivity of polystyrene by the chain-end group could be explained by the presence of oligoaniline-rich domains dispersed in the polystyrene matrix. The formation of these nanoscale domains would significantly enhance the interfacial area of highly polarizable nanodipoles. This hypothesis is further supported by the higher permittivity of low molecular weight PS compared to that of higher molecular weight PS when doped with same reagents, as the weight fraction of oligoaniline plus dopant in the lower molecular weight PS was in the range of 8-12 wt %, which was sufficient to have nanoscale phase separation between chain ends and the polystyrene matrix (Scheme 1). However, this phase separation would be much less prominent in high molecular weight PS as the weight fraction of oligoaniline plus dopant was only around 2 wt %, which would lead to totally disorganized systems. To support this hypothesis, SAXS measurement was carried out on polymers 6a-8b. For the high molecular weight polymers 6a, 7a, and 8a, no ordered peaks were observed, as shown in Figure 9A. Given that polymers 6a, 7a, and 8a had only 2 wt % oligoaniline/acid dopant, these polymers probably formed homogeneous systems. However, for the low molecular weight polymers 6b, 7b, and 8b, a weak correlation peak at the 5 nm length scale  $(d = 2\pi/q)$  was observed (Figure 9B). Since there were no additional higher order peaks present, it can be concluded that these polymers did not form well-ordered nanodomains of oligoaniline/acid dopant complex,



**Figure 7.** Dielectric polarization versus applied electric field for PS and OANI-capped PS doped with (A) HCl, (B) DBSA, and (C) CSA. All measurements carried out with 100 Hz cycle frequency.

but rather disordered domains with broad interfaces between them and polystyrene matrix. Nevertheless, these results suggest that these highly polarizable nanodomains led to significant enhancements in dielectric permittivity.

## CONCLUSION

In conclusion, we prepared oligoaniline end-functionalized polystyrene polymers via click chemistry between azide-ended polystyrene and alkyne-containing oligoaniline. The oligoaniline



**Figure 8.** Stored energy density ratio ( $\hat{W}_{OANLPS}$  divided by  $\hat{W}_{PS}$  measured at the same frequency and field strength) as a function of OANI weight percent. All measurements carried out at 100 Hz cycle frequency with energy densities determined at 12.9 kV/cm field strength.



units were doped by various acids, including HCl, DBSA, and CSA. The dielectric properties of these oligoaniline-ended PS polymers indicated that doping with large, organic acids resulted in increases of up to an order of magnitude in permittivity and energy storage density relative to PS, while maintaining a relatively low dielectric loss, especially in the high frequency range. Given its simplicity, this novel strategy could be generalized to improve dielectric permittivity of many other commodity polymers.

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#### Notes

The authors declare no competing financial interest.

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