Pi-Conjugated Chain Extenders for the Synthesis of Optoelectronic Segmented Polyurethanes

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ABSTRACT: The optical properties of mechanochromic materials change under mechanical stress. Segmented polyurethanes are elastomers composed of amorphous, saturated chain soft segments, and rigid pi-conjugated hard domains. Within aggregates of hard domains pi–pi interactions may form and result in perturbation of the optoelectronic properties of the system. Disruption and restoration of these electronic interactions within the material may lead to observable mechanochromic response. A series of oligothiophene diols and diamines, as well as a naphthalene diimide diol, have been synthesized for incorporation into the hard domains of segmented polyurethanes and polyureas using long poly(tetramethylene oxide) chains as soft segments. The resulting polymers were evaluated to determine their extent of polymerization and their thermal stability. The optical properties of the materials were studied in solution and as thin films. Where possible the electrochemical properties of the polymers were also explored. The length of the soft segment chains in the segmented polyurethanes hindered electronic coupling of hard domains. Future work involving smaller, more solubilizing soft segments may allow for easier material characterization and mechanochromic response. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4861–4874, 2011

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INTRODUCTION Pi-conjugated electronic materials are now recognized as viable and competitive active components for lightweight and processable device applications requiring light emission, charge transport, or energy storage.[1–3] Although small molecule pi-conjugated organics can be grown into high-quality single crystals suitable for inclusion in sophisticated device architectures, these materials often lack the solution processability of their polymeric counterparts. New synthesis technologies have led to the construction of highly regioregular conjugated polymers where the solubilizing side-chain orientations provide critical control of interpolymer packing of the pi-conjugated backbones.[4] These and other types of supramolecular organizations will play key roles in the enhancement of pi-electron delocalization at the molecular level that is ultimately parlayed functionally into macroscopic substrates.[5]

With respect to supramolecular organization, natural silk proteins exploit phase segregation en route to high-performance structural polymers.[6] In these elastomeric materials, there is a partitioning of a repetitive polymer into domains of “soft” amorphous chain segments composed of disordered peptide sequences accompanied by domains of “hard” crystalline chain segments rich in β-sheet peptide conformations. The unique mechanical properties of these silks arise from the strong restoring forces leading a mechanically deformed material back to the initial state as driven by the re-establishment of the enthalpically favorable hydrogen-bonding interactions among the β-sheets that make up the hard domains. A variety of synthetic elastomers have been prepared that mimic these mechanical properties such as the segmented polyurethanes (Spandex/Lycra).[7] We report here the syntheses of segmented polyurethanes and polyureas where well-defined pi-conjugated oligomers (both potential p-channel and n-channel materials) have been incorporated into the hard domains of the polymer backbone as a means to facilitate pi-electron delocalization within the hard domains of the bulk polymeric material.

Our interest in segmented polyurethanes was inspired by Rubner’s work with mechanochromic polydiacetylenes.[8–10] This polymer design involved the preparation of a soft macromonomer through the endcapping of poly(tetramethylene oxide) (PTMO) with a diisocyanate. This macromonomer was subjected to chain extension polymerization with a butadiynyl diol thus yielding the segmented polymer. The

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diacetylenes were confined to the hard domain after phase segregation and subsequently cross-linked through topochemical polymerization. It was anticipated that mechanical stresses would disrupt the chromophore arrangements within the hard domains thus leading to altered optical responses. Reversible chromic behavior was observed, but these effects were attributed to changes in interactions among the cross-linked hard domains rather than to specific changes in interchromophore interactions.

Chromic materials that are responsive to external mechanical stimuli are important as sensors for applied stresses or loads being borne by a composite material.[11] Segmented polyurethanes containing pendent liquid crystal segments exhibit changes in liquid-crystalline phase ordering in response to mechanical stress.[12–14] Another class of mechanochromic materials is the broad family of self-assembled colloidal particle arrays whose effects are rendered by altered lattice spacings among silica or polymer particles dispersed within a polymerized matrix upon application of a mechanical stress.[15,16] Compression of the array alters the spacing and the Bragg conditions thus impacting the optical properties associated with reflected and refracted light. Related mechanochromic effects can also be envisioned from deformations of spherical block copolymer morphologies that exhibit specific photonic bandgaps.[17] Mechanochromic responses can also be triggered from molecular dyes dispersed within supporting polymer matrices, whereby mechanical alterations of interchromophore interactions will lead to altered absorption or photoluminescence profiles.[18–20] These effects arise from altered influences of exciton coupling among dye aggregates that allow for excimer/exciplex photoluminescence when the dyes form nanoscopic aggregates in the relaxed polymer, and regular fluorescence properties arising from a "molecularly dispersed" dye when the polymers are stretched and the aggregates are disrupted or broken up to a greater extent. Mechanical deformation of the molecular dye–polymer composite upon the application of mechanical stress led to irreversible spectral shifts due to the disruption of the aggregated chromophore dopants. Mechanochromism was reported where the application of mechanical stresses led to specific and irreversible chemical alterations within embedded photochromic dyes leading to direct color changes rather than those through the light irradiation commonly used for photochromic switching.[21,22] The potential use of mechanical stress to direct chemical reactions within polymeric materials is also being investigated.[23]

In this report, we describe the synthesis of segmented polyurethanes and polyureas bearing well-defined pi-conjugated units for potential use as mechanochromic materials with reversible optical responses due to the restoring forces present in the covalent polymer backbone. The phase segregation is expected to be disrupted under applied mechanical stress due to the disruption of weak interactions such as hydrogen bonding within the hard domains of the relaxed polymer. More important from a chromic perspective is that this disruption may also change the optoelectronic properties of the polymer due to alterations in exciton coupling. The motivation behind this work was to explore the prospects for new polymers that would undergo clear and reversible chromicity changes due to the re-establishment of exciton coupling or other types of pi–pi interactions within the hard domains, as they reform in the absence of applied stresses.

In addition to preliminary synthetic work, we present the optical and thermal characterization of the resulting polymeric materials. Recent work has examined the incorporation of functional electronic units such as 3,4-ethylenedioxythiophene (EDOT) monomer, rylene diimides, and oligophenylene vinylenes into polyurethane-type materials.[19,24–26] The pi systems embedded within the macromonomers here consist of a series of telechelic oligothiophene diols and diamines as chain extenders for complex polymer synthesis.

EXPERIMENTAL

All air or water sensitive syntheses were performed using oven or flame dried glassware and air-free Schlenk line techniques. Solvents were degassed by purging with N_2 for at least 30 min prior to use. All chemicals were used as received from the supplier (Aldrich, Acros, Alfa Aesar), and the palladium catalysts were obtained from Strem Chemicals. 2,5-Bis(tributylstannyl)thiophene[27] and 5,5′-bis(tributylstannyl)-2,2′-bithiophene[28] were prepared by lithiation of thiophene or 2,2′-bithiophene with *n*-BuLi then quenching with tributyl tin chloride followed by distillation. Molecular weights and molecular weight distributions were determined via gel permeation chromatography (GPC) using a Waters chromatograph containing a two-column bed (styragel HR 7.8 × 300 mm columns with 5 μm beads size; 500–30,000 and 2,000–600,000 Da), a Waters 2414 refractive index detector, and a Waters 2489 UV–visible detector (254 nm). GPC samples were run in tetrahydrofuran (THF) at a flow rate of 1 mL/min at 30 °C and calibrated against polystyrene standards. Analysis was done using Empower 2 software. Differential scanning calorimetry (DSC) was performed using TA Instruments DSC Q1000 V9.8 Build 296, and thermogravimetric analysis (TGA) was performed using TA Instruments TGA Q500 V6.7 Build 203. NMR data were obtained on Bruker Avance instruments at either 400 or 300 MHz for ^{1}H spectra or 100 or 75 MHz for ^{13}C spectra. A Varian Cary 50 Bio UV-Visible spectrophotometer was used to acquire UV–vis data. Electrochemical measurements were conducted using an Autolab PGSTAT 302 bipotentiostat. Solutions for electrochemical experiments were prepared in THF containing 0.1*M* tetrabutylammonium hexafluorophosphate (TBAP) as an electrolyte. Potentials were recorded at a 2 mm^2 platinum button electrode versus a quasi-internal Ag/Ag$^+$ reference.

tert-Butyldimethyl(thiophen-2-ylmethoxy)silane (**2**): 2-thiophenemethanol (**1**; 3.224 g, 28.20 mmol), imidazole (2.320 g, 34.08 mmol), and 12 mL of degassed dimethylformamide (DMF) were added to a 50-mL flask. Then *tert*-butyldimethylsilyl chloride (5.142 g, 34.10 mmol) was added. After 24 h the cloudy, white reaction mixture was diluted with ether (100 mL) and filtered. The filtered solution was placed in a separation funnel and washed with water (2× 75 mL), then with saturated ammonium chloride solution (4× 50 mL), and then with water again (2× 75 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide the slightly yellow oil product (6.194 g, 27.11 mmol, 97%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.23 (dd, $J = 4.9$, 1.4 Hz, 1H), 6.98–6.95 (m, 2H), 4.92 (s, 2H), 0.98 (s, 9H), 0.15 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 145.3, 126.5, 124.6, 123.8, 60.8, 26.0, 18.4, −5.2. HRMS (EI) m/z calculated for ($C_{11}H_{20}OSSi$) 228.10042, found 228.09971 [$M^{+}\cdot$].

((5-Bromothiophen-2-yl)methoxy)(*tert*-butyl)dimethylsilane (**3**): **2** (10.251 g, 44.876 mmol) and 100 mL degassed DMF were added to a dried 250-mL Schlenk flask. The reaction vessel was wrapped in foil to exclude light then *N*-bromosuccinamide (NBS; 8.801 g, 49.45 mmol) was added portion-wise. After 18 h, the dark red reaction mixture was diluted with ether to 700 mL total volume. The resulting mixture was washed with saturated ammonium chloride solution (4× 150 mL) and then with water (2× 200 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to a dark red oil. This oil was loaded onto a silica gel plug packed in hexane and eluted with 1 L of 20% dichloromethane in hexane. The solvent was concentrated under reduced pressure to provide the oil product (11.93 g, 38.82 mmol, 86%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 6.90 (d, $J = 3.68$ Hz, 1H), 6.68 (d, $J = 3.64$ Hz, 1H), 4.82 (d, $J = 1.04$ Hz, 2H), 0.98 (s, 9H), 0.15 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 147.21, 129.25, 123.62, 111.10, 60.90, 25.90, 18.35, −5.21. HRMS (EI) m/z calculated for ($C_{11}H_{19}BrOSSi$) 306.01093, found 306.01133 [$M^{+}\cdot$].

Compound previously reported by Cama et al.[29] and Rivero et al.[30]

tert-Butyldimethyl((5-(tributylstannyl)thiophen-2-yl)methoxy) silane (**4**): **2** (1.094 g, 4.789 mmol) and 10 mL dry THF were added to a dried 50-mL flask. The reaction vessel was cooled in an ice bath, and then, 1.47*M* *n*-butyl lithium in hexane (3.4 mL, 5.0 mmol) was added drop-wise. During this addition, the reaction mixture became tan/yellow. After 1 h, tributyltin chloride (1.665 g, 5.115 mmol) was added in one portion, which caused the solution to turn a light golden color. The ice bath was removed, and after 3 h the reaction mixture was loaded onto a silica gel plug packed and eluted with hexane (300 mL). The collected solvent was concentrated under reduced pressure to provide the yellow oil product (2.167 g, 4.188 mmol, 87%) with slight tributyltin impurity which was used without further purification. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ: 7.00 (m, 2H), 4.96 (s, 2H), 1.62 (m, 6H), 1.39 (m, 6H), 1.14 (m, 6H), 0.98 (s, 9H), 0.92 (m, 9H), 0.15 (s, 6H).

tert-Butyl thiophen-2-ylmethylcarbamate (**6**): 2-thiophenemethylamine (**5**; 4.858 g, 42.92 mmol) and 100 mL dry dichloromethane were added to a dried 250-mL Schlenk flask. Then, triethylamine (6.721 g, 66.42 mmol) was added to the solution. Di-*tert*-butyl dicarbonate (11.282 g, 51.693 mmol) was then added portion-wise which caused bubbles to evolve from the solution. Once the di-*tert*-butyl dicarbonate addition was complete, the bubbling continued for ~90 min. After 4 h, the reaction mixture was placed in a separation funnel and washed with water (3× 75 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide a yellow oil. This oil was crystallized from boiling hexane. The crystallites were collected by filtration and after rinsing with additional hexane yielded the product as a white solid (7.883 g, 36.99 mmol, 86%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.19 (dd, $J = 4.4$, 2.0 Hz, 1H) 6.93 (m, 2H), 4.98 (br, 1H), 4.46 (d, $J = 5.4$ Hz, 2H), 1.46 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 155.8, 142.2, 127.0, 125.2, 80.0, 39.8, 28.7. HRMS (EI) m/z calculated for ($C_{10}H_{15}NO_2S$) 213.08235, found 213.08247 [$M^{+}\cdot$].

Compound previously reported by Klare et al.[31]

tert-Butyl (5-bromothiophen-2-yl)methylcarbamate (**7**): **6** (1.003 g, 4.707 mmol) was added to a 50-mL flask and dissolved in 10 mL of degassed DMF. The reaction vessel was then wrapped in foil to exclude light, and NBS (0.907 g, 5.10 mmol) was then added portion-wise. After 18 h, the light yellow reaction mixture was diluted with ether to 200 mL total volume. This mixture was washed with saturated ammonium chloride solution (4× 100 mL) and then with water (2× 100 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide the light yellow oil product that was used without further purification (1.37 g, 4.69 mmol, quantitative). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 6.82 (d, $J = 3.6$ Hz, 1H), 6.64 (d, $J = 3.5$ Hz, 1H), 5.21 (br, 1H), 4.32 (d, $J = 5.7$ Hz, 2H), 1.42 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 155.8, 144.3, 129.6, 125.83, 111.5, 80.0, 39.9, 28.6. HRMS (EI) m/z calculated for ($C_{10}H_{14}BrNO_2S$) 290.99286, found 290.99243 [$M^{+}\cdot$].

Compound previously reported by Klare et al.[31]

tert-Butyl (5-(tributylstannyl)thiophen-2-yl)methylcarbamate (**8**): **6** (1.606 g, 7.537 mmol) was added to a 100-mL Schlenk flask and dissolved in 30 mL of dry THF. The reaction mixture was cooled in an ice bath. *n*-Butyl lithium (1.59*M*) in hexane (10.4 mL, 16.5 mmol) was added to the reaction drop-wise forming a dark purple/brown mixture. The reaction was maintained at 0 °C for 45 min, and then Bu_3SnCl (5.426 g, 16.67 mmol) was added drop-wise resulting in a dark purple solution. The ice bath was removed, and after 6 h the reaction mixture was diluted with THF (350 mL) and washed with brine (4× 100 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide a dark brown oil. This oil was dissolved in 10% EtOAc/hexane and loaded onto a silica gel plug packed and eluted with 10% EtOAc/hexane (1 L). Collected eluent was concentrated under reduced pressure to provide the dark red oil product (3.770 g, 7.505 mmol, 99%) with slight tributyltin impurity which was used without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.05 (bs, 1H), 7.00 (d, $J = 4.3$ Hz, 1H), 4.81 (bs, 1H), 4.51 (d, $J = 7.7$ Hz, 2H), 1.56–1.53 (m, 6H), 1.46 (s, 9H), 1.37–1.29 (m, 6H), 1.11–1.05 (m, 6H), 0.92–0.87 (m, 9H).

5,5′-Bis((*tert*-butyldimethylsilyloxy)methyl)-2,2′-bithiophene (**9**): **3** (1.464 g, 4.764 mmol), **4** (2.506 g, 4.843 mmol), and 20 mL degassed DMF were added to a dried 100-mL Schlenk flask. $Pd(PPh_3)_4$ (0.097 g, 0.084 mmol) was added, and reaction mixture was heated to 75 °C in an oil bath. After 2 days, the dark brown reaction mixture was diluted with 600 mL of ether, and the resulting mixture was washed with saturated ammonium chloride solution (4× 150 mL) and water (2× 200 mL). The organic layer was collected, dried over magnesium sulfate, and the solvent was concentrated under reduced pressure to provide a light brown oil. This oil was loaded onto a silica gel column packed in hexane and eluted with 30% dichloromethane in hexane. The fractions containing product were concentrated under reduced pressure to provide a green oil which solidified in the freezer. Pale green crystals were collected by filtration (1.078 g, 2.370 mmol, 50%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 6.96 (d, $J = 3.6$ Hz, 2H), 6.79 (d, $J = 3.6$ Hz, 2H), 4.83 (d, $J = 0.9$ Hz, 4H), 0.93 (s, 9H), 0.11 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 144.5, 137.2, 124.6, 123.1, 61.1, 26.2, 18.7, −4.9. HRMS (FAB-MS) *m/z* calculated for ($C_{22}H_{38}O_2S_2Si_2$) 454.18518, found 454.18414 [$(M+H)^+$].

2,2′-Bithiophene-5,5′-diyldimethanol (**10**): **9** (1.078 g, 2.370 mmol) and 50 mL THF were placed in a 250-mL flask. Twenty milliliters of 1*M* tetrabutylammonium fluoride (TBAF; 20 mmol) in THF (with 5% water) solution was added which caused the initially light green reaction mixture to become light yellow. After 2 days, the light brown reaction mixture was loaded onto a silica gel plug packed and eluted with ethyl acetate (800 mL). The collected solvent was concentrated under reduced pressure to provide a light yellow oil, which was crystallized from boiling chloroform. The yellow solid product was collected by filtration (0.250 g, 1.105 mmol, 46%). ^{1}H-NMR (300 MHz, CD_3OD, ppm) δ: 7.02 (d, $J = 3.6$ Hz, 2H), 6.89 (dt, $J = 3.6, 0.8$ Hz, 2H), 4.69 (d, $J = 0.5$ Hz, 4H). ^{13}C-NMR (75 MHz, CD_3OD, ppm) δ: 145.3, 138.5, 126.8, 124.0, 60.0. HRMS (EI/CI) *m/z* calculated for ($C_{10}H_{10}O_2S_2$) 226.01222, found 226.01229 [$M^{+}\cdot$].

Compound previously reported by Joo et al.[32]

tert-Butyl 2,2′-bithiophene-5,5′-diylbis(methylene)dicarbamate (**11**): DMF (250 mL) was placed into a 500-mL Schlenk flask and degassed with nitrogen purge for 1 h. **8** (6.034 g, 12.01 mmol) was added to the solvent forming a red solution. **7** (3.527 g, 12.07 mmol) and $Pd(PPh_3)_4$ (0.395 g, 0.342 mmol) were added. The reaction flask was placed in an oil bath and heated to 65 °C. After 3 days the reaction mixture was cooled to room temperature, diluted with ether (500 mL), and washed with saturated ammonium chloride solution (4× 150 mL) and water (2× 150 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide a red/brown solid. Hexane (500 mL) was added to the collected solid, and the mixture was sonicated for several minutes. The brown solid product was collected by filtration (2.746 g, 6.468 mmol, 54%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 6.94 (d, $J = 3.6$ Hz, 2H), 6.82 (d, $J = 3.1$ Hz, 2H), 4.91 (bs, 2H), 4.43 (d, $J = 4.9$ Hz, 4H), 1.47 (s, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 155.7, 141.3, 137.1, 126.2, 123.3, 80.0, 39.8, 28.5. HRMS (FAB-MS) *m/z* calculated for ($C_{20}H_{28}N_2O_4S_2$) 424.14905, found 424.14880 [$M^{+}\cdot$].

2,2′-Bithiophene-5,5′-diyldimethanaminium chloride (**12**): **11** (2.704 g, 6.369 mmol) was added to a 1-L round bottom flask and dissolved in dioxane (450 mL) forming a red solution. Concentrated HCl (150 mL) was added to the vigorously stirred solution, which clouded over time. After 18 h, the reaction mixture was filtered and the gray solid product was collected and dried under vacuum (1.633 g, 5.493 mmol, 86%). ^{1}H-NMR (400 MHz, D_2O, ppm) δ: 7.27 (d, $J = 5.0$ Hz, 2H), 7.21 (d, $J = 5.0$ Hz, 2H), 4.42 (s, 4H), 3.78 (s, 6H)

Compound previously reported by Muguruma et al.[33]

2,2′-Bithiophene-5,5′-diyldimethanamine (**13**): **12** (1.621 g, 5.453 mmol) was added to a 1-L round bottom flask and dissolved in water (400 mL.) Aqueous KOH (2*M*, 20 mL, 40 mmol) was added, which caused the solution to cloud. After 6 h, the reaction mixture was filtered, and the collected liquid was extracted with dichloromethane (4× 200 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure to provide the gray/tan solid product (1.180 g, 5.260 mmol, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 6.96 (d, $J = 3.6$ Hz, 2H), 6.79 (d, $J = 3.5$ Hz, 2H), 4.02 (s, 4H), 1.66 (bs, 4H). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm) δ: 149.2, 136.2, 125.1, 123.8, 42.2. HRMS (EI/CI) *m/z* calculated for ($C_{10}H_{12}N_2S_2$) 224.04419, found 224.04428 [$M^{+}\cdot$].

Synthesis previously reported by Muguruma et al.[33]

5,5″-Bis(((*tert*-butyldimethylsilyl)oxy)methyl)-2,2′:5′,2″-terthiophene (**15**): **3** (6.628 g, 21.57 mmol) was added to a 250-mL flask and dissolved in 100 mL degassed DMF. 2,5-Bis(tributylstannyl)thiophene (**14**; 7.137 g, 10.78 mmol) and $Pd(PPh_3)_4$ (0.745 g, 0.645 mmol) were added to the solution. The reaction vessel was placed in an oil bath and heated to 60–70 °C. After 5 days, the cloudy, black reaction mixture was diluted with ether to 700 mL total volume. The resulting mixture was filtered through a cotton plug into a separation funnel and washed with saturated ammonium chloride solution (4× 150 mL) and then with water (2× 200 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide an amber/yellow solid. This solid was recrystallized from methanol to yield clean product as a red/brown solid (4.033 g, 7.511 mmol, 70%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.02 (s, 2H), 6.99(d, $J = 3.6$ Hz, 2H), 6.81 (d, $J = 3.6$ Hz, 2H), 4.84 (s, 4H), 0.94 (s, 18H), 0.12 (s, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 145.0, 136.7, 136.6, 124.8, 124.3, 123.4, 61.2, 26.2, 18.7, −4.9. HRMS (FAB-MS) *m/z* calculated for ($C_{26}H_{40}O_2S_3Si_2$) 536.17290, found 536.17186 [$(M+H)^+$].

[2,2′:5′,2″-Terthiophene]-5,5″-diyldimethanol (**16**): **15** (1.495 g, 2.784 mmol) was placed in a 250-mL flask and dissolved in 80 mL THF forming a red/amber solution. TBAF (1*M*) in THF (12 mL, 12 mmol; with 5% water) solution was added to flask. After 20 h, the reaction mixture was loaded onto a silica gel plug packed in ethyl acetate. This plug was eluted with 1 L of 10% methanol in ethyl acetate solution. Collected solvent was concentrated under reduced pressure to provide a red/orange solid. This solid was recrystallized from boiling chloroform. The yellow/orange solid product was collected by filtration (0.466 g, 1.51 mmol, 54%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.09 (s, 2H), 7.07 (d, $J = 3.6$ Hz, 2H), 6.92 (d, $J = 3.6$ Hz), 4.71 (s, 4H).

Compound previously reported by Joo et al.[32] and Kim et al.[34]

Di-*tert*-butyl ([2,2′:5′,2″-terthiophene]-5,5″-diylbis(methylene))dicarbamate (**17**): **7** (0.413 g, 1.41 mmol) was added to a 100-mL Schlenk flask, and 25 mL DMF was added. The resulting solution was degassed with a nitrogen purge for 60 min. 2,5-Bis(tributylstannyl)thiophene (**14**; 0.485 g, 0.732 mmol) was added to the flask forming a greenish solution. $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol) was added to the solution, which turned yellow. The reaction vessel was placed in an oil bath and heated to 65 °C. After 3 days, the dark brown/black reaction mixture was diluted with 350 mL of ether and washed with saturated ammonium chloride solution (4× 50 mL) and then with water (2× 50 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide an orange solid. This solid was recrystallized from boiling ethanol and filtered providing the desired product as a red solid (0.124 g, 0.245 mmol, 35%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.00 (s, 2H), 6.97 (d, $J = 3.6$ Hz, 2H), 6.84 (d, $J =$ 3.5 Hz, 2H), 4.93 (br, 2H), 4.44 (d, $J = 5.3$ Hz, 4H), 1.47 (s, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 137.0, 136.5, 126.6, 124.5, 123.6, 40.0, 28.7. HRMS (FAB-MS) m/z calculated for ($C_{24}H_{30}N_2O_4S_3$) 506.13677, found 506.13486 [M^+].

[2,2′:5′,2″-Terthiophene]-5,5″-diyldimethanammonium chloride (**18**): **17** (0.196 g, 0.387 mmol) and dioxane (18 mL) were added to a 50-mL flask. Concentrated HCl (6 mL) was added drop-wise. After 24 h, the cloudy, yellow reaction mixture was filtered and the collected pale yellow solid product was rinsed with ethanol (0.134 g, 0.353 mmol, 91%). ^{1}H-NMR (400 MHz, D_2O, ppm) δ: 7.26 (s, 2H), 7.25 (d, $J = 3.8$ Hz, 2H), 7.18 (d, $J = 3.8$ Hz, 2H), 4.39 (s, 4H)

Compound previously reported by Muguruma et al.[33]

[2,2′:5′,2″-Terthiophene]-5,5″-diyldimethanamine (**19**): **18** (0.040 g, 0.105 mmol) was placed in a 250-mL flask and dissolved in 100 mL water. KOH solution (2*M*, 4.5 mL, 9.0 mmol) was added drop-wise causing the initially yellow reaction mixture to cloud. After 2 h, the reaction mixture was filtered, and the collected solid was rinsed with additional water. The collected orange/brown solid product was dried under high vacuum (0.015 g, 0.049 mmol, 47%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.01 (br, 4H), 6.8 (s, 2H), 4.04 (s, 4H).

Synthesis previously reported by Muguruma et al.[33]

5,5‴-Bis(((*tert*-butyldimethylsilyl)oxy)methyl)-2,2′:5′,2″:5″,2‴-quaterthiophene (**21**): **3** (0.791 g, 2.57 mmol) was added to a dried 100-mL Schlenk flask and dissolved in 30 mL DMF. The resulting solution was degassed with a nitrogen purge for 1 h. 5,5′-Bis(tributylstannyl)-2,2′-bithiophene (**20**; 0.946 g, 1.27 mmol) and $Pd(PPh_3)_4$ (0.093 g, 0.080 mmol) were added to the solution. The reaction vessel was placed in an oil bath and heated to 70 °C. After 5 days, the reaction mixture was diluted with 500 mL ether and filtered removing a red/brown solid. The collected liquid was added to a separation funnel and washed with saturated ammonium chloride solution (4× 100 mL) and then with water (2× 100 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide a red/orange solid. This solid was washed with boiling ethanol and filtered to collect the dark red solid product (0.266 g, 0.430 mmol, 34%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.34 (d, $J = 3.8$ Hz, 2H), 7.29 (d, $J = 3.8$ Hz, 2H), 7.23 (d, $J = 3.6$ Hz, 2H), 6.00 (d, $J = 3.6$ Hz, 2H), 4.89 (s, 4H), 0.94 (s, 18H), 0.14 (s, 12H). HRMS (FAB-MS) m/z calculated for ($C_{30}H_{42}O_2S_4Si_2$) 618.16062, found 618.16059 [M^+].

[2,2′:5′,2″:5″,2‴-Quaterthiophene]-5,5‴-diyldimethanol (**22**): **21** (0.101 g, 0.163 mmol) was added to a 25-mL round bottom flask and dissolved in 10 mL THF forming a dark amber solution. 1*M* TBAF in THF solution (0.5 mL, 0.5 mmol) was added to the solution, which caused it to cloud. After 20 h, the reaction mixture was diluted with 500 mL of ether. Resulting mixture was filtered through a cotton plug into a separation funnel and washed with brine (4× 75 mL). The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure to provide a red/orange solid. This solid was washed in boiling chloroform, and the red/orange solid product was collected by filtration (0.039 g, 0.100 mmol, 61%). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm) δ: 7.29 (d, $J = 3.7$ Hz, 2H), 7.23 (d, $J = 3.9$ Hz, 2H), 7.19 (d, $J = 2.7$ Hz, 2H), 6.93 (d, $J = 3.7$ Hz, 2H), 5.56 (t, $J = 5.3$ Hz, 2H), 4.63 (d, $J = 5.0$ Hz, 4H).

Compound previously reported by Joo et al.[32]

Di-*tert*-butyl ([2,2′:5′,2″:5″,2‴-quaterthiophene]-5,5‴-diylbis(methylene))dicarbamate (**23**): **7** (0.734 g, 2.51 mmol) was added to a 100-mL Schlenk flask, and 30 mL DMF was added. The resulting solution was degassed with a nitrogen purge for 1 h. 5,5′-Bis(tributylstannyl)-2,2′-bithiophene (**20**; 0.850 g, 1.15 mmol) and $Pd(PPh_3)_4$ (0.093 g, 0.080 mmol) were added to the solution. The reaction vessel was placed in an oil bath and heated to 70 °C turning the initially yellow solution red/orange. After 4 days, the dark brown/black reaction mixture was diluted with 500 mL ether, and the resulting mixture was filtered. The collected liquid was washed with saturated ammonium chloride solution (3× 100 mL) and then with water (2× 100 mL). The combined aqueous layers were extracted with ether (2× 100 mL). The combined organics were dried over magnesium sulfate and concentrated under reduced pressure to provide a red/orange solid. This red/orange solid was washed in boiling ethanol, cooled, and filtered providing the red/orange solid product (0.105 g, 0.270 mmol, 23%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.04 (quartet, $J = 3.8$ Hz, 4H), 6.99 (d, $J = 3.6$ Hz, 2H), 6.85 (d, $J = 3.4$ Hz, 2H), 4.89 (br, 2H), 4.44 (d, $J = 5.8$ Hz, 4H), 1.48 (s, 18H). HRMS (FAB-MS) m/z calculated for ($C_{28}H_{32}N_2O_4S_4$) 588.12449, found 588.12506 [M^+].

[2,2′:5′,2″:5″,2‴-quaterthiophene]-5,5‴-diyldimethanammonium chloride (**24**): **23** (2.123 g, 0.3606 mmol) and dioxane (450 mL) were added to a 1-L flask. The resulting suspension was heated with a heat gun, until the solid was in solution and subsequently cooled to room temperature. Concentrated HCl (150 mL) was added, which caused a precipitate to form. After 18 h, the reaction mixture was filtered and the tan/orange solid product is collected (1.428 g, 3.094 mmol, 86%).

Compound is too insoluble for NMR characterization.

Compound previously reported by Muguruma et al.[33]

[2,2′:5′,2″:5″,2‴-Quaterthiophene]-5,5‴-diyldimethanamine (**25**): **24** (0.104 g, 0.225 mmol) was placed in 200-mL flask, and 150 mL water was added. The resulting suspension was heated but the solid never fully dissolved. KOH solution (2*M*, 3.0 mL, 6.0 mmol) was added drop-wise, which caused a precipitate to form immediately. After 3 h, the reaction mixture was filtered, and the collected solid was rinsed with additional water. The collected red solid product was dried under high vacuum (0.060 g, 0.154 mmol, 67%). ^{1}H-NMR (300 MHz, DMSO-d_6, ppm) δ: 7.26 (d, J = 3.8 Hz, 2H), 7.19 (d, J = 3.8 Hz, 2H), 7.15 (d, J = 3.5 Hz, 2H), 6.89 (m, 2H), 3.89 (s, 4H).

Synthesis previously reported by Muguruma et al.[33]

Bis-*N*,*N*′-(2-hydroxyethyl)-1,4,5,8-naphthalenetetracarboxylic diimide (**27**): ethanolamine (125 mL, 2.0 mol) was added to a 250-mL flask. Naphthalene tetracarboxylic dianhydride (**26**; 6.659 g, 24.83 mmol) was added to the flask which caused a gas to evolve. The reaction mixture became a dark slurry. After 24 h, the dark purple reaction mixture was diluted with 600 mL of methanol and filtered. Light purple solid product was collected by filtration and dried under high vacuum (7.017 g, 19.80 mmol, 80%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 8.79 (s, 4H), 4.49 (t, J = 5.5 Hz, 4H), 4.02 (t, J = 5.5 Hz, 4H).

Compound previously reported by Fierz-David and Rossi.[35]

Bithiophene Diol Polyurethane (29)

4,4′-Methylenebis(phenyl isocyanate) (0.520 g, 2.078 mmol) and dry toluene (15 mL) were added to a 100-mL Schlenk flask. The reaction vessel was placed in an oil bath and heated to 65 °C. Then, PTMO (2,900 g/mol average molecular weight; 3.018 g, 1.039 mmol), which had been dried under high vacuum at 60 °C for several days, was dissolved in 15 mL of dry toluene. This PTMO solution was added to the reaction vessel over 1 h via syringe pump. **10** (0.236 g, 1.039 mmol) was added to the reaction 3 h after the PTMO addition was complete. The cloudy, pale yellow/tan reaction mixture was maintained at 80 °C. After 46 h, the reaction mixture was allowed to cool to room temperature and was poured into a flask containing 300 mL of methanol. The resulting mixture was filtered, and pale yellow solid product was isolated (3.113 g, mass yield: 82%). GPC: M_w 58,000 Da, M_n 23,700 Da.

All polymerizations are based on synthesis reported by Rubner.[8]

Bithiophene Diamine Polyurea (30)

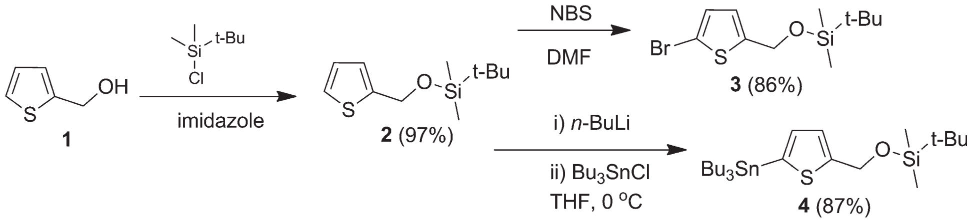
4,4′-Methylenebis(phenyl isocyanate) (0.245 g, 0.979 mmol) and dry toluene (10 mL) were added to a 100-mL Schlenk flask. The reaction vessel was placed in an oil bath and heated to 70 °C. Then PTMO (2,900 g/mol average molecular weight; 1.421 g, 0.4900 mmol), which had been dried under high vacuum at 65 °C for several days, was dissolved in 12 mL of dry toluene. This PTMO solution was added to the reaction vessel over 1 h via syringe pump. **13** (0.110 g, 0.4903 mmol) and 20 mL of dry toluene were mixed in a separate flask and heated to 90 °C. The resulting mixture was cannulated into the reaction flask, and after 2.5 h, the PTMO addition was complete. The resulting cloudy white reaction mixture was maintained at 80 °C. After 5 days, the reaction mixture was allowed to cool to room temperature and was poured into a flask containing 600 mL of methanol. The resulting mixture was filtered and yellow solid product was isolated (1.080 g, mass yield: 61%). GPC: M_w 77,400 Da, M_n 43,600 Da.

Terthiophene Diol Polyurethane (31)

4,4′-Methylenebis(phenyl isocyanate) (0.180 g, 0.719 mmol) and dry toluene (60 mL) were added to a 250-mL two-neck round bottom flask. The reaction vessel was placed in an oil bath and heated to 60 °C. Then, PTMO (2900 g/mol average molecular weight; 1.044 g, 0.360 mmol), which had been dried under high vacuum at 60 °C for several days, was dissolved in 15 mL of dry toluene. This PTMO solution was added to the reaction vessel over 1 h via syringe pump. The oil bath temperature was raised to 80 °C. **16** (0.111 g, 0.360 mmol) was added to the reaction, and after 3 h, the PTMO addition was complete. The cloudy yellow reaction mixture was heated to reflux. After 5 days, the reaction mixture was allowed to cool to room temperature and was poured into a flask containing 400 mL of methanol. The resulting mixture was filtered, and tan/yellow solid product was isolated. More material precipitated from the filtered liquid, and this was also collected by filtration. The collected product was a yellow/tan solid (0.356 g, mass yield: 27%). Polymer is too insoluble for GPC analysis.

Terthiophene Diamine Polyurea (32)

4,4′-Methylenebis(phenyl isocyanate) (0.252 g, 1.007 mmol) and dry toluene (10 mL) were added to a 100-mL Schlenk flask. The reaction vessel was placed in an oil bath and heated to 65 °C. Then, PTMO (2900 g/mol average molecular weight; 1.465 g, 0.5052 mmol), which had been dried under high vacuum at 65 °C for several days, was dissolved in 10 mL of dry toluene. This PTMO solution was added to the reaction vessel over 1.25 h via syringe pump. **19** (0.154 g, 0.503 mmol) and 25 mL of dry toluene were mixed in a separate flask and heated to 90 °C. The resulting mixture was cannulated into the reaction flask, and after 4 h, the PTMO addition was complete. The resulting cloudy orange reaction mixture was maintained at 75 °C. After 3 days, the reaction mixture was allowed to cool to room temperature and was poured into a flask containing 500 mL of methanol. The resulting mixture was filtered and brown solid product was



SCHEME 1 2-Thiophenemethanol-based precursor syntheses.

isolated (1.071g, mass yield: 57%). GPC: M_w 41,500 Da, M_n 22,600 Da.

Quaterthiophene Diol Polyurethane (33)

4,4′-Methylenebis(phenyl isocyanate) (0.101 g, 0.404 mmol) and dry toluene (10 mL) were added to a 100-mL three-neck flask. The reaction vessel was placed in an oil bath and heated to 60 °C. Then, PTMO (2,900 g/mol average molecular weight; 0.583 g, 0.201 mmol), which had been dried under high vacuum at 60 °C for several days, was dissolved in 9 mL of dry toluene. This PTMO solution was added to the reaction vessel over 1 h via syringe pump. **22** (0.079 g, 0.202 mmol) was added to the reaction, and after 3 h, the PTMO addition was complete. A condenser was attached to the reaction vessel, and the reaction mixture was heated to reflux. After 24 h, an additional 10 mL of dry toluene was used to rinse down the sides of the reaction vessel. After 6 days, the reaction mixture was allowed to cool to room temperature and was poured into a flask containing 300 mL of methanol. The resulting mixture was filtered and dark red solid product was isolated (0.149 g, mass yield: 20%). Polymer was too insoluble for GPC analysis.

Quaterthiophene Diamine Polyurea (34)

4,4′-Methylenebis(phenyl isocyanate) (0.255 g, 1.019 mmol) and *o*-dichlorobenzene (10 mL) were added to a 250-mL Schlenk flask. The reaction vessel was placed in an oil bath and heated to 70 °C. Then, PTMO (2,900 g/mol average molecular weight; 1.478 g, 0.5097 mmol), which had been dried under high vacuum at 65 °C for several days, was dissolved in 10 mL of *o*-dichlorobenzene. This PTMO solution was added to the reaction vessel over 1 h via syringe pump. **25** (0.199 g, 0.5121 mmol) and 150 mL of *o*-dichlorobenzene were mixed in a separate flask and heated to reflux. The resulting mixture was cannulated into the reaction flask, and after 5.5 h, the PTMO addition was complete. The resulting dark red reaction mixture was maintained at 100 °C. After 4 days, the reaction mixture was allowed to cool to room temperature and was poured into a flask containing 600 mL of methanol. The resulting mixture was filtered, and brown solid product was isolated (>1.932 g, mass yield: quant.). GPC: M_w 37,600 Da, M_n 14,300 Da.

Naphthalene Diimide Diol Polyurethane (35)

4,4′-Methylenebis(phenyl isocyanate) (0.247 g, 0.987 mmol) and *o*-dichlorobenzene (10 mL) were added to a 100-mL Schlenk flask. The reaction vessel was placed in an oil bath and heated to 60 °C. Then PTMO (2900 g/mol average molecular weight; 1.436 g, 0.4952 mmol), which had been dried under high vacuum at 60 °C for several days, was dissolved in 8 mL of *o*-dichlorobenzene. This PTMO solution was added to the reaction vessel over 75 min via syringe pump. **27** (0.174 g, 0.491 mmol) and 20 mL *o*-dichlorobenzene were mixed in a separate flask and heated with a heat gun. The resulting suspension was cannulated into the reaction flask, and after 3 h, the PTMO addition was complete. Once this cannulation was complete, the reaction mixture was heated to 110 °C. After 2 days, the reaction mixture was allowed to cool to room temperature and was poured into a flask containing 300 mL of methanol. The resulting mixture was filtered, and the dark red solid product was isolated (1.429 g, mass yield: 77%). GPC: M_w 70,700 Da, M_n 34,100 Da.

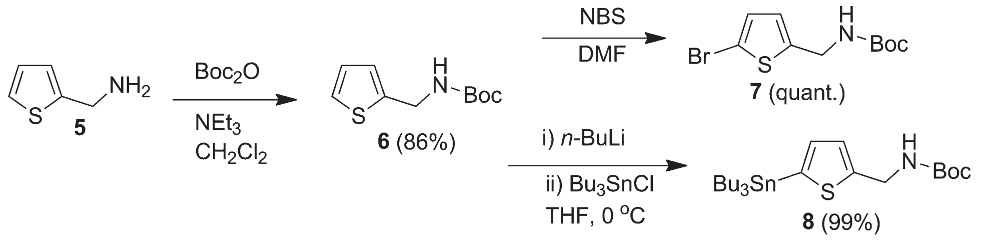
RESULTS AND DISCUSSION

The segmented polyureas and polyurethanes that are the focus of this work have three components: a PTMO soft segment chain, an oligothiophene diol (to form polyurethanes) or diamine (to form polyureas), and a diisocyanate, 4,4′-methylenebis(phenyl isocyanate) (MDI). The PTMO chain utilized in this work has a number average molecular weight (M_n) of 2900 g/mol. The diamine or diol segments used contain two, three, or four thiophene rings and were prepared by Stille cross-coupling reactions. Naphthalene diimide has also been utilized as a hard segment. We present the syntheses of the requisite chain extenders and polymer syntheses with thermal, optical, electrochemical, and characterization data.

Precursor Syntheses

The synthesis of Stille cross-coupling precursors to oligothiophene diols is shown in Scheme 1. 2-Thiophenemethanol **1** was protected with *tert*-butyldimethylsilyl (TBDMS) chloride using imidazole as a base. The protected alcohol **2** was brominated using NBS in DMF, while excluding light to form the thienyl bromide cross-coupling partner **3**.[29,30] The tributylstannane **4** was generated from **2** by deprotonation of the α-position of the thiophene ring with *n*-BuLi then quenching with tributyl tin chloride. This reaction proceeded well, although the crude product was difficult to purify due to problems with decomposition on silica gel or during distillation. Because of these difficulties the crude stannylated product **4** was carried forward without purification.

Likewise, the syntheses of building blocks for the oligothiophene diamines are shown in Scheme 2. The amine of 2-



SCHEME 2 2-Thiophenemethylamine-based precursor syntheses.

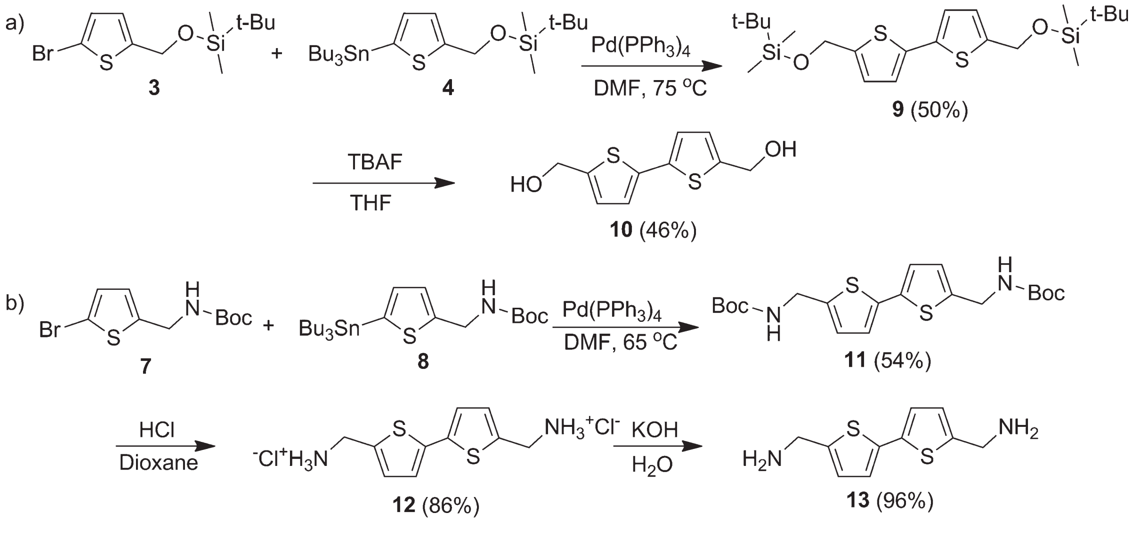
thiophenemethylamine **5** was protected with the *tert*-butyloxycarbonyl (Boc) group using triethylamine as a base to form **6**.[31] Boc-protected amine **6** was then brominated using NBS in DMF while shielding the reaction from light to give bromide **7**.[31] Similar to the protected alcohol **2**, the Boc-protected amine **6** was lithiated at the thiophene α-position using *n*-BuLi and then quenched with tributyl tin chloride to form the tributylstannane **8**. This stannane also could decompose on silica or during distillation, so the crude product **8** was also used without purification.

Chain Extender Syntheses

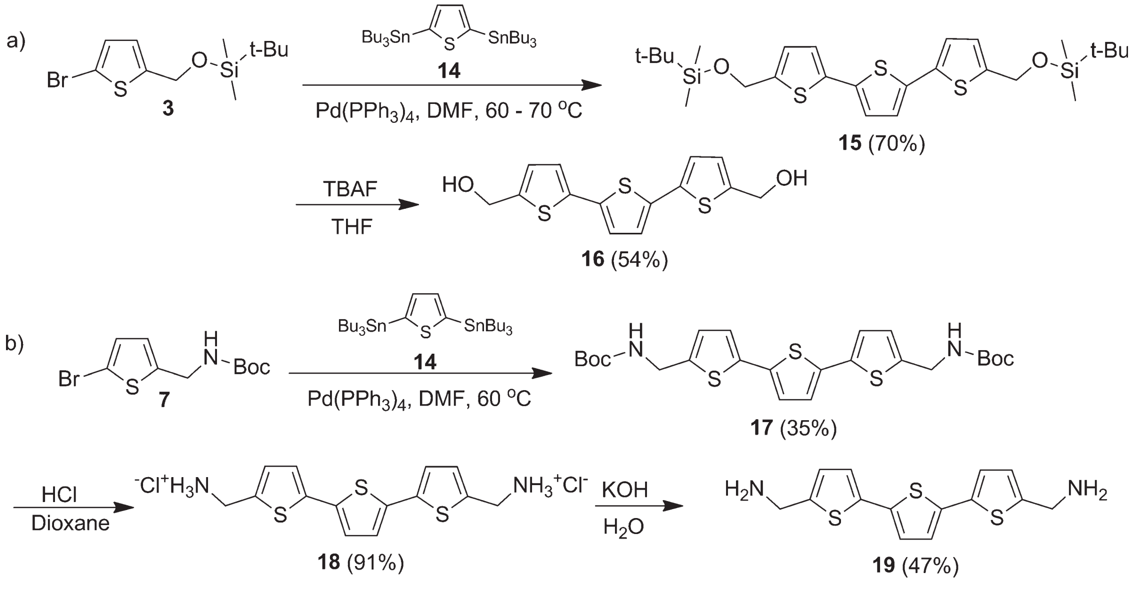
Scheme 3 shows the syntheses of the bithiophene chain extenders. The previously synthesized bromide **3** and stannane **4** were joined through a Stille cross-coupling reaction to form the protected diol bithiophene **9** [Scheme 3(a)]. This coupling reaction was performed in DMF with mild heating and a palladium (0) catalyst. The TBDMS protecting groups were then removed with TBAF in THF to provide the bithiophene diol **10**.[32] Similarly, the bromide **7** and the stannane **8** derived from the Boc-protected amine **6** were coupled under Stille conditions to form the Boc-protected diamine bithiophene **11** [Scheme 3(b)]. The Boc protecting groups were removed by treatment with HCl forming the hydrochloride salt **12**, which was then treated with KOH to form the free-base diamine bithiophene **13**.[33] Both protected bithiophenes have been synthesized on gram scales.

The syntheses of bifunctionalized terthiophenes, **16** and **19**, utilized 2,5-bis(tributylstannyl)thiophene **14**[27] as a coupling partner in twofold Stille couplings with the thienyl bromides described earlier (**3** and **7**, respectively), as shown in Scheme 4. Once the terthiophenes were formed the protecting groups were removed as before. The TBDMS groups of **15** were removed by TBAF treatment to give the free diol **16**.[32,34] The Boc-protected amines of **17** were first treated with HCl forming the hydrochloride salt **18**, then treatment with KOH gave the free-base diamine **19**.[33] The protected terthiophenes have been synthesized on 100s of milligrams to gram scales.

Bifunctionalized quaterthiophenes were synthesized in a similar manner as was employed for the terthiophene syntheses, as shown in Scheme 5. Using 5,5′-bis(tributylstannyl)-2,2′-bithiophene **20**[28] in twofold Stille couplings with brominated compounds **3** and **7** allowed for the preparation of the protected quaterthiophenes, **22** and **25**, respectively. As with the previous oligomers, the protecting groups were removed to provide the free diol or free diamine. The silyl protecting groups of **21** were removed by TBAF to give the diol **22**.[32] Boc-protecting groups of **23** were removed with HCl, and the resulting hydrochloride salt **24** was treated with KOH to give the free-base diamine **25**.[33] The protected quaterthiophenes have been synthesized on 100 mg scales. The oligothiophene diamines prepared in this work (**13**, **19**, **25**) were previously reported by Muguruma



SCHEME 3 Syntheses of (a) bithiophene diol **10** and (b) bithiophene diamine **13**.

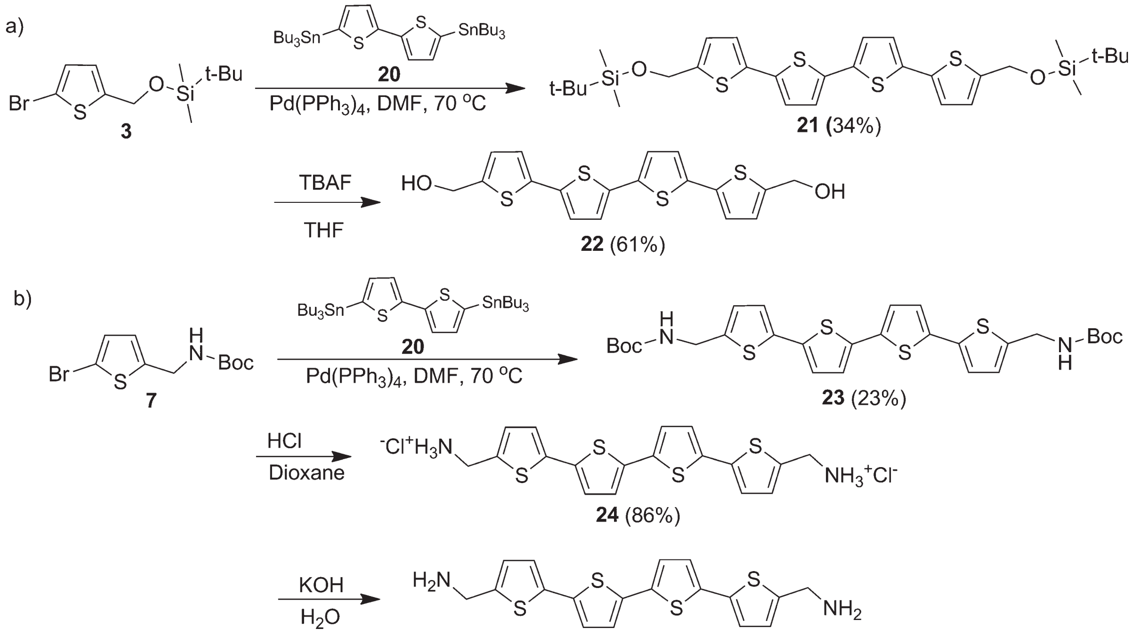


SCHEME 4 Syntheses of (a) terthiophene diol **16** and (b) terthiophene diamine **19**.

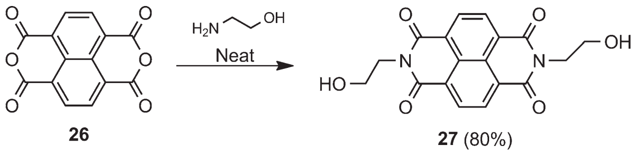
et al.[33] Attempts to reproduce the preparative chemistry described in this work either failed completely or led to impure product mixtures which could not be purified due to the instability of the silane derived "STABASE" protecting group used. After attempts to follow these reported synthetic pathways failed, Stille-based cross-coupling approaches were developed as described here.

In addition to oligothiophenes, a diimide derivative of 1,4,5,8-naphthalenetetracarboxylic dianhydride **26** was studied. **26** was treated with ethanolamine to produce the desired naphthalene diimide **27**,[35] which was used to form polymers in the same way as the oligothiophenes. This synthesis is shown in Scheme 6.

Oligothiophenes and naphthalene diimides have interesting optoelectronic properties. The protected alcohol and amine precursors described above may be easily incorporated into other systems. These molecules may be of interest for the construction of field-effect transistor sensors that rely on active semiconductor layers with polar functional groups.[36] However, the final deprotected diol and diamine monomers can be challenging to work with due to poor solubility resulting from a lack of solubilizing side chains. The chain



SCHEME 5 Syntheses of (a) quaterthiophene diol **22** and (b) quaterthiophene diamine **25**.



SCHEME 6 Synthesis of naphthalene diimide **27**.

extenders are sparingly soluble in common chlorinated solvents, ethereal solvents, methanol, ethanol, and toluene. Better but still poor solubility was observed in dimethylsulfoxide (DMSO) and DMF.

Polymer Syntheses

The diol and diamine chain extenders were used as components in the synthesis of segmented polyurethanes or polyureas, respectively. Polymerization reactions were carried out in the same manner as those in the Rubner work,[8] as shown in Scheme 7. The first step in this sequence, forming the macromonomer **28**, had to be performed under pseudo high dilution conditions via slow addition (utilizing a syringe pump) of a PTMO solution into the MDI solution with vigorous stirring. MDI and PTMO were mixed in a 2:1 ratio, so that the PTMO was end-capped with MDI. Once the macromonomer was generated, a diol or diamine chain extender was added quickly to allow for reaction with the isocyanate groups at the termini of the macromonomer to form the segmented polymer. After 2–6 days, the polymerization reaction was cooled to room temperature then poured into methanol and filtered to collect the product. This method was used to form a variety of segmented polyurea (R = NH) and polyurethane (R = O) materials (Scheme 8).

Molecular Weights

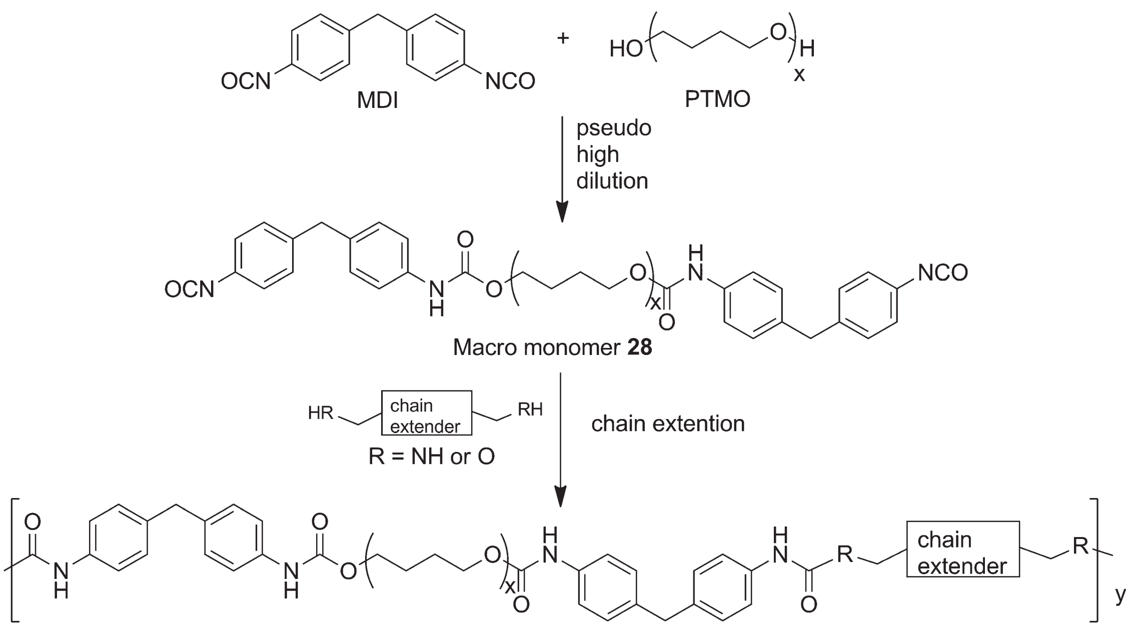
The polymers synthesized through this method are very poorly soluble in a variety of common solvents. This poor solubility extended to dichloromethane and THF, which are commonly used as mobile phases for GPC. To obtain GPC data, polymer samples were refluxed in THF but did not dissolve completely. The filtered solutions containing soluble materials were then evaluated by GPC—these data are presented in Table 1. The measured degree of polymerization is low, but these data only represent the soluble fraction of the polymer. In some cases, elastomeric free-standing films were isolated after filtration (e.g., ref. [32]) suggesting an entangled material with a higher actual molecular weight. Such insolubilities have been reported[24,37] for these types of systems, and we expect to solve this problem in the future through the use of a more solubilizing soft segment.[26]

Thermal Data

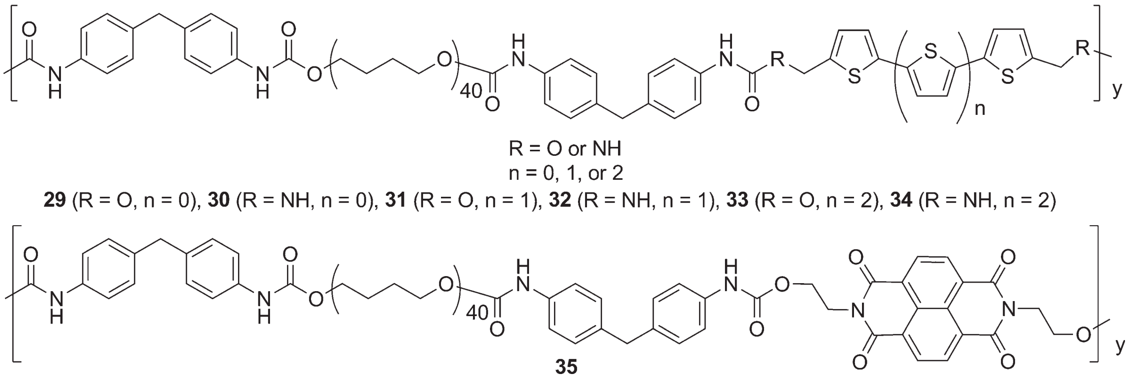
The thermal properties of these polymers were fairly comparable, and representative DSC and TGA data are shown in Figure 1. DSC measurements indicate the phase change behavior of the polymer. In this case, the two signals recorded are likely melting and solidification of the polymer at slightly above room temperature. For all polymers, these thermal properties of the material are dominated by the PTMO segments rather than by differences in hard domain interactions. TGA provides data on the decomposition of the polymer. This experiment measured the decrease in mass, as temperature is increased. As shown, polymer **29** was stable up to ~300 °C and then began to decompose.

NMR Spectra

The bithiophene diol containing polymer **29** was soluble enough to allow acquisition of NMR data in deuterated DMF. Figure 2 shows the NMR spectra of bithiophene containing polymer **29** (top), bithiophene diol monomer **10** (middle), and MDI (bottom). The aromatic region peaks of **10** and MDI shift and coalesce into the aromatic peaks of the polymer. The spectrum of **29** shows two distinct urethane N—H peaks



SCHEME 7 Representative chain-extension polymerization of diisocyanate macromonomers.



SCHEME 8 Structures of synthesized segmented polyurethanes.

TABLE 1 GPC Data for Synthesized Polymers

Polymer	Repeat Unit Mass (g/mol)	M_w	M_n	Number of Repeats (y)	Polydispersity Index
29	3628.8	58,800	23,700	6.5	2.48
30	3626.9	77,400	43,600	12.0	1.78
31	Polymer too insoluble for analysis				
32	3709.0	41,500	22,600	6.1	1.84
33	Polymer too insoluble for analysis				
34	3791.1	37,600	14,300	3.8	2.63
35	3756.8	70,700	34,100	9.1	2.07

at above 9 ppm, indicating that the alcohol/isocyanate polycondensation was successful. The dominant signals in the polymer NMR are from the PTMO chains (marked with asterisks). The other polymers were too insoluble to obtain NMR data in common solvents such as $CDCl_3$, CD_2Cl_2, DMSO, and DMF. These materials did dissolve in a mixture of trifluoroacetic acid-d and $CDCl_3$ but decomposition also occurred.

UV–Vis

UV–vis absorption spectra of the protected diamine oligothiophenes (**11**, **17**, and **23**) and the polymers formed from them (**30**, **32**, and **34**) are presented in Figure 3. The general trend with relation to oligomer length is maintained for both the monomers and the polymers. Longer oligothiophenes absorb longer wavelength, lower energy light as expected due to the longer conjugation pathway. The absorption maxima (λ_{max}) for the monomers and respective polymers occur at nearly the same wavelength: the bithiophene diamine **13** λ_{max} is at 315 nm, while the polymer **30** λ_{max} is 318 nm. Terthiophene diamine **19** has a λ_{max} at 363 nm, and polymer **32** has a λ_{max} at 370 nm. The λ_{max} of **25**, the quaterthiophene diamine, is at 398 nm, and in the corresponding polymer **34**, the λ_{max} is at 400 nm. This indicates that

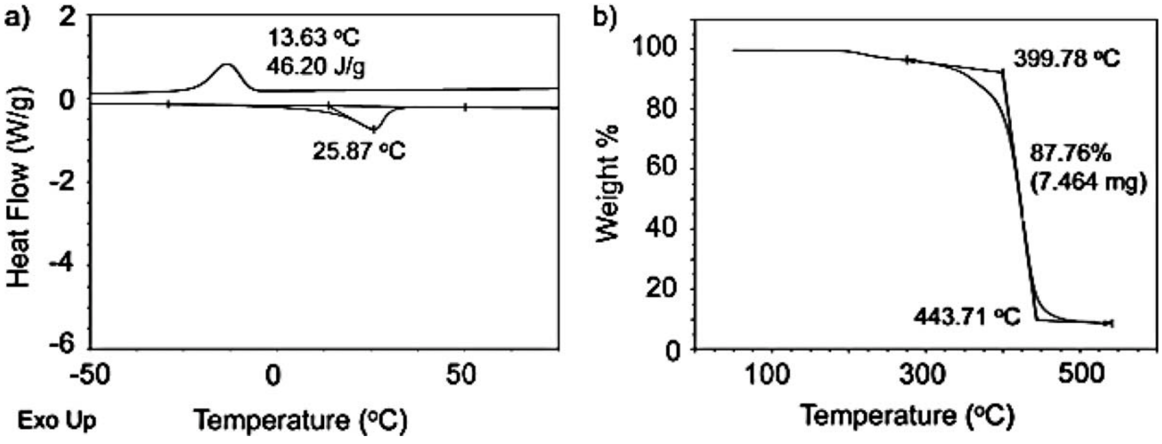


FIGURE 1 (a) DSC and (b) TGA data for bithiophene derived polymer **29**.

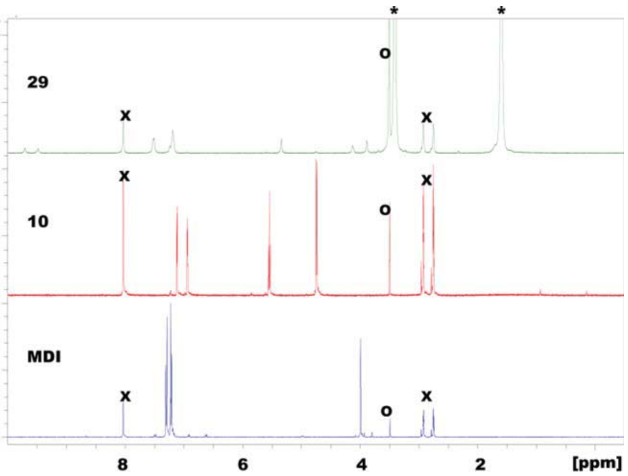


FIGURE 2 NMR spectra (400 MHz, DMF-d_7) of bithiophene containing polymer **29** (top), bithiophene diol monomer **10** (middle), and MDI (bottom). * denotes peaks from PTMO chains, x denotes protio DMF peaks, and o denotes the residual water peak.

the optoelectronic properties of the chromophores are not being perturbed once incorporated into the polyureas and that the polymers are well-solvated in acetic acid solution rather than involved in any hard-segment segregation that should also perturb the observed electronic properties.

In addition to the solution phase UV–vis spectra, data have been obtained for polymer films drop-cast from solution onto glass slides. Representative spectra are shown in Figure 4. Drop-cast films of the oligothiophene containing polymers, such as terthiophene diamine containing polymer **32**, show a broad, featureless absorption centered around 376 nm with the low-energy band edge red shifted from the solution values. This is not uncommon for conjugated polymer thin films and reflects chromophore aggregation in the solid state, enhanced solid state planarity, excitonic coupling, and other such factors. The UV–vis spectra of the naphthalene diimide containing polymer **35** show similar vibronic fine structure in both the solution and the film. The major vibronic peaks in solution were observed at 357 and 378 nm. This fine structure is less distinct in the film spectrum, and the peaks were observed at 363 and 380 nm.

Cyclic Voltammetry

Figure 5 shows solution cyclic voltammetry (CV) data which were collected for the naphthalene diimide monomer **27** and the corresponding polymer **35** incorporating this unit. The samples analyzed were filtered solutions in THF containing 0.1M TBAP as an electrolyte. These measurements were taken using a platinum button working electrode versus a Ag/Ag$^+$ reference. The peak reduction current of the polymer was observed at a slightly less negative potential (−0.93 V) than that for the monomer (−0.98 V). We could not observe the second reduction for the diimide core under ambient conditions. Anodic CV experiments were also attempted on solutions the oligothiophene containing polymers but no oxidation was observed due to the poor solubility of these materials in the electrolyte solutions. A solution of polymer and electrolyte was drop-cast onto electrodes but dissolved in solution when the CV experiment was attempted, resulting in no signal being observed.

CONCLUSIONS

A series of oligothiophene and naphthalene diimide chain extenders have been synthesized and utilized in the synthesis of segmented polyurethanes and polyureas. These materials have been evaluated through a variety of characterization techniques. The polymers are thermally robust and maintain the optoelectronic properties of the chromophore incorporated into the system. Although the solubilities were poor and the thermal properties were dominated by the soft PTMO segment, we expect this approach to be generally applicable to the incorporation of other soft segments with greater solubilities. Future studies will examine the effect of using shorter PTMO chains to form polymers, because smaller PTMO segments may allow greater interaction

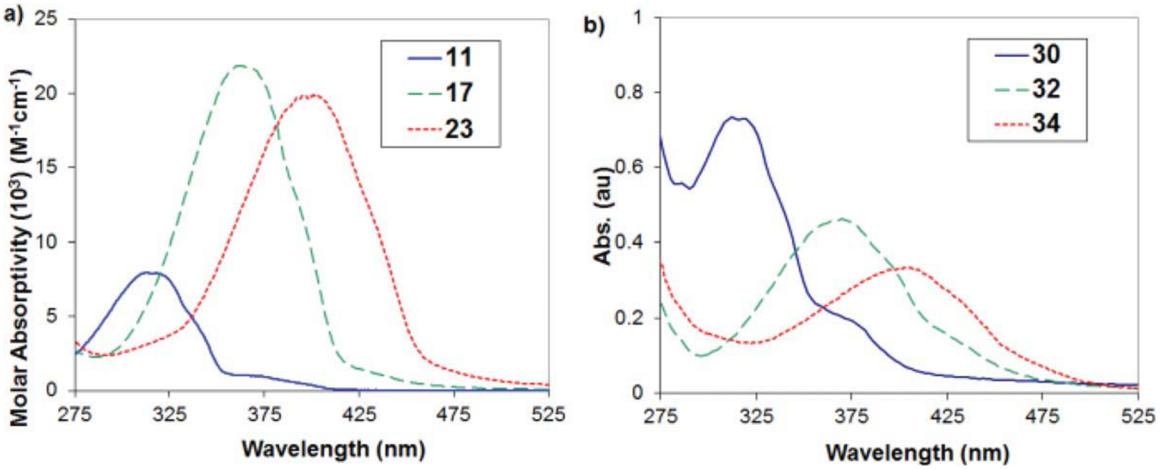


FIGURE 3 UV–vis spectra (in acetic acid) of (a) protected oligothiophene diamines and (b) polymers synthesized utilizing them. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

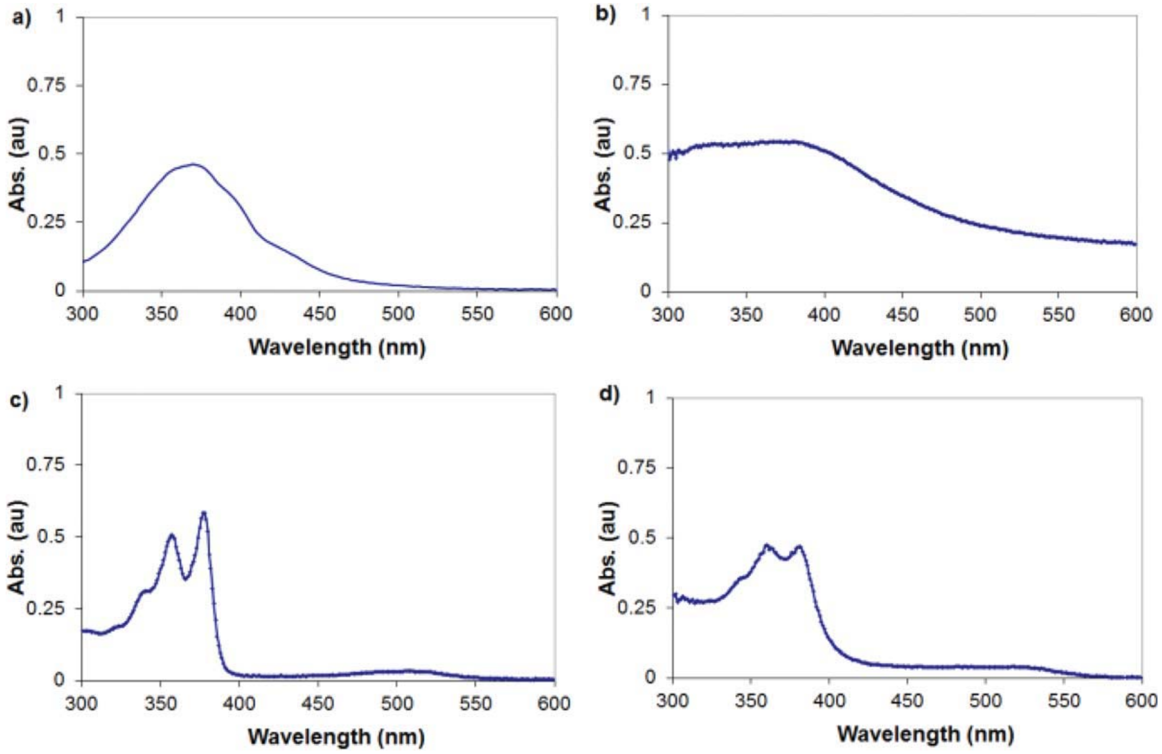


FIGURE 4 UV–vis spectra of (a) polymer **32** in acetic acid solution, (b) drop-cast film of polymer **32**, (c) polymer **35** in acetic acid solution, and (d) drop-cast film of polymer **35**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

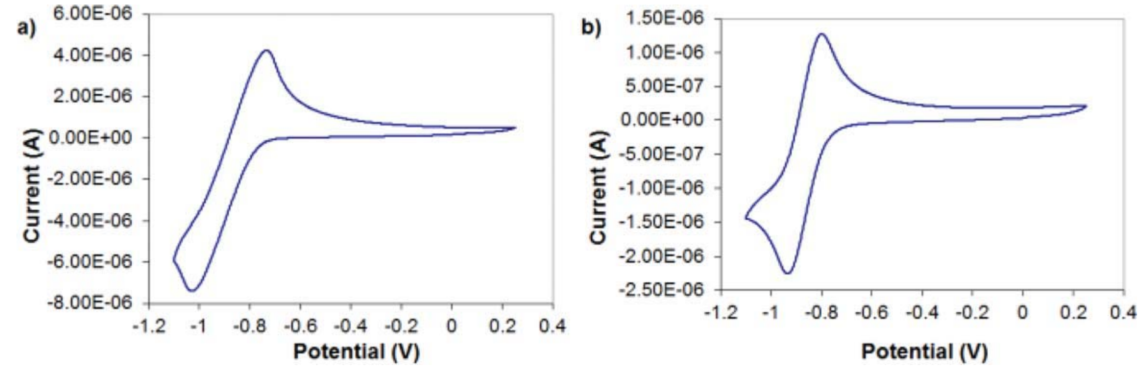


FIGURE 5 Cyclic voltammetry (vs. Ag/Ag$^+$ reference) of (a) the naphthalene diimide **27** and (b) polymer **35** in THF containing 0.1*M* TBAP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between hard domains in the resulting material. The presence of these interactions may perturb the optoelectronic properties of the systems in a way not observed in this study.

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