Conductive Triethylene Glycol Monomethyl Ether Substituted Polythiophenes with High Stability in the Doped State

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Received 3 February 2019; accepted 1 March 2019 DOI: 10.1002/pola.29362

ABSTRACT: Synthesis of two conducting polymers containing 3-hexylthiophene and 3-[2-(2-(2-methoxyethoxy)ethoxy)] thiophene is demonstrated. In thin-film transistors, the high-molecular-weight polymer shows an average mobility of 4.2×10^{-4} cm² V⁻¹ s⁻¹. Most importantly, the polymers have high conductivity upon doping with iodine and also have high stability in the doped state with high conductivities measured even after 1 month. Furthermore, the doping causes transparency to thin films of the polymer and the films are resistant to common organic solvents. All these properties indicate a great potential

INTRODUCTION Polythiophenes (PTs) are attractive due to their demonstrated use as semiconducting materials in various applications such as organic field effect transistors,^{1,2} organic photovoltaic devices,³ and sensors,^{4,5} Electrical and optical properties of PTs depend on the type of substituents on thiophene⁶ and regiochemistry.^{7,8} Regioregular poly(3-hexylthiophene) (P3HT) is a widely studied polymer among poly(alkyl thiophene)s which easily self-assembles to form a well-ordered two-dimensional lamellar structure,^{9,10} a crucial requirement in charge transport. P3HT also has good solubility in organic solvents,¹¹ and it has good conductivities $(>100 \text{ S cm}^{-1})^{12}$ in a doped or oxidized state. However, P3HT is not stable over time in its doped state, and upon exposing to air, the conductivity drops very fast.^{13,14} However, poly(alkoxythiophene)s such as poly[3-(2-(2-methoxyethoxy)ethoxy)thiophene-2,5-diyl] (P3MEET) has been reported with increased conductivity upon doping and were stable over time.^{15–17} Attachment of alkoxy substituents on a thiophene ring can make the resulting polymer insoluble in organic solvents due to α,β' coupling (crosslinking) between thiophene rings.¹⁵ Many attempts have been made to overcome issues associated with

for the iodine-doped polymer to be used as an alternative to commercially available poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate). © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: 3-hexylthiophene; alternative to poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate); conductivity; triethylene glycol monomethyl ether; conducting polymers; transparency; atomic force microscopy (AFM)

both poly(alkylthiophenes)s and poly(alkoxythiophene)s and to synthesize polymers with improved properties. For example, sulfonated-P3MEET-based polymers have drawn attention as an improved alternative to commercially available poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS).18-20 PEDOT: PSS is not an ideal hole transporting layer due to its hygroscopicity and acidity which negatively impact the stability of the devices.²¹⁻²³ A published study by McCulloch and coworkers highlighted the importance of MEEET-based units on organic electrochemical transistor applications.²⁴ Furthermore, diblock copolymers of P3HT and P3MEEET have been reported, and showed a composition-dependent helical nanowire formation via complexation with K⁺ ions and polymers with amphiphilic nature.^{25,26} In our previous paper, we have reported a pyrimidine containing polymer with MEEET and 3HT units,²⁷ but a copolymer of bithiophene units composed of 3HT and MEEET has not yet been reported. Here, we report a polymer containing bithiophene units composed of 3HT and MEEET synthesized by McCullough method.²⁸ This polymer revealed a range of promising optical, electrical, and thermal properties such as better ordering in the

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solid state, reduced band gap, better thermal stability, and most importantly high conductivity upon doping with iodine which persisted for days.

EXPERIMENTAL

Materials and Methods

All commercial chemicals were purchased either from Sigma Aldrich Chemical Co., LLC., Saint Louis, MO, USA, or from Fisher Scientific Co., LLC., Pittsburgh, PA, USA, and were used without further purification unless otherwise noted. All glassware and syringes were dried at 120 °C for at least 24 h before use and cooled in a desiccator under a nitrogen atmosphere. Tetrahydro-furan (THF) and toluene were dried over sodium/benzophenone ketyl and freshly distilled under nitrogen before use.

Nuclear magnetic resonance (¹H and ¹³C NMR) spectra and all two-dimensional (2D)-NMR analysis were recorded at 25 °C using a Bruker AVANCE III 500 MHz NMR spectrometer, as indicated, and were referenced to residual protic solvent (CHCl₃: δ 7.26 ppm). The data are reported as follows: chemical shifts are reported in ppm on δ scale, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

Gas chromatography/mass spectrometry (GC/MS) analysis was performed on an Agilent 6890-5973 GC/MS work station. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethylsiloxane. Helium was the carrier gas (1 mL min⁻¹). The conditions used for GC/MS analysis: injector and detector temperature = $250 \,^{\circ}$ C; initial temperature = $70 \,^{\circ}$ C; temperature ramp = $10 \,^{\circ}$ C min⁻¹; final temperature = $280 \,^{\circ}$ C.

The molecular weights of the synthesized polymers were measured by size exclusion chromatography (SEC) analysis on a ViscoTec VE 3580 system equipped with ViscoGEL columns (GMHHR-M), connected to a refractive index detector. A gel permeation chromatography (GPC) solvent/sample module (GPC_{max}) was used with high-performance liquid chromatography grade THF as the eluent, and calibration was based on polystyrene standards. The conditions used: flow rate = 1.0 mL min⁻¹, injector volume = 100 μ L, column temperature = 35 °C, detector temperature = 30 °C. The polymer sample was dissolved in THF, and the solution was filtered through poly(tetrafluoroethylene) filters (0.2 μ m) before injection.

Ultraviolet-visible (UV-vis) absorption spectra of the polymer solution in chloroform solvent were carried out in 1 cm cuvettes using an Agilent 8453 UV-vis spectrometer. Thin films of polymer were obtained by evaporation of chloroform solvent from polymer solution on glass microscope slides.

Cyclic voltammograms were obtained with a BAS CV-50W voltammetric analyzer (Bioanalytical Systems, Inc., West Lafayette, IN, USA). The electrochemical cell was comprised with three electrode systems: platinum disk working electrode, a platinum wire auxiliary electrode, and an Ag/Ag^+ reference electrode. The electrolyte solution: 0.1 M electrochemical grade tetrabutylammoniumhexafluoro phosphate in freshly distilled

acetonitrile (acetonitrile was distilled under nitrogen over calcium hydride and collected over molecular sieves). The electrolyte solution was placed in a cell and purged with argon. A drop of the polymer solution in chloroform was evaporated in ambient air. The film was immersed into an electrochemical cell containing the electrolyte, and the oxidation and reduction potentials were recorded. For calibration, the half of the redox potential of ferrocene/ferrocenium (Fc/Fc⁺) was measured under the same condition and located at 0.09 V versus Ag/Ag⁺ reference electrode.

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated by using eqs 1 and 2:

HOMO (eV) =
$$(E_{ox} + 4.71)$$
 eV (1)

LUMO (eV) =
$$(E_{red} + 4.71)$$
 eV (2)

where E_{ox} and E_{red} are the measured potentials relative to Ag/Ag⁺.

Tapping mode atomic force microscopy (TMAFM) studies were carried out on a VEECO Dimension 5000 Scanning Probe Microscope with a hybrid xyz head equipped with the NanoScope software.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out at beamline 7.3.3 of Advanced Light Source in Lawrence Berkeley National Laboratory. Beamline 7.3.3 operates at an energy of 10.0 keV with $\lambda = 1.2398$ Å. Scattering data were acquired at an incident angle of 0.15°. In-plane data were extracted as line cuts from the 2D images and is presented as a function of the scattering vector, q ($q = 4\pi \sin(\theta/2)/\lambda$). GIWAXS intensities were also azimuthally averaged and presented versus q.

Thermogravimetric analysis (TGA) of the polymer was carried out on the SDT Q600 Instrument. Differential scanning calorimetry (DSC) was carried out using MettlerToledo DSC 1 Star System. Aluminum standard pans were filled with polymer sample (2.55 mg). The polymer sample was subjected to heat–cool–heat cycle and data were recorded by heating and cooling the sample from 25 to 200 °C and vice versa at the rate of 10 °C min⁻¹.

The conductivity of the polymers was measured using a fourpoint conductivity meter. The polymer solution in chloroform was drop-casted on a cleaned glass substrate in chloroform chamber. After complete solvent evaporation, polymers were chemically oxidized by exposure to iodine vapor for various amounts of time. The conductivities were calculated by eq 3. At least five consecutive measurements were performed per one measurement.

$$\sigma = \frac{1}{4.53 \times \text{Rl}} \tag{3}$$

where σ is the conductivity, *R* is the resistance (S), *R* is *V*/*I*, and *l* is the film thickness (cm).

Resistance was measured by using a four-point probe, and the film thickness was measured by using a Veeco Dektak VIII profilometer.

Vertical charge carrier mobility was measured using Schottky diodes which were made with the device structure of indium tin oxide (ITO)/PEDOT:PSS/polymer/Al. The measurements of space charge limited current (SCLC) of pure polymers were carried out in Keithley 2400 source meter interfaced with the LabVIEW software under nitrogen atmosphere under dark conditions. The voltage was increased from 0 to 2.5 V. Each pixel had an area of 10 mm² with the film thickness of ~33 nm. The mobility was calculated by eq 4:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3} \tag{4}$$

where μ is the charge mobility, *J* is the current density, ε_0 is the vacuum permittivity (equal to 8.854×10^{-12} F m⁻¹), ε_r is the relative permittivity of semiconducting materials (3.5 was used), *V* is the applied bias on the diode, and *L* is the film thickness.

Field-effect mobilities were extracted from thin-film transistors with the polymer as the active layer and a bottom-gate, bottomcontact configuration fabricated as previously reported.²⁹ Borondoped p-type silicon wafers with a 300 nm thick thermally grown SiO₂ layer to serve as the gate electrode and gate dielectric (C = 10.6nF cm⁻², Process Specialties). Gold source and drain electrodes were approximately 100 nm thick and were deposited using conventional double-layer photolithography. Self-assembled monolayers were not applied (UV-Ozone treatment only). **P2** was spun cast at 1000 rpm for 4 min from 10 mg mL⁻¹ in 1,2,4-trichlorobenzene solutions and annealed at 150 °C for 3 h before electrical measurements. The device channel width was 220 µm, and the length was 320 µm.

UV-vis-near infrared (NIR) transmittance spectra were recorded using an Agilent Cary 7000 UV-Vis-NIR spectrometer for spin-coated thin films of polymer **P2** from chloroform solution on ITO substrate followed by iodine doping to compare it with the transmittance of PEDOT:PSS.

Synthesis of Materials Synthesis of 3MEEET (3)

NaH (3.68 g, 153 mmol) was introduced to a three-necked round-bottom flask equipped with a condenser and mixed with dry dimethylformamide (20 mL) under nitrogen. Triethylene glycol monomethyl ether (20.5 g, 116 mmol) was added dropwise from a syringe during 30 min while maintaining the temperature at 0 °C. The mixture was stirred for 1 h at 0 °C to assure complete consumption of NaH. 3-Bromothiophene (12.9 g, 79.1 mmol) and CuBr (0.45 g, 3.14 mmol) were added to the reaction mixture at this point, and it was heated to 110 °C.³⁰ After 30 min at the elevated temperature, an aliquot was taken out, quenched with a 1 M aqueous solution of NH₄Cl, extracted with diethyl ether and subjected to GC-MS analysis. As the abundance of starting materials was present in the reaction mixture an additional amount of (CuBr or CuI) CuBr (0.57 g, 3.97 mmol) was added at this point, and the reaction was allowed to proceed at the elevated temperature for 1 h. The progress of the reaction was monitored with GC-MS analysis, and more CuBr (1.51 g, 10.5 mmol) was added until 3-bromothiophene was consumed. The reaction mixture was heated at 110 °C for 12 h after which no 3-bromothiophene was present. The mixture was poured into a 1 M aqueous solution of NH₄Cl (100 ml) and stirred for



Synthesis of 2-Bromo-3MEEET (4)

The crude 3MEEET (4.93 g, 20.0 mmol) was dissolved in THF: hexane mixture (9:1, 150 mL) in a round-bottom flask and cooled down to -5 °C. *N*-bromosuccinimide (NBS, 3.58 g, 20.0 mmol) was added into the reaction mixture in small portions over 1 h period. After all the NBS was added the reaction mixture was stirred for 2 h at 0 °C. The mixture was poured into deionized water and extracted with hexane (3× 100 mL). Combined organic layers were washed with deionized water, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The crude compound was purified by column chromatography using ethyl acetate: hexane (2:3) as the eluting solvents (4.04 g, 62%). ¹H NMR (500 MHz, CDCl₃, δ , ppm): 7.18 (d, J = 6.0, 1H), 6.77 (d, J = 6.0, 1H), 4.20 (t, 2H), 3.83–3.54 (m, 10H), 3.38 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, δ , ppm): 154.44, 124.31, 118.04, 92.30, 72.00, 71.73, 71.01, 70.72, 70.62, 69.90, 59.10.

Synthesis of 3-Hexyl-3'-[2-(2-(2-methoxyethoxy)ethoxy) ethoxy]bithiophene (5)

Mg (0.4 01 g, 16.5 mmol) was kept under vacuum in a 100 mL three-necked round-bottom flask equipped with a reflux condenser before the addition of THF (10 mL) and 2-bromo-3HT (2.73 g, 11.0 mmol) under nitrogen. The Grignard reaction was allowed to proceed for 2 h at 60 °C. Ni(dppp)Cl₂ (0.357 g, 0.659 mmol) was kept under vacuum in another 100 mL threenecked round-bottom flask equipped with a reflux condenser prior to the addition of THF (50 mL) and 2-bromo-3MEEET (0.390 g, 11.0 mmol) under nitrogen. The Grignard reagent was cannulated to the other flask containing 2-bromo-3MEEET and the catalyst Ni(dppp)Cl₂. The resultant mixture was stirred under reflux for 24 h, quenched in water, extracted with hexane (3× 100 mL). Combined organic layers were washed with deionized water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to get the crude product. Purification was carried out by column chromatography using ethyl acetate: hexane (2:3) as eluting solvents (1.82 g, 37%). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 7.22 (d, J = 5.2, 1H), 7.18 (d, J = 5.8, 1H), 6.90 (d, J = 5.2, 1H), 6.88 (d, J = 5.6, 1H) 4.16 (t, 2H), 3.78-3.46 (m, 10H), 3.37 (s, 3H), 2.67 (t, 2H), 1.32 (m, 8H), 0.88 (t, 3H). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 153.24, 140.85, 128.85, 127.50, 124.56, 123.27, 118.16, 114.31, 71.95, 71.35, 70.85, 70.67, 70.56, 69.91, 59.05, 31.70, 30.55, 29.35, 29.26, 22.63, 14.11.

Synthesis of 2-Bromo-3-hexyl-3'-(2-(2-(2-methoxyethoxy) ethoxy)bithiophene (6)

3-Hexyl-3'-(2-(2-(2-methoxy)ethoxy) ethoxy)-2,2'-bithiophene (1.82 g, 4.42 mmol) was dissolved in THF:hexane mixture (9:1, 300 mL) in a round-bottom flask and cooled down to 0° C.



NBS (0.788 g, 4.42 mmol) was added to the reaction mixture in small portions over 30 min. After all the NBS was added, the reaction mixture was stirred for 2 h at 0 °C. The mixture was poured into deionized water and extracted with diethyl ether (3× 100 mL). Combined organic layers were washed with deionized water (3× 100 mL), dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The crude compound was purified by column chromatography using ethyl acetate: hexane (1:4) as the eluting solvents to obtain the orange-colored oil (1.32 g, 61%). ¹H NMR (500 MHz, CDCl₃, δ , ppm): 7.19 (d, J = 5.6, 1H), 6.86 (s, 1H), 4.18 (t, 2H), 3.81–3.53 (m, 10H), 3.37 (s, 3H), 2.62 (t, 2H), 1.27 (m, 8 H), 0.88 (t, 2H). ¹³C NMR (125 MHz, CDCl₃, δ , ppm): 153.53, 140.95, 131.52, 129.33, 123.58, 117.75, 113.26, 111.08, 71.95, 71.38, 70.87, 70.68, 70.58, 69.86, 59.06, 31.64, 30.37, 29.44, 29.16, 22.60, 14.10.

Synthesis of Poly[3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy) ethoxy)bithiophene] (P1)

Freshly distilled isopropylamine (0.40 mL, 2.849 mmol) was added to a three-necked round-bottom flask equipped with a reflux condenser. It was diluted with dry THF (10 mL) and cooled down to -78 °C. *n*-BuLi (1.00 mL, 2.442 mmol) was added while stirring and the reaction mixture was allowed to stir at the same temperature for 30 min. 2-Bromo-3-hexyl-3'-[2-(2-(2-methoxy)ethoxy)ethoxy]bithiophene (1.00 g, 2.035 mmol) in dry THF (10 mL) was added at -78 °C and the reaction mixture was stirred at the same temperature for 1 h. After 1 h, ZnCl₂ (0.444 g, 3.256 mmol) was added and stirred for 2 h. The reaction mixture was allowed to warm up to room temperature, and Ni(dppp)Cl₂ (0.0 22 g, 0.0407 mmol) (monomer:catalyst = 50:1) was added at room temperature while stirring. The

reaction mixture was heated to $40 \,^{\circ}$ C, stirred for 24 h and then was cooled down to room temperature and precipitated in methanol. The solid was filtered, and the polymer was purified by Soxhlet extractions with methanol, hexane, and chloroform. The polymer was obtained as a dark blue solid after the evaporation of chloroform.³¹ The experiment was repeated with monomer: catalyst ratio 200:1 to generate polymer (**P2**).

RESULTS AND DISCUSSION

The synthesis of the monomer of poly[3-hexyl-3'-(2-(2-(2-methoxyethoxy) ethoxy)ethoxy)bithiophene] is shown in Scheme 1 (Additional synthetic procedures are given in Experimental, Supporting Information). Starting material 2-bromo-3HT(2) was synthesized by a nickel catalyzed Kumada coupling reaction between 3-bromothiophene and hexylmagnesium bromide followed by bromination with NBS. Starting material 2-bromo-3MEEET (4) was synthesized by copper-mediated substitution of 3-bromothiophene,³⁰ followed by bromination with NBS. The dimer 2-bromo-3-hexyl-3'-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]-2,2'-bithiophene (6) was synthesized by nickel catalyzed Kumada coupling reaction between compounds (2) and (4), followed by bromination with NBS. The position of the monobromination of compound (6) was confirmed via 2D NMR analvsis, and the spectra are given in Appendix S1, Supporting Information [Fig. S13(a,b)]. Heteronuclear multiple bond correlation of hexyl α carbon with thiophene singlet proton revealed that the monobromination occurred on the hexyl thiophene ring. McCullough method was used for polymerization of the monomer (6), in which lithium diisopropylamide was used to abstract the bithiophene proton at the 5'-position followed by metal exchange via the addition of ZnCl₂. The polymerization was then



SCHEME 1 Synthetic scheme for the synthesis of poly[3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)bithiophene].

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Polymer	Monomer: Catalyst	Molecular Weight (<i>M_n</i>) ^a (g mol ⁻¹)	Polydispersity Index	λ _{max} (CHCl ₃) ^b (nm)	λ _{max} (film) ^c (nm)	Optical Band Gap (eV)	HOMO (eV) ^d	LUMO (eV) ^e	Eg (eV)
P1	50:1	6010	1.73	471	541, 575, 640	1.50	-4.71	-3.00	1.71
P2	200:1	14,790	1.72	476	549, 579, 640	1.50	-4.71	-2.91	1.80

^a Determined by SEC (THF eluent).

^b UV-vis absorption maxima of polymer solution in chloroform solution.

 $^{\rm c}$ UV-vis absorption maxima of polymer film drop-casted from chloroform solution.

catalyzed with Ni(dppp)Cl₂.³¹ Two different monomer:catalyst ratios (50:1 and 200:1) were used to obtain polymers **P1** and **P2**, respectively (Table 1).

The polymer formation was confirmed by SEC analysis (Table 1) and ¹H-NMR analysis. The ¹H-NMR spectrum of the polymer **P2** is shown in Figure S14. The two signals around 7 ppm are due to the thiophene protons. The triplet at 4.3 ppm is due to the α -CH₂ in the alkoxy chains, and the singlet at 3.3 ppm is due to the methoxy protons. The two triplets around 2.7 and 0.9 ppm are due to the α -CH₂ protons in hexyl chains and terminal methyl groups, respectively.

The HOMO and LUMO energy levels of the polymers were estimated by cyclic voltammetry from the onset of oxidation and reduction peaks, respectively (Figs. S18 and S19). Due to the strong electron donating properties of MEEE [2-(2-(2-methoxyethoxy)ethoxy] side chains, the resultant polymers showed high HOMO levels and hence lower band gap. The values are given in Table 1.

The optical properties of these polymers were characterized by using UV-vis spectroscopy [Fig. S15(a,b)]. The UV-vis spectra in chloroform solution showed one absorption maximum around 470 nm for both polymers (Table 1). The absorption maximum in thin film was redshifted by \sim 70 nm with shoulder peaks indicating the increased intermolecular ordering of the polymer in the solid state compared with solution.

Furthermore, the polymers showed solvatochromism in THF/ water solvent mixtures [Fig. S15(c,d)]. Incremental addition of water (nonsolvent for PTs) to a solution of polymers in THF (a suitable solvent for the polymer) resulted in a redshifted absorption and concentration-independent vibronic structures. We observed the same phenomenon in our previous work of regioregular P3HT-based block copolymers and speculated that it is due to the formation of micellar or vesicular aggregates formed by self-assembly to generate core–shell type structure.^{32–34} In this case, we believe that the observed redshift may be due to a fibrillar aggregate as we have observed in tapping mode atomic force microscopy (AFM) images of polymers on mica, drop-casted from THF/water (3:2) solvent mixture [Fig. 1(c,f)].

Interestingly, the polymers displayed different morphologies in different solvents. The morphology of the polymers drop-casted from toluene, chloroform, and THF/water (3/2, v/v) on mica surface was studied using TMAFM and the resultant images are

^d Estimated from the onset of oxidation peak of the cyclic voltammogram.

^e Estimated from the onset of reduction peak of the cyclic voltammogram.

shown in Figure 1. In less polar solvents, the hydrophilic MEEE segments might tend to self-assemble so that the hydrophilic chains stay away from the less polar solvent. Upon increasing solvent polarity, the MEEE segments form more favorable interactions with the more polar solvents to self-assemble in well-separated nanowires.

Furthermore, the crystallinity of the polymers was tested using X-ray diffraction studies, and it displayed peaks for lamellar packing and π - π stacking with *d*-spacing of 15.3 and 4.2 Å for **P1** and 15.2 and 4.2 Å for **P2**, respectively (Figs. S16 and S17). Lamellar packing distances of these polymers are less than that of regioregular P3HT, and π - π stacking distances are larger than that of regioregular P3HT.³⁵

Furthermore, GIWAXS measurements were also obtained from a film of the polymer **P2**, and the data is shown in Figure 1 (2a and 2b). We assigned the peak at $q \sim 0.4$ Å⁻¹ to the distance between polymer backbones through the alkyl side chains. The broad peak at q of 1.53 Å⁻¹ corresponds to a π - π stacking distance of 4.1 Å, which is larger than that of P3HT.³⁶ Another peak was visible at 0.83 Å⁻¹ in the in-plane data shown in Figure 2(b). This peak suggested the crystal structure of MEEE substituted PT may differ from that of P3HT.^{36,37}

Comparing the π -stacking peak of MEEE replaced PT to regiorandom P3HT, which is amorphous, the breadth and position are similar.³⁸ The broad π -stacking peak suggests a weak coupling between chains. As a consequence, the GIWAXS data suggest that MEEE substituted PT will exhibit lower charge mobilities when compared to regioregular P3HT.

Thermal stability of the polymers was analyzed using TGA, and polymer **P1** were stable up to ~300 °C and showed 5% weight loss at 320 °C. Polymer **P2** displayed 5% weight loss at 274 °C. According to the DSC analysis of the polymer **P2**, the glass transition temperature around 90 °C, melting of the polymer around 160–170 °C and the crystallization temperature around 125 °C was observed (Fig. S22).

The high conductivity upon doping with iodine vapor and the conductivity persisting for days under ambient conditions is a prominent feature in MEET-based polymers.¹⁶ Our polymers showed similar behavior when the conductivity measurements were carried out using a four-point probe. The results are summarized in Tables 2 and 3.





FIGURE 1 Tapping mode AFM images (phase) of **P1** (1a, 1b, 1c) and **P2** (1d, 1e, 1f) on mica drop-casted from toluene (1a, 1d) chloroform (1b, 1e) THF/water (3:2) solvent mixture (1c, 1f) with 0.30 mg mL⁻¹ (2a) GIWAXS data from a film of the polymer **P2** (2b) GIWAXS intensity versus scattering vector *q*. Both azimuthally averaged data and in-plane line cuts are shown.

The conductivity increased upon doping of the polymers with iodine for both polymers, with and without thermal annealing. **P2** had exhibited higher conductivity compared to that of **P1**, possibly due to its relatively higher molecular weight. Thermal annealing did not help in increasing conductivity. Nonannealed samples showed slightly higher conductivities in doped states compared to thermally annealed samples. To study the stability of the doped state of the polymers, polymer films doped with iodine vapors for 12 h were kept in the air, and the conductivities were measured over time. Results are summarized in Table 3. Conductivities remained nearly constant for 30 days, indicating that these polymers have stable oxidized states. This could be due to the better stabilization of charge carriers by alkoxy side chains on the polymer.

To study the mobility of the charge carriers, the high-molecularweight polymer **P2** was tested in field effect transistors as well as in a Schottky diode. Field-effect mobilities were extracted from the electrical characterization of thin-film transistors with the polymer as the active layer. Devices were fabricated with a bottom-gate, bottom-contact configuration. Surfaces were cleaned by UV-Ozone treatment for 10 min. No other surface treatment was applied because the self-assembled monolayers such as octadecyltrichlorosilane deposited on the dielectric surface led to de-wetting of the polymer. I_D (drain current) versus V_D (drain–source voltage) curves are given in Figure 2(a). The linear behavior at low source-drain voltages suggests a lack of significant contact barriers. I_D versus V_G is shown in Figure 2(b), and the average threshold voltage is $-30 \text{ V} (\pm 22.2 \text{ V})$ and the on/off ratio is $8.8 \times 10^1 (\pm 5.1 \times 10^1)$. The field-effect mobility was obtained from the slope of $I_D^{1/2}$ versus V_G (saturation regime) using:

$$\mu_{\text{sat}} = (2L/WC_i) m^2 \tag{5}$$

where μ_{sat} is the field-effect mobility obtained in the saturation regime, *L* is the channel length, *W* is the channel width, *C_i* is the capacitance of the dielectric, and *m* is the slope of the plot of $I_D^{1/2}$ versus V_G at saturation. The average mobility of devices with **P2** as the active layer was 4.2×10^{-4} cm² V⁻¹ s⁻¹ (±4.8 × 10⁻⁵ cm² V⁻¹ s⁻¹), which is lower than that of devices with regioregular P3HT as the active layer, even when devices lack self-assembled monolayers at the dielectric surface.²⁹ SCLC model in Schottky diode revealed that the polymer had a hole mobility of 3.47 × 10^{-7} cm² V⁻¹ s⁻¹ (±6.67 × 10^{-8} cm² V⁻¹ s⁻¹) (Fig. S23).

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FIGURE 2 (a) Output curves of **P2** at different gate voltages (I_D vs. V_D curves), (b) I_D versus V_G , and (c) transmittance of doped polymer **P2** compared with that of PEDOT:PSS.

Due to the conductivity features upon doping, we have investigated the applicability of polymer **P2** as a hole injection layer for photovoltaic applications. Different concentrations of the polymer were spin coated from chloroform solution on ITO substrates with different spin rates. The resultant polymer films were doped with iodine vapor for 30 min, and their transmittance was measured [Fig. 2(c)]. The 30 min was more reasonable timescale for doping in real applications, and the conductivity does not change considerably as doping time increases (Table 2).

Upon doping with iodine vapors, the polymer films became more transparent [inset of Fig. 2(c)] and no longer soluble in common organic solvents such as chloroform and chlorobenzene. This is a

TABLE 2 Average Conductivity upon Increasing Doping Time

	Doping Time	Average Conductivity (S cm ⁻¹)		
		P1	P2	
	Before doping	$9 imes 10^{-5}$	$8 imes 10^{-4}$	
Thermally annealed at	30 min	200	648	
100 °C for 5 min	1 h	181	654	
	3 h	181	703	
	12 h	179	655	
Without thermal	30 min	274	779	
annealing	1 h	274	829	
	3 h	275	789	
	12 h	275	782	

Film thickness: P1 annealed 6013.3 Å, P1 nonannealed 4001.8 Å, P2 annealed 1623.8 Å, P2 nonannealed 1388.7 Å

crucial requirement in active layer deposition in photovoltaic applications as the active layer is deposited on top of the hole injection layer by using a common organic solvent. Both 5 mg mL⁻¹ samples showed similar transmittance as PEDOT:PSS in infrared regions and above 80% transmittance in UV-vis regions. Since both 5 mg mL⁻¹ samples showed similar behavior, 5 mg mL⁻¹ sample spin coated at 3000 rpm could consider as best conditions as this speed gives a reasonable average film thickness of ~16 nm. This film thickness is comparable with the PEDOT: PSS film thickness.³⁹ PEDOT:PSS needs an additional annealing step before active layer deposition and shows hygroscopicity and acidity. By contrast, our polymer does not require any annealing before active layer deposition. Our group is currently investigating device performances by using **P2** as the hole injection layer.

TABLE 3 Stability of the Oxidized State

	Time (Days) afte Treatment in Ai	Avera er Cond r (S cn	age luctivity n ⁻¹)
		P1	P2
Thermally annealed at	1	179	662
100°C for 5 min	3	179	732
	4	182	691
	5	185	647
	30	175	647
Without thermal annea	lling 1	266	760
	3	268	766
	4	264	794
	5	279	764
	30	263	757



CONCLUSIONS

In conclusion, triethylene glycol monomethyl ether substituted PTs synthesized by McCullough method displayed a range of promising optical, electrical, and thermal properties such as better ordering in solid state compared with solution, reduced band gap due to the high lying HOMO level, thermal stability up to $\sim 300 \,^{\circ}$ C and in thin-film transistors of high-molecular-weight polymer showed an average mobility of $4.2 \times 10^{-4} \, \mathrm{cm}^2 \, \mathrm{V}^{-1} \, \mathrm{s}^{-1}$. Furthermore, polymers showed high conductivity upon chemical doping with iodine vapors which persisted for days due to the stable oxidized states. Due to the increased transparency upon doping this polymer revealed great potential as an alternative to commercially available PEDOT:PSS.

ACKNOWLEDGMENTS

We are gratefully acknowledging the financial support Welch Foundation (AT-1740). The authors would like to thank Qing Wang, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA for grazingincidence wide-angle X-ray scattering data analysis and Elizabeth A. Rainbolt (liz.rainbolt@gmail.com) for X-ray diffraction analysis.

REFERENCES AND NOTES

1 C. B. Nielsen, I. McCulloch, Prog. Polym. Sci. 2013, 38(12), 2053.

2 M. Zhu, S. Pan, Y. Wang, P. Tang, F. Qiu, Z. Lin, J. Peng, *Angew. Chem. Int. Ed.* 2018, *57*(28), 8644.

3 L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao, L. Yu, *Chem. Rev.* **2015**, *115*(23), 12666.

4 S. Pan, L. He, J. Peng, F. Qiu, Z. Lin, *Angew. Chem. Int. Ed.* 2016, 55(30), 8686.

5 T. P. Huynh, P. S. Sharma, M. Sosnowska, F. D'Souza, W. Kutner, *Prog. Polym. Sci.* **2015**, *47*, 1.

6 M. Leclerc, K. Faid, Adv. Mater. 1997, 9(14), 1087.

7 K. Y. Kao, R. Y. Pei, H. L. Chen, J. H. Chen, S. A. Chen, *RSC Adv.* **2016**, *6*(82), 79209.

8 K. A. Mazzio, A. H. Rice, M. M. Durban, C. K. Luscombe, J. Phys. Chem. C 2015, 119(27), 14911.

9 H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280* (5370), 1741.

 M. P. Bhatt, H. D. Magurudeniya, E. A. Rainbolt, P. Huang,
D. S. Dissanayake, M. C. Biewer, M. C. Stefan, *J. Nanosci. Nanotechnol.* 2014, 14(2), 1033.

11 R. D. McCullough, Adv. Mater. 1998, 10(2), 93.

12 M. Â. J. Panzer, C. Â. D. Frisbie, *Adv. Funct. Mater.* 2006, *16*(8), 1051.

13 K.-Y. Jen, G. G. Miller, R. L. Elsenbaumer, *J. Chem. Soc. Chem. Commun.* **1986**, (17), 1346.

14 M. C. lovu, C. R. Craley, M. Jeffries-El, A. B. Krankowski, R. Zhang, T. Kowalewski, R. D. McCullough, *Macromolecules* 2007, *40*(14), 4733.

15 S. A. Chen, C. C. Tsai, Macromolecules 1993, 26(9), 2234.

16 E. E. Sheina, S. M. Khersonsky, E. G. Jones, R. D. McCullough, *Chem. Mater.* **2005**, *17*(13), 3317.

17 M. R. Bryce, A. Chissel, P. Kathirgamanathan, D. Parker, N. R. M. Smith, J. Chem. Soc. Chem. Commun. 1987, (6), 466.

18 D. Belaineh, R. O. Png, C. L. McGuiness, M. Mathai, V. Seshadri, P. K. H. Ho, *Chem. Mater.* **2014**, *26*(16), 4724.

19 S. A. Mauger, J. Li, O. T. Ozmen, A. Y. Yang, S. Friedrich, M. D. Rail, L. A. Berben, A. J. Moule, *J. Mater. Chem.* C **2014**, *2*(1), 115.

20 S. A. Mauger, A. J. Moulé, Org. Electron. 2011, 12(11), 1948.

21 E. Voroshazi, B. Verreet, A. Buri, R. Müller, D. Di Nuzzo, P. Heremans, *Org. Electron.* **2011**, *12*(5), 736.

22 M. Jørgensen, K. Norrman, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* 2008, *92*(7), 686.

23 K. Norrman, S. A. Gevorgyan, F. C. Krebs, ACS Appl. Mater. Interfaces 2009, 1(1), 102.

24 C. B. Nielsen, A. Giovannitti, D. T. Sbircea, E. Bandiello, M. R. Niazi, D. A. Hanifi, M. Sessolo, A. Amassian, G. G. Malliaras, J. Rivnay, I. McCulloch, *J. Am. Chem. Soc.* **2016**, *138*(32), 10252.

25 E. Lee, B. Hammer, J. K. Kim, Z. Page, T. Emrick, R. C. Hayward, *J. Am. Chem. Soc.* 2011, *133*(27), 10390.

26 J. Kim, A. Siva, I. Y. Song, T. Park, Polymer 2011, 52(17), 3704.

27 S. S. Gunathilake, H. D. Magurudeniya, P. Huang, H. Nguyen, E. A. Rainbolt, M. C. Stefan, M. C. Biewer, *Polym. Chem.* **2013**, *4* (20), 5216.

28 R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, J. Org. Chem. 1993, 58(4), 904.

29 K. Vakhshouri, B. H. Smith, E. P. Chan, C. Wang, A. Salleo, C. Wang, A. Hexemer, E. D. Gomez, *Macromolecules* **2016**, *49* (19), 7359.

30 M. A. Keegstra, T. H. A. Peters, L. Brandsma, *Tetrahedron* **1992**, *48*(17), 3633.

31 R. D. McCullough, R. D. Lowe, *J. Chem. Soc. Chem. Commun.* **1992**, (1), 70.

32 M. G. Alemseghed, S. Gowrisanker, J. Servello, M. C. Stefan, Macromol. Chem. Phys. 2009, 210(23), 2007.

33 M. G. Alemseghed, J. Servello, N. Hundt, P. Sista, M. C. Biewer, M. C. Stefan, *Macromol. Chem. Phys.* 2010, *211*(12), 1291.

34 N. Hundt, Q. Hoang, H. Nguyen, P. Sista, J. Hao, J. Servello, K. Palaniappan, M. Alemseghed, M. C. Biewer, M. C. Stefan, *Macromol. Rapid Commun.* **2011**, *32*(3), 302.

35 R. D. McCullough, S. Tristram-Nagle, S. P. Williams, R. D. Lowe, M. Jayaraman, *J. Am. Chem. Soc.* **1993**, *115*(11), 4910.

36 T. J. Prosa, M. J. Winokur, J. Moulton, P. Smith, A. J. Heeger, *Macromolecules* **1992**, *25*(17), 4364.

37 B. H. Smith, M. B. Clark, H. Kuang, C. Grieco, A. V. Larsen, C. Zhu, C. Wang, A. Hexemer, J. B. Asbury, M. J. Janik, E. D. Gomez, *Adv. Funct. Mater.* **2015**, *25*(4), 542.

38 C. Wang, J. Rivnay, S. Himmelberger, K. Vakhshouri, M. F. Toney, E. D. Gomez, A. Salleo, *ACS Appl. Mater. Interfaces* 2013, *5*(7), 2342.