

Supporting information

Poly(5-alkyl-[3,4-c]thienopyrrole-4,6-dione)s: A study of π -conjugated redox polymers as anode materials in Lithium-ion batteries

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Characterization:

^1H spectra were recorded using a Varian AS400 in deuterated chloroform at 298 K. Chemical shifts were reported as δ values (ppm) relative to chloroform value of 7.26 ppm.

For our size-exclusion chromatography (SEC) measurements, we used a Varian Polymer Laboratories GPC220 equipped with a RI detector, a PL BV400 HT Bridge Viscometer, 2 PLgel Mixed C (300 x 7.5 mm) columns and a PLgel Mixec C Guard column. The temperature of the system was set to 110°C and the 1,2,4-trichlorobenzene (TCB) (with 0.0125% BHT w/v) flow was set to 1 mL/min. The samples (2 mg) were dissolved in 2 mL of TCB in a 5 mL chromatography vial then stirred and heated to 110°C for 1 hour to let aggregates completely dissolve. Then, a filtration through a .45 μm cellulose fiber film in a 5 mL chromatography vial lead to a homogenous polymeric solution. The sample was injected through a loop of 200 μL with a Varian Polymer Laboratories PL-SP 260VC sample preparation system. Calibration was set with narrow polystyrene standards.

UV vis-NIR absorption spectra were recorded using a Varian Cary 500 UV-vis-NIR spectrophotometer using 1 cm path length quartz cells. A polymeric solution was spin coated on untreated glass substrate in order to perform the solid-state measurement. The optical bandgap was calculated from the onset of the absorption band.

IR spectrum were recorded using a Fourier transformed infrared Magna-850 Nicolet from Thermo equipped with a liquid-nitrogen cooled a MCT detector with a beam splitter of

potassium bromide. Spectra were recorded using a Nicolet Magna 850 Fourier transform infrared spectrometer (Thermo Scientific, Madison, WI) with a liquid nitrogen cooled narrow-band MCT detector using an ATR accessory (Golden-Gate™, Specac Ltd, London, UK). The electric field of the infrared beam was s-polarized (perpendicular to the plane of incidence) using a ZnSe wire-grid polarizer (Specac Ltd.). Spectrums were recorded with a resolution of 4 cm⁻¹ resulting from an accumulation of 128 scans. A Happ-Ganzel adipozation and a zero-filling with a factor 2 were applied to every spectrum. The OMNIC (ThermoElectron, Madison, WI) software was monitoring the parameters and the acquisition of the scans. Spectral corrections were achieved using the GRAMS/AI 8.0 software (Thermo Galactic, Salem, NH). A linear baseline was subtracted to account for the background drift.

Thermogravimetric analyses of the polymers were performed with a TGA/SDTA 851e from Metler-Toledo. The acquisitions were recorded under argon with a 10 °C/min scan rate from 50 to 600 °C. The reported degradation temperatures (DT) correspond to a 5% mass lost.

Materials:

Chemicals: Thiophene-3,4-dicarboxylic acid was bought from Frontier. Monomers have been synthesized following the reported literature and were carefully purified prior to use in the polymerization reaction ^[1,2]. Other monomers, 2,5-dibromothiophene and 3,4-ethylenedioxythiophene, have been purchase from Sigma Aldrich and use as received. Trans-Bis(acetato)bis[o-(di-o-tolylphosphino)benzyl]dipalladium (II) (Pd(Herrmann-Beller)), Tri(o-anisyl) phosphine, pivalic acid, cesium carbonate and extra dry toluene have been purchase from Sigma Aldrich and use as received.

Monomers synthesis

5-octyl-[3,4-c]thienopyrrole-4,6-dione (M1): In a round bottom flask, 5g (29.11mmol) of thiophene-3,4-dicarboxylic acid was dissolved in 125mL of acetic anhydride (0.232mol/L) and the solution is heated at 140°C over night. After cooling to room temperature, the solution is evaporated under reduced pressure to afford off-white slurry and use for the next step without further purification. The compound is dissolves in 268mL of toluene (0.11mol/L). 5,64g (43.67mmol) of octylamine is added and the solution is reflux for 24h. Subsequently, the solvent is evaporated under reduced pressure and the brownish slurry is dissolved in 225mL (0.13mol/L) of thionyl chloride and heated to reflux for 4h. After cooling to room temperature, thionyl chloride is evaporated under reduced pressure to afford a brown solid. After two recrystallizations in methanol, pure 5-octyl-[3,4-

c]thienopyrrole-4,6-dione was collected as 4,31g of white crystals representing a yield of 56% .

RMN ¹H (400MHz, CDCl₃, ppm): 7.80 (s, 2H); 3.61 (t, 2H, J=7.36 Hz); 1.64 (m, 2H); 1.27 (m, 10H); 0.86 (t, 3H, J=6.84 Hz)

5-octyl-4,6-dihydro-[3,4-c]-thienopyrrole (M2): 620mg (16.34mmol) of LiAlH₄ is poured in 60mL (0.27mol/L) of dry diethyl ether. Then a solution of 1.39g (6.65mmol) 5-octyl-[3,4-c]thienopyrrole-4,6-dione in 80mL (0.083mol/L) dry diethyl ether is added drop-wise to the solution of LiAlH₄. Then, the mixture is stirred at reflux 18h. The solution is chilled to room temperature and water is added drop-wise. The mixture is wash with water and extracted with ethyl ether. Organic phases are combined, dried with MgSO₄, filtrated and evaporated under reduced pressure. The brown oil is purified by silica column chromatography using methylene chloride as eluent and filtrated over activated carbon to afford 5-octyl-4,6-dihydro-[3,4-c]-thienopyrrole as a yellowish oil with 41% yield.

RMN ¹H (400MHz, CDCl₃, ppm) : 7.80 (s, 2H); 3.71 (s, 4H); 2.70 (t, 2H, J=7.55 Hz); 1.56 (quint, 2H, J=7.18 Hz); 1.28 (m, 10H); 0.89 (t, 3H, J=6.78 Hz)

5-butyl-[3,4-c]thienopyrrole-4,6-dione (M3): In a round bottom flask, 1g (5.82mmol) of thiophene-3,4-dicarboxylic was dissolved in 25mL of acetic anhydride (0.232mol/L) and the solution is heated at 140°C over night. After cooling to room temperature, the solution is evaporated under reduced pressure to afford off-white slurry and use for the next step without further purification. The compound is dissolves in 53mL of toluene (0.11mol/L). 0.64g (8.73mmol) of butylamine is added and the solution is reflux for 24h. Subsequently, the solvent is evaporated under reduced pressure and the yellow solid is dissolved in 45mL (0.13mol/L) of thionyl chloride and heated to reflux for 4h. After cooling to room temperature, thionyl chloride is evaporated under reduced pressure to afford a brown solid. After two recrystallizations in methanol, pure 5-butyl-[3,4-c]thienopyrrole-4,6-dione was collected as 462 mg of white crystals representing a yield of 38% .

RMN ¹H (400MHz, CDCl₃, ppm): 7.80 (s, 2H); 3.60 (t, 2H, J=7.31 Hz); 1.61 (quint, 2H, J=7.48 Hz); 1.34 (six, 2H, J=7.45 Hz); 0.93 (t, 3H, J=7.346 Hz)

5-tetradecyl-[3,4-c]thienopyrrole-4,6-dione (M4): In a round bottom flask, 1g (5.82mmols) of thiophene-3,4-dicarboxylic was dissolved in 25mL of acetic anhydride (0.232mol/L) and the solution is heated at 140°C over night. After cooling to room temperature, the solution is evaporated under reduced pressure to afford off-white slurry and use for the next step without further purification. The compound is dissolves in 53mL of toluene (0.11mol/L). 1.86g (8.73mmol) of tetradecylamine is added and the solution is reflux for 24h. Subsequently, the solvent is evaporated under reduced pressure and the yellow solid is dissolved in 45mL (0.13mol/L) of thionyl chloride and heated to reflux for 4h. After cooling to room temperature, thionyl chloride is evaporated under reduced pressure to afford a brown solid. After two recrystallizations in methanol, pure 5-

tetradecyl-[3,4-*c*]thienopyrrole-4,6-dione was collected as 750 mg of off-white crystals representing a yield of 37% .

RMN 1H (400MHz, CDCl₃, ppm): 7.79 (s, 2H); 3.60 (t, 2H, J=7.35 Hz); 1.63 (m, 2H); 1.26 (m, 22H); 0.88 (t, 3H, J=6.75 Hz)

*5-(2-ethylhexyl)-[3,4-*c*]thienopyrrole-4,6-dione (M5)*: In a round bottom flask, 10g (58.21mmols) of thiophene-3,4-dicarboxylic was dissolved in 250mL of acetic anhydride (0.232mol/L) and the solution is heated at 140°C over night. After cooling to room temperature, the solution is evaporated under reduced pressure to afford off-white slurry and use for the next step without further purification. The compound is dissolves in 536mL of toluene (0.11mol/L). 11.28g (87.32mmol) of 2-ethylhexylamine is added and the solution is reflux for 24h. Subsequently, the solvent is evaporated under reduced pressure and the yellow solid is dissolved in 452mL (0.13mol/L) of thionyl chloride and heated to reflux for 4h. After cooling to room temperature, thionyl chloride is evaporated under reduced pressure to afford a brown solid. After two recrystallizations in methanol, pure 5-(2-ethylhexyl)-[3,4-*c*]thienopyrrole-4,6-dione was collected as 6.51g of off-white crystals representing a yield of 42% .

RMN 1H (400MHz, CDCl₃, ppm): 7.80 (s, 2H); 3.51 (d, 2H, J=7.28 Hz); 1.80 (sept, 1H, J=6.21 Hz); 1.31 (m, 2H); 0.89 (m, 6H)

*2,8-dibromo-5-octyl-[3,4-*c*]thienopyrrole-4,6-dione (M6)*: In a round bottom flask, 1g (3.77mmols) of 5-octyl-[3,4-*c*]thienopyrrole-4,6-dione is dissolved in 5.6mL of sulfuric acid and 18.9mL of trifluoroacetic acid. Then, 2.01g (11.3mmols) of N-bromosuccinimide is added in portions and the solution is stirred in the dark overnight. Afterward, a 2M KOH solution is added until the solution turn from red to yellowish-green. The solution is wash with water and extracted with methylene chloride. Organic phases are combined and dry with MgSO₄, filtrated and evaporated under reduced pressure. The yellowish cristals are purified by silica column chromatography using a 6:4 (v/v) Hexane: Methylene chloride mix as eluent to afford 2,8-dibromo-5-octyl-[3,4-*c*]thienopyrrole-4,6-dione as a white crystal with 78% yield.

RMN 1H (400MHz, CDCl₃, ppm): 3.51 (d, 2H, J=7.28 Hz); 1.80 (sept, 1H, J=6.21 Hz); 1.31 (m, 2H); 0.89 (m, 6H)

Polymers synthesis

Polymerization reactions were carried out as described in literature [3].

*Poly[5-octyl-[3,4-*c*]thienopyrrole-4,6-dione-alt-2,5-thiophene] (P1)*: In a 10mL oven dry biotage microwave vial with a magnetic stirring bar, 150mg (0.57mmol) of 5-octyl-[3,4-*c*]thienopyrrole-4,6-dione (**M1**), 136.9mg (0.57mmol) of 2,5-dibromothiophene, 21.2mg (0.023mmol) of Pd(Herrmann-Beller), 15.9mg (0.045mmol) of Tri(*o*-anisyl) phosphine,

17.3mg (0.17mmol) of pivalic acid and 424mg (1.3mmol) of cesium carbonate is added. The vial is sealed and purged by vacuum and filled with argon three times. Then, 2.3mL of degassed dry toluene is added and the solution is stirred at 120°C for 48 hours. The reaction was cooled at room temperature and the polymer was precipitated in methanol, filtered through 0.45mm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, chloroform and ortho-dichlorobenzene (ODCB). The solvent was reduced to about 10 mL and precipitated in methanol, filtered through 0.45mm nylon filter and air-dried to afford the insoluble polymer P1 with 32% yield. DT=360°C

Poly[5-octyl-4,6-dihydro-[3,4-c]-thienopyrrole-alt-2,5-thiophene] (P2): In a 20mL oven dry biotage microwave vial with a magnetic stirring bar, 453.6mg (1.91mmol) 5-octyl-4,6-dihydro-[3,4-c]-thienopyrrole (**M2**), 458.8mg (1.91mmol) of 2,5-dibromothiophene, 71.7mg (0.077mmol) of Pd(Herrmann-Beller), 53.9mg (0.153mmol) of Tri(o-anisyl) phosphine, 58.6mg (0.574mmol) of pivalic acid and 1.4333g (4.4mmol) of cesium carbonate is added. The vial is sealed and purged by vacuum and filled with argon three times. Then, 7.65mL of degassed dry toluene is added and the solution is stirred at 120°C for 24 hours. The reaction was cooled at room temperature and the polymer was precipitated in methanol, filtered through 0.45mm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, chloroform and ortho-dichlorobenzene (ODCB). The solvent was reduced to about 10 mL and precipitated in methanol, filtered through 0.45mm nylon filter and air-dried to afford the insoluble polymer P2 with 52% yield. DT=270°C

Poly[5-butyl-[3,4-c]thienopyrrole-4,6-dione-alt-2,5-thiophene] (P3): In a 10mL oven dry biotage microwave vial with a magnetic stirring bar, 150mg (0.717 mmol) of 5-butyl-[3,4-c]thienopyrrole-4,6-dione (**M3**), 173.6mg (0.717mmol) of 2,5-dibromothiophene, 26.9mg (0.0287mmol) of Pd(Herrmann-Beller), 20.2mg (0.057mmol) of Tri(o-anisyl) phosphine, 22.0mg (0.215mmol) of pivalic acid and 537.7mg (1.65mmol) of cesium carbonate is added. The vial is sealed and purged by vacuum and filled with argon three times. Then, 2.8mL of degassed dry toluene is added and the solution is stirred at 120°C for 48 hours. The reaction was cooled at room temperature and the polymer was precipitated in methanol, filtered through 0.45mm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, chloroform and ortho-dichlorobenzene (ODCB). The solvent was reduced to about 10 mL and precipitated in methanol, filtered through 0.45mm nylon filter and air-dried to afford the insoluble polymer P3 with 27% yield. DT=340°C

Poly[5-tetradecyl-[3,4-c]thienopyrrole-4,6-dione-alt-2,5-thiophene] (P4): In a 20mL oven dry biotage microwave vial with a magnetic stirring bar, 524.3mg (1.5mmol) 5-tetradecyl-[3,4-c]thienopyrrole-4,6-dione (**M4**), 362.9mg (1.5mmol) of 2,5-dibromothiophene, 56.3mg (0.06mmol) of Pd(Herrmann-Beller), 42.3mg (0.12mmol) of Tri(o-anisyl) phosphine, 45.6mg (0.45mmol) of pivalic acid and 1.1241g (3.45mmol) of

cesium carbonate is added. The vial is sealed and purged by vacuum and filled with argon three times. Then, 6mL of degassed dry toluene is added and the solution is stirred at 120°C for 48 hours. The reaction was cooled at room temperature and the polymer was precipitated in methanol, filtered through 0.45mm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, chloroform and ortho-dichlorobenzene (ODCB). The solvent was reduced to about 10 mL and precipitated in methanol, filtered through 0.45mm nylon filter and air-dried to afford the insoluble polymer P4 with 51% yield. DT=440°C

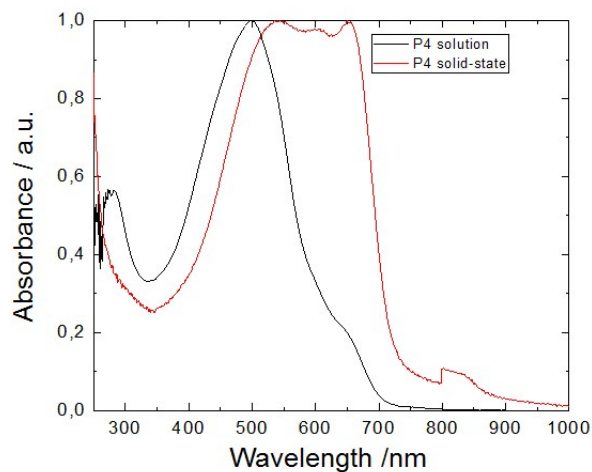
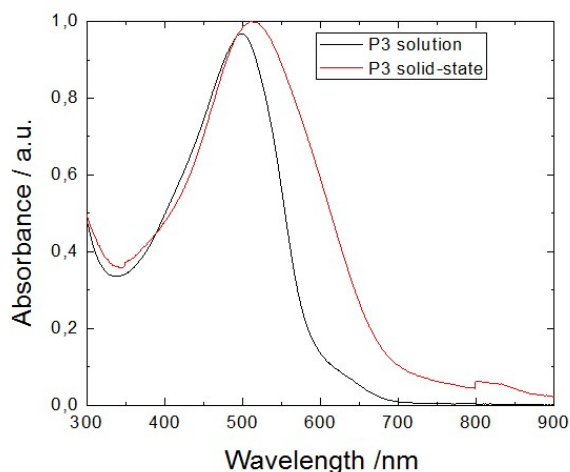
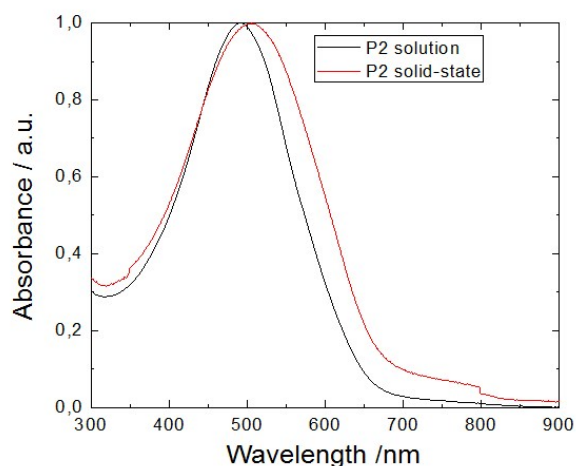
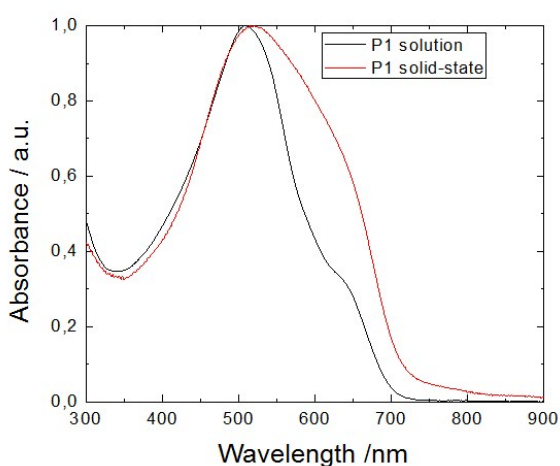
Poly[5-(2-ethylhexyl)-[3,4-c]thienopyrrole-4,6-dione-alt-2,5-thiophene] (P5): In a 20mL oven dry biotage microwave vial with a magnetic stirring bar, 397.7mg (1.5mmol) 5-(2-ethylhexyl)-[3,4-c]thienopyrrole-4,6-dione (**M5**), 362.9mg (1.5mmol) of 2,5-dibromothiophene, 56.3mg (0.06mmol) of Pd(Herrmann-Beller), 42.3mg (0.12mmol) of Tri(o-anisyl) phosphine, 45.6mg (0.45mmol) of pivalic acid and 1.1241g (3.45mmol) of cesium carbonate is added. The vial is sealed and purged by vacuum and filled with argon three times. Then, 6mL of degassed dry toluene is added and the solution is stirred at 120°C for 48 hours. The reaction was cooled at room temperature and the polymer was precipitated in methanol, filtered through 0.45mm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, chloroform and ortho-dichlorobenzene (ODCB). The solvent was reduced to about 10 mL and precipitated in methanol, filtered through 0.45mm nylon filter and air-dried to afford the insoluble polymer P5 with 42% yield. DT=370°C

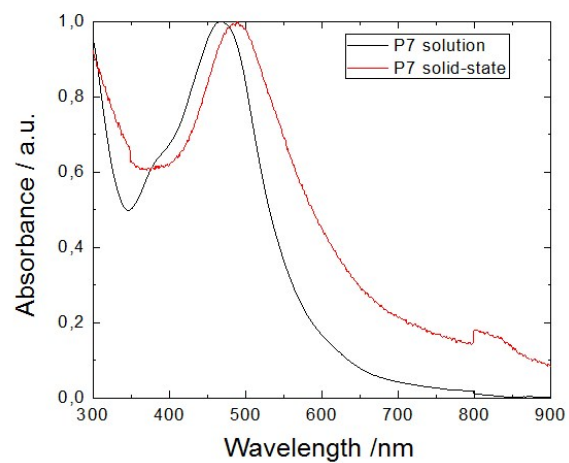
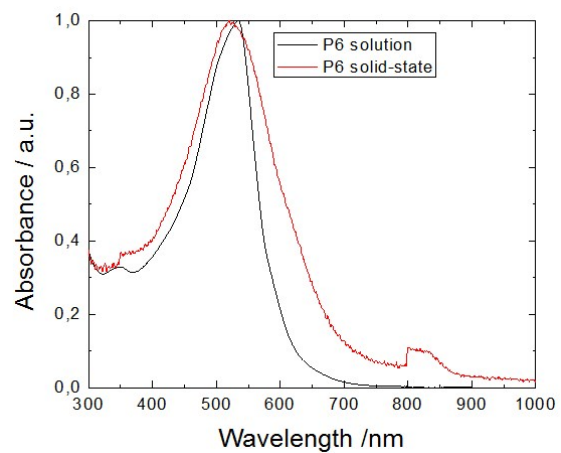
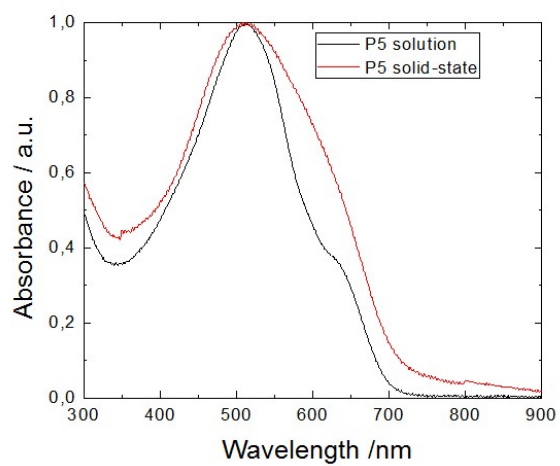
Poly[5-octyl-3,4-c]thienopyrrole-4,6-dione-alt-2,5-ethylenedioxythiophene] (P6): In a 10mL oven dry biotage microwave vial with a magnetic stirring bar, 150mg (0.354mmol) of 2,8-dibromo-5-octyl-[3,4-c]thienopyrrole-4,6-dione (**M6**), 50.3mg (0.345mmol) of 3,4-ethylenedioxythiophene, 12.9mg (0.0138mmol) of Pd(Herrmann-Beller), 10mg (0.028mmol) of Tri(o-anisyl) phosphine, 10.8mg (0.1062mmol) of pivalic acid and 265.3mg (0.8142mmol) of cesium carbonate is added. The vial is sealed and purged by vacuum and filled with argon three times. Then, 1.4mL of degassed dry toluene is added and the solution is stirred at 120°C for 48 hours. The reaction was cooled at room temperature and the polymer was precipitated in methanol, filtered through 0.45mm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, chloroform and ortho-dichlorobenzene (ODCB). The solvent was reduced to about 10 mL and precipitated in methanol, filtered through 0.45mm nylon filter and air-dried to afford the insoluble polymer P6 with 45% yield. DT=340°C

Poly[5-octyl-[3,4-c]thienopyrrole-4,6-dione] (P7): In a 10mL oven dry biotage microwave vial with a magnetic stirring bar, 150mg (0.57mmol) of 5-octyl-[3,4-c]thienopyrrole-4,6-dione (**M1**), 241.2mg (0.57mmol) of 2,8-dibromo-5-octyl-[3,4-c]thienopyrrole-4,6-dione (**M6**), 21.2mg (0.023mmol) of Pd(Herrmann-Beller), 15.9mg (0.045mmol) of Tri(o-anisyl) phosphine, 17.3mg (0.17mmol) of pivalic acid and 424mg

(1.3mmol) of cesium carbonate is added. The vial is sealed and purged by vacuum and filled with argon three times. Then, 2.3mL of degassed dry toluene is added and the solution is stirred at 120°C for 48 hours. The reaction was cooled at room temperature and the polymer was precipitated in methanol, filtered through 0.45mm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, chloroform and ortho-dichlorobenzene (ODCB). The solvent was reduced to about 10 mL and precipitated in methanol, filtered through 0.45mm nylon filter and air-dried to afford the insoluble polymer P7 with 21% yield. DT=390°C

UV-visible absorption spectra of the resulting copolymers





References for supporting information

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- [3] a) Mercier, L. G.; Aïch, B. R.; Najari, A.; Beaupré, S.; Berrouard, P.; Pron, A.; Robitaille, A.; Tao, Y.; Leclerc, M. *Polym. Chem.* **2013**, 4, 5252-5260 b) Berrouard, P.; Najari, A.; Pron, A.; Gendron, D.; Morin, P.-O.; Pouliot, J.-R.; Veilleux, J.; Leclerc, M. *Angew. Chem. Int. Ed.* **2012**, 51, (9), 2068-2071