Electroactive Polyacrylates bearing Linear Conjugated Systems based on EDOT moieties

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ABSTRACT: New polyacrylates bearing an electropolymerizable bi or terthiophene group have been synthesized via classical radical polymerization and via RAFT process. Polymerizations can be controlled if thiophene moieties have protected α positions; otherwise polymerization is difficult or impossible. Cross-linked polymers can be obtained after film electropolymerizations on different electrodes (gold, carbon and platinum).

Introduction

Since the publication of the first conducting polymer,1 extended pi-conjugated systems have aroused by researchers a growing interest on the one hand for accessibility and diversity and on the other hand for their many and varied applications. Indeed, such materials, depending on their semi-conducting or conducting properties, can be used as active layers in many devices, as OLED2 (television screen commercialized), OFET,3 bioelectronics,4 electrochromics,5,6 organic electronics.7 The use of organic conjugated polymers has also appeared in other domains. For example, the superhydrophobicity of polythiophene in its oxidized state has allowed its use as surface protection against biofouling.8 Moreover, a modified polythiophene bearing zwitterionic functions has also been investigated for its conductive properties and its excellent antifouling/biocompatibility at biointerfaces. Very recently, a modified poly(3,4-
ethylenedioxythiophene) (PEDOT) has been developed and presents antifouling properties against whole blood and bacteria.\(^9\) Besides, the material can be switched from cationic antimicrobial to zwitterionic antifoulant just by applying different potentials. If conjugated polymers do appear as promising candidates for antifouling applications, their formulation in paints appears difficult due to their mode of synthesis (chemical or electrochemical way) which does not allow an easy control of the polymer chains length and architecture. In this context, it appears interesting to link acrylate moieties with thiophene lateral groups to synthesize electroactive polymers via conventional radical polymerization and via reversible-deactivation radical polymerizations to control their architectures.

Examples of controlled (or not) radical polymerization with acrylate in the presence of thiophene groups have been described in the literature. Most of examples are block copolymers grown from P3HT strands and perylene bisimide acrylate,\(^10,11\) fullerene acrylate,\(^12\) lactide,\(^13\) vinylpyridine,\(^14,15\) fullerene,\(^16,17\) styrene-fullerene\(^18\) and others. In these cases, the thiophene is present in the final polymer but not on the acrylate moiety. Methacrylic esters have been successfully inserted at each extremity of ter or pentathiophene units to produce cross-linked materials\(^19\) for pattern formation by stamping. In all these examples, alpha positions of thiophenes are not available. The only example showing free alpha positions was presented by Xu and coll who have successively polymerized and electropolymerized acrylic ester linked to EDOT moieties to target electrochromic films.\(^20\)
Figure 1. Representation of the targeted polymer.

In this context, post-electropolymerizable polyacrylates have been investigated by designing the polymer presented on figure 1. This polymer exhibits a terthienyl moiety terminated on both side by one EDOT moiety well-known for allowing easy polymerization by chemical or electrochemical oxidation. In this paper, we describe our various efforts (resumed on scheme 1) to obtain this target polymer and draw the conditions to synthesize thienyl containing acrylic polymers with high yields via the RAFT polymerization.

Experimental part

Reagents. Solvents were purified and dried using standard protocols. 2,2’-azobis(isobutyronitrile) (AIBN) was purchased from Sigma-Aldrich and purified by recrystallization from methanol. Cyanomethyl dodecyl trithiocarbonate (CTA, Sigma-Aldrich) was used as received.

Instrumentation. 1H NMR and 13C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 300.1 and 75.4 MHz; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. High resolution mass spectra were recorded under FAB mode on a Jeol JMS 700 spectrometer. Chloroform (CDCl3) and tetrahydrofuran (THF-d8) were used as solvents. The number-average molar mass (Mn) and dispersity (D) of polymers were determined by triple detection size exclusion...
chromatography (TD-SEC). Analyses were performed on a Viscotek apparatus, composed of a GPC Max (comprising a degasser, a pump and an autosampler) with a TDA-302 (RI refractive index detector, right and low angle light scattering detector at 670 nm and viscometer) and an UV detector (λ = 298 nm). The following columns were used: a Viscotek HHR-H precolumn and two Viscotek ViscoGel GMHHR-H columns. THF was used as the eluent with a flow rate of 1.0 ml.min⁻¹ at 30 °C. For each precipitated polymer, the refractive index increment (dn/dc) was determined using the OmniSec software, from a solution of known concentration (ca. 10 mg.ml⁻¹) filtered through a 0.2 mm PTFE filter. IR spectra were recorded on a Bruker Vertex 70.

**Synthesis of precursors.**

3-(2-cyanoethylsulfanyl) thiophene 1 was synthesized according to the preparation developed in literature.²⁰ To a solution of 3-bromothiophene (7.05 g, 42.98 mmol, 1.00 eq) in anhydrous diethylether (Et₂O) (50 ml) under N₂ at -78 °C was added dropwise a solution of n-BuLi 1.6 M in hexane (18.1 ml, 1.05 eq) over a period of 30 min. After 15 min of stirring at -78 °C, the lithiated salt precipitated, and then elemental sulfur (1.44 g, 1.05 eq) was added in one portion. After 30 min of additional stirring at -78 °C, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. Then the solution was cooled down to 0°C and 3-bromopropionitrile (11.51 g, 7.13 ml, 2 eq) was added dropwise. The reaction mixture was stirred for 7 h at room temperature. After careful addition of a 0.5 M aqueous solution of HCl (40 ml), the mixture was extracted with dichloromethane (CH₂Cl₂) (200 ml). The organic phases were dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (eluent: 1:1 CH₂Cl₂(DCM)/petroleum ether (PE)) to give compound 1 as lightly yellow oil (5.8 g; 80% yield). ¹H NMR (300MHz, CDCl₃): δ (ppm)
1.86-1.95 (m, 2H); 2.99 (t, 2H, J=7.1 Hz); 7.08 (dd, 1H, J= 4.9 Hz, J= 1.3 Hz); 7.37 (dd, 1H, J=1.3 Hz, J=3.0 Hz); 7.38 (dd, 1H, J= 3.0 Hz, J= 4.9 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 31.7, 61.2, 123.4, 126.0, 129.5.

3-((2,5-dibromothiophen-3-yl)thio)propanenitrile 2. A solution of N-bromosuccinimide (11.00 g, 64.38 mmol) in DMF (25 ml) was added dropwise to 1 (7.00 g, 30.66 mmol) in DMF (40 ml) under N$_2$ at 0°C in the absence of light. The mixture was stirred 12 h at room temperature, concentrated and the residue was diluted with saturated aqueous NaCl and extracted with ethyl acetate (AcOEt) (200 ml). The organic phase was washed with water (100 ml), dried over MgSO$_4$ and evaporated in vacuum to furnish an oily residue which was purified by chromatography on silica gel (Et$_2$O/PE 90:10) to give a yellow oil (2.8 g; 32% yield). $^1$H NMR (300MHz, CDCl$_3$): $\delta$ (ppm) = 2.58 (t, 2H, J= 7.2 Hz); 3.02 (t, 2H, J= 7.2 Hz); 6.97 (s, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$), $\delta$ (ppm): 18.7, 31.0, 112.0, 117.6, 117.7, 130.7, 133.5. IR: 2250, 1495, 1392, 1281, 1010 and 901 cm$^{-1}$. HRMS calculated for C$_7$H$_5$NS$_2$Br$_2$: 324.8230; found: 324.8232.

3-((2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-3-yl)thio)propanenitrile 3. Compound 2 (800 mg, 2.46 mmol, 1 eq), tributylstannyl EDOT (3190 mg, 7.38 mmol, 3 eq), and [Pd(PPh$_3$)$_4$] (284 mg, 0.246 mmol, 0.1 eq) in 40 ml DMF were refluxed for 12 h under inert atmosphere (N$_2$). After concentration, the residue was dissolved in AcOEt. The organic phase was washed twice with an aqueous saturated solution of NaCl then with water. After drying with MgSO$_4$ and evaporation of solvent, the product was purified by chromatography on silica gel (CH$_2$Cl$_2$/PE 50/50 to 100/0) to give corresponding yellow solid (800 mg, 88%). Mp 166-167°C. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ (ppm) = 2.57 (t, 2H, J = 7.5 Hz); 3.00 (t, 2H, J= 7.5 Hz); 4.25 (m, 4H); 4.37 (m, 2H); 6.26 (s, 1H); 6.38 (s, 1H); 7.17 (s, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 18.4, 32.0, 64.5,
64.7, 65.2, 65.3, 97.8, 100.3, 110.4, 111.2, 118.3, 123.2, 128.0, 133.5, 135.0, 138.3, 139.5, 141.4, 142.0. IR : 2250, 1496, 1477, 1362, 1063 cm⁻¹. HRMS (FAB) calculated for C₁₉H₁₅NO₄S₄ : 448.9884; found: 448.9883.

3-((2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-3-yl)thio)propan-1-ol 4. To a solution of compound 3 (0.40 g, 1.28 mmol, 1 eq) in anhydrous dimethylformamide (DMF) (10 ml) was added, under argon, cesium hydroxide (0.29 g, 1.94 mmol, 1.5 eq) in solution of methanol (5 ml) followed by bromopropanol (1.07 g, 7.74 mmol, 6 eq) in solution in anhydrous DMF (1.50 ml). The mixture was stirred for 12 h. Solvent was removed at reduced pressure and the resulting residue was taking up in AcOEt (100 ml). The organic layer was washed with water (2 x 80 ml), dried over MgSO₄ and filtered. The solvent was removed under vacuum. The resulting brown oil was purified by chromatography on silica gel (cyclohexane to cyclohexane/AcOEt 50/50) to give corresponding viscous yellow oil (263 mg, 65%). ¹H NMR (300MHz, CDCl₃): δ (ppm) = 1.56 (s, 1H, OH), 1.85 (m, 2H), 2.95 (t, 2H, J= 7.1 Hz), 3.73 (t, 2H, J= 6.6 Hz), 4.23 (m, 4H), 4.35 (m, 2H), 6.23 (s, 1H), 6.35 (s, 1H), 7.17 (s, 1H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 23.3, 33.3, 61.6, 64.6, 64.7, 65.1, 65.2, 97.4, 99.8, 111.1, 111.6, 126.6, 127.5, 132.6, 132.9, 138.0, 139.0, 141.3, 142.0. IR : 2922, 1521, 1497, 1363, 1167, 1065 cm⁻¹. HRMS FAB calculated for C₁₉H₁₈O₅S₄ : 454.0037; found: 454.0027.

3-(thiophen-3-ylthio) propyl acrylate 6. To a solution of 3-bromothiophene (15 g, 92 mmol, 1.1 eq) in anhydrous Et₂O (100 ml) under N₂ at -78 °C was added dropwise a solution of n-ButLi 1.6 M in hexane (63.6 mL, 1.1 eq) over a period of 30 min. After 15 min of stirring at -78 °C, the lithiated salt precipitated, and then elemental sulfur (3.26 g, 1.1 eq) was added in one portion. After 30 min of additional stirring at -78 °C, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. Then the
solution was cooled to 0 °C, and 3-bromopropanol (12.2 g, 8.00 ml, 0.95 eq) was added dropwise. The reaction mixture was stirred for 10 h at room temperature. 10 ml of triethylamine and then acryloyl chloride (29 g, 27 ml, 272 mmol, 3 eq) were added dropwise. After 4 hours 50 ml of water were added then the mixture was extracted with Et2O (200 ml). The organic phases were dried over MgSO4 and evaporated in vacuum. The resulting oil crude was purified by chromatography on silica gel (PE to PE/Et2O 90:10) to give compound 6 as lightly yellow oil (11.7 g; 56% yield). 'H NMR (300MHz, CDCl3): δ(ppm) = 1.90-1.99 (m, 2H); 2.89 (t, 2H, J = 7.4 Hz); 4.23 (t, H, J = 6.2 Hz); 5.80 (dd, 1H, J = 1.3 and 10.4 Hz); 6.09 (dd, 1H, J = 10.4 and 17.3 Hz); 6.38 (dd, 1H, J = 1.3 and 17.3Hz); 7.00 (dd, 1H, J = 1.3 and 4.8 Hz); 7.15 (dd, 1H, J = 1.3 and 15.0 Hz); 7.29 (dd, 1H, 3.0 and 4.8 Hz). 13C NMR (75 MHz, CDCl3): δ (ppm) = 28.5, 31.8, 62.8, 124.1, 126.3, 128.3, 129.8, 130.8, 131.2, 166.0. HRMS EI for C10H12O2S2, calculated: 228.0279; found: 228.0273.

3-((2,5-dibromothiophen-3-yl)thio)propyl acrylate 7. A solution of N-bromosuccinimide (11.00 g, 64.38 mmol, 2.2 eq) in DMF (25 ml) was added dropwise to 6 (7.00 g, 30.66 mmol, 1 eq) in DMF (40 ml) under N2 at 0 °C in the absence of light. The mixture was stirred 12 h at room temperature, and concentrated and the residue was diluted with saturated aqueous NaCl and extracted with AcOEt (200 ml). The organic phase was washed with water (100 ml), dried over MgSO4 and evaporated in vacuum to furnish an oily residue which was purified by chromatography on silica gel (Et2O/PE 90:10) to give 7 a yellow oil (2.8 g; 32 % yield).'H NMR (300MHz, CDCl3): δ (ppm) = 1.97 (q, 2H, J = 6.5 Hz); 2.94 (t, 2H, J= 7.2 Hz); 4.30 (t, 2H, J = 6.2 Hz); 5.87 (dd, 1H, J = 13.3 Hz; J= 1.4 Hz); 6.15 (dd, 1H, J= 17.4 Hz; J= 17.2 Hz); 6.45 (dd, 1H, J= 17.3 Hz; J= 1.37 Hz); 6.96 (s, 1H). 13C NMR (75 MHz, CDCl3): δ (ppm) = 28.6, 31.7, 62.5, 111.1, 114.2, 128.2, 130.9, 132.5, 132.9, 165.9. HRMS calculated for C10H10Br2O2S2: 383.8489; found: 383.8488.
3-((2-bromothiophen-3-yl)thio)propyl acrylate 8. A solution of N-bromosuccinimide (3.89 g, 22.89 mmol) in DMF (25 ml) was added dropwise to 6 (5 g, 21.8 mmol) in DMF (25 ml) under N₂ at 0°C in the absence of light. The mixture was stirred 12 h at room temperature, concentrated under reduced pressure. The residue was saturated with aqueous NaCl and extracted with AcOEt (200 ml). The organic phase was washed with water (100 ml), dried over MgSO₄ and evaporated in vacuum to furnish an oily residue which was chromatographed on silica gel (Et₂O/PE 10:90) to give 8 as a white oil (3.0 g; 50% yield). ¹H NMR (300MHz, CDCl₃): δ (ppm) = 1.92 (m, 2H); 2.92 (t, 2H, J= 6.8 Hz); 4.26 (t, 2H, J= 6.2 Hz); 5.81 (dd, 1H, J= 1.5 and 10.4 Hz); 6.10 (dd, 1H, J= 10.4 Hz, J= 17.3 Hz)); 6.38 (dd, 1H, J= 1.5 and 17.3 Hz); 6.93 (d, 1H, J= 5.6 Hz); 7.26 (d, 1H, J = 5.6 Hz). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 28.8, 31.8, 62.8, 115.2, 126.3, 128.4, 130.6, 131.0, 132.2, 166.1. HRMS El for C₁₀H₁₁BrO₂S₂, calculated: 305.9384; found: 305.9382.

3-((2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-3-yl)thio)propyl acrylate 5. Compound 7 (1.30 g, 3.36 mmol, 1eq), stannyl derivative (3.64 g, 8.42 mmol, 2.5 eq), and [Pd(PPh₃)₂Cl₂] (0.12 mg, 0.168 mmol, 0.05 eq) were refluxed in dry DMF (50 ml) for 12 h under inert atmosphere (N₂). After concentration, the residue was dissolved in AcOEt. The organic phase was washed twice with an aqueous saturated solution of NaCl then with water. After drying with MgSO₄ and evaporation of solvent, the product was purified by chromatography on silica gel (cyclohexane/AcOEt 0/100 to 50/50) to give corresponding viscous oil (1.20 g, 75 %). ¹H NMR (500MHz, CDCl₃): δ (ppm) = 1.95 (m, 2H); 2.91 (t, 2H, J= 7.2 Hz); 4.28 (m, 10H); 5.79 (dd, 1H, J= 1.4 and 10.4 Hz); 6.08 (dd, 1H, J= 10.4 and 17.3 Hz); 6.23 (s, 1H); 6.37 (m, 2H); 7.16 (s, 1H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 28.7, 33.1, 63.1, 64.5, 64.6, 65.1, 65.2.8, 97.4, 99.8, 110.9, 111.5, 126.0, 127.5, 128.4, 130.8, 132.9, 133.0, 138.0, 138.9, 141.2, 141.9, 166.1. IR 1717, 1521, 1364, 1167, 1065 cm⁻¹. HRMS El calculated for C₂₂H₂₀O₆S₄: 508.0143; found: 508.0114.
3-((2-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-3-yl)thio)propyl acrylate 9. Compound 8 (1.75 g, 5.69 mmol, 1 eq), stannyl derivative (3.69 g, 8.54 mmol, 1.5 eq), and [Pd(PPh3)4] (0.131 g, 0.114 mmol, 0.02 eq) were refluxed in dry DMF (50 ml) for 12 h under inert atmosphere (N2). After concentration, the residue was dissolved in AcOEt. The organic phase was washed twice with an aqueous saturated solution of NaCl then with water. After drying with MgSO4 and evaporation of solvent, the product was purified by chromatography on silica gel (cyclohexane to cyclohexane/AcOEt 20/80) to give corresponding 9 as a viscous oil (800 mg, 29%). 1H NMR (300MHz, CDCl3): δ (ppm) = 1.93 (m, 2H); 2.87 (t, 2H, J= 7.2 Hz); 4.26 (m, 10 H); 5.80 (dd, 1H, J = 1.5 and 10.4 Hz); 6.08 (dd, 1H, J = 10.4 and 17.3 Hz); 6.35 (s, 1H); 6.36 (dd, 1H, J= 1.5 and 17.3 Hz); 7.01 (d, 1H, J= 5.3 Hz); 7.21 (d, 1H, J= 5.3 Hz). 13C NMR (75 MHz, CDCl3): δ (ppm) = 28.6, 33.0, 63.0, 64.4, 65.1, 99.7, 110.7, 123.9, 126.0, 128.4, 130.8, 131.9, 134.7, 139.1, 141.2, 166.1. HRMS EI for C16H16O4S3, calculated: 368.0211; found: 368.0205.

Conventional polymerization.

Conventional polymerization was performed in a dried schlenk flask with a magnetic stirring bar and a rubber septum. It was charged with AIBN and monomer at a molar ratio of 40:100 with dried THF. The solution was deoxygenated by bubbling N2 for 30 min before heating at 100°C. Polymerizations were also carried out in a high pressure/vacuum Wilmad NMR tube using CDCl3 or THF-d8 as solvents. Poly- 6 was prepared according to the conventional polymerization from compound 6 (600 mg, 2.63 mmol, 1 eq) and AIBN (13 mg, 0.079 mmol, 0.4 eq). After 3 hours of reaction full conversion is obtained by TLC. The crude product was purified by precipitation in methanol to afford corresponding poly- 6 (570 mg).
Poly- 7: A solution of Br₂ (0.92 g, 5.78 mmol, 2.2 eq) in CHCl₃ (30 mL) was added dropwise to poly- 6 (0.520 g, 1 eq) in CHCl₃ (10 mL) under N₂ at 0 °C in the absence of light for 12 h. An excess of Br₂ (0.23 g, 1.44 mmol, 0.5 eq) was added, and the medium was stirred one more hour. The mixture was concentrated and the residue was diluted with saturated aqueous NaCl and extracted with CH₂Cl₂ (100 ml). The organic phase was washed with water (100 ml), dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by precipitation in methanol to afford the corresponding poly- 7 (620 mg). ¹H NMR (300MHz, CDCl₃): δ (ppm) = 2.15 (s, 2H); 2.91 (s, 2H); 4.20 (s, 2H); 7.35 (s, 1H).

Poly- 5 was prepared from compound poly- 7 (0.33 g, 0.87 mmol, 1 eq), stannyl derivative (1.50 g, 3.50 mmol, 4.0 eq), and [Pd(PPh₃)₂Cl₂] (20 mg, 0.174 mmol, 0.02 eq) in DMF. After 24 h stirring at 110 °C, the crude mixture was precipitated in methanol. It has been purified by dissolution-precipitation in CH₂Cl₂ and methanol respectively. ¹H NMR (300MHz, CDCl₃), δ (ppm): 0.77-2.55 (m), 2.87 (sl, 2H), 4.15-4.40(m, 10H), 6.18 (s, 1H), 6.29 (m, 1H), 7.14 (s, 1H).

Controlled radical polymerization

All polymerizations were carried out in a high pressure/vacuum Wilmad NMR tube using THF-d₈ or CDCl₃ as solvent. Experimental procedures are given for procedures conducted in THF-d₈. Poly- 7: 0.75 ml of a solution composed of AIBN (4.2 mg, 0.025 mmol), cyanomethyl dodecyl trithiocarbonate (CTA) (23.5 mg, 0.074 mmol), 7 (342.5 mg, 1.112 mmol) in THF-d₈ were charged into an NMR tube. The solution was then deoxygenated via three freeze pump thaw cycles. The NMR tube was placed in NMR machine preheated to 65 °C. A ¹H-
NMR spectrum (8 scans) was taken every 15 minutes. At the end of the reaction, the reaction mixture was cooled to room temperature and precipitated in methanol. The obtained polymer was rinsed with methanol three times and dried under vacuum at 40 °C to a constant weight. The monomer conversion was evaluated by 'H NMR comparing the signals of the reactive double bond (6.38 ppm) from monomers with the methylene protons –S–CH₂– from monomers and corresponding polymers (2.91 ppm). 'H NMR (300MHz, CDCl₃), δ (ppm): 1.29 (s, 2H); 2.93 (s, 1H); 3.78 (s, 1H); 4.00 (s, 2H); 4.24 (s, 2H); 5.62 (s, 2H); 6.99 (s, 1H).

Poly- 8: 0.75 ml of a solution composed of AIBN (1.0 mg, 0.006 mmol), CTA (5.6 mg, 0.017 mmol), 7 (97.0 mg, 0.316 mmol) in THF-d₈ were charged into an NMR tube. The solution was then deoxygenated via three freeze pump thaw cycles. The NMR tube was placed in NMR machine preheated to 65 °C. A 'H NMR spectrum (8 scans) was taken every 15 minutes. At the end of the reaction, the reaction mixture was cooled to room temperature and precipitated in methanol. The obtained polymer was rinsed with methanol three times and dried under vacuum at 40 °C to a constant weight. The monomer conversion was evaluated by 'H NMR comparing the signals of the reactive double bond (6.36 ppm) from monomers with the methylene protons –S–CH₂– from monomers and corresponding polymers (2.91 ppm). 'H NMR (300MHz, CDCl₃): δ (ppm) = 1.26 (s, 2H); 2.93 (s, 2H); 4.20 (s, 2H); 6.98 (s, 1H); 6.99 (s, 1H); 7.30 (s, 1H).
RESULTS AND DISCUSSION

The cross-linked polymer poly-5 (Figure 1) can be obtained by radical polymerization of compound 5. This acrylic monomer was envisioned following several routes, all starting from 3-bromothiophene (Scheme 1). We first explored the synthesis from 3-(2-cyanoethylsulfanyl) thiophene 1 obtained in 80% yield, \(^{21}\). Its bis-bromination in 2,5-positions led to compound 2 in 32% yield. Then, Stille cross-coupling with stannylated EDOT led to 3 in 88% yield. Deprotection of the thiolate carried on 3 with cesium hydroxide and nucleophilic substitution with bromopropanol afforded the target alcohol 4. Unfortunately, the last step to introduce acrylic ester was not successful whatever the conditions used, this alcohol does not seem nucleophilic enough. Thus, a second route, in which the acrylate function is first introduced was developed. The latter is conducted in one single pot sequence from 3-bromothiophene by successive addition of n-BuLi, sulfur, 3- bromopropanol and 4-acryloyl chloride in 56% yield.
The bis-bromination of 6 appeared tricky, the target compound 7 was isolated in a moderate yield of 32% together with the monobrominated compound 8 as main product (50%). In all cases, a partial hydrolysis of the acrylate group was also observed. Then Stille cross-coupling of 7 and 8 with stannylated EDOT led to terthiophene 5 and bithiophene 9 in good yields.

We first tested the abilities of these two monomers to be electropolymerized. Application of recurrent potential scans to acetonitrile solution of 5 leads to the progressive emergence of a new redox system at lower potential associated with the electrodeposition of a polymer (Figure 2a). The CV of the polymers recorded in a monomer-free electrolytic medium (Figure 2b) presents a broad reversible oxidation wave increasing from 0.5 V for electropolymerized 5. We also tested 9 in the same conditions (Figure 2c), however it seems that electropolymerization can't proceed since no increase of current is visible when cycling.

Then, first attempts of polymerization from monomers 5 or 9 were realized by conventional radical polymerization using AIBN in THF without success (Scheme 2). In this context, more attempts have been tested from monomer 6, easier to synthesize. The
polymerization proceeded only after addition of 40% mol of AIBN. No reaction took place with lower loading of radical promotor. The hydrogen at position 2 of thiophene being quite labile, its exchange with growing chains could be responsible of early radical termination. Indeed, if this phenomenon has not really been pointed out in literature, similar results have been described for the synthesis of block copolymers containing organic semiconductor like polythiophene or perylene diimide.22 In this case, the monomer was completely consumed and polymer chains with low molar masses were obtained. As a first attempt towards poly-5, poly-6 was post-functionalized (Scheme 3). In absence of acrylic group, the bisbromination of the pendent thiophene, followed by NMR, appeared quantitative as well as the final Stille cross-coupling with stannylated-EDOT leading easily to poly-5.

**Scheme 2. Conventional radical polymerization of 5, 6, and 9**

![Scheme 2. Conventional radical polymerization of 5, 6, and 9](image)

**Scheme 3. Classical polymerization of 6 and post-functionalization with stannylated-EDOT.**
The advantage of post-functionalization is to avoid complicated purification on column chromatography. Even if poly-5 can be obtained following this route, the global yield is limited due to the difficult polymerization of 6. The polymer weight remains low (<1000 g/mol) and the large addition of added AIBN does not allow to envision a RAFT controlled polymerization. Thus, in order to better understand the limitation of this method, other attempts were conducted from intermediates 7 and 8 (Scheme 4).

Scheme 4: Controlled polymerization of 7 and 8.

Polymerizations have been realized in NMR tubes to follow the disappearance of monomers. Figure 3 shows that 7 reached more than 90% conversion meanwhile 8 leveled out 60%. The assumption that labile hydrogen atoms could interact with the
growing radicals could be confirmed as higher yield of conversion was obtained for the totally brominated protected synthons 7. RAFT polymerization of monomers 7 and 8 was carried out to control the growth and the molar mass distribution of the polymer chains. Cyanomethyl dodecyl trithiocarbonate was used as chain transfer agent (CTA). Optimization of the conditions has been done in NMR tubes with THF-d₈ and/or CDCl₃ as solvent. Monomer conversion rates have been determined by integrating peaks assigned to polymer and monomer on 'H NMR spectra.

![Figure 3. Classical polymerization of compounds 7 and 8 in THF-d₈ at 65°C with [Monomer]₀ = 0.4 M and [AIBN]₀ = 8x10⁻³ M.](image)

In all cases, the RAFT polymerization occurs and moderate to high conversion rates have been obtained (Table 1, Figure 4 b, d). A good correlation of Mn both measured by NMR and TD-SEC analyses is noteworthy observed. Experimental Mn values are close to the predicted calculated ones. All polymers exhibit low dispersity values whatever the solvent of polymerization (Table 1). Higher conversion rates are obtained for both monomers in THF-d₈ while the more acidic CDCl₃ solvent leads to lower yields (Table 1). Moreover, in these RAFT conditions, the poisoning influence of the thiophenic acidic proton is still slightly observed as the conversion yields in Poly-8 never exceeds 72% vs a higher rate of 94% in the case of the RAFT polymerization of 7 in THF-d₈.
Table 1: Comparison between RAFT-synthesized polymers using THF-d$_8$ and CDCl$_3$ as solvent.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Solvent</th>
<th>Conv (%)</th>
<th>$M_n^{ab}$ (g.mol$^{-1}$)</th>
<th>$M_n$ (g.mol$^{-1}$) NMR</th>
<th>$M_n$ (g.mol$^{-1}$) SEC</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-8</td>
<td>THF-d$_8$</td>
<td>72</td>
<td>4,300</td>
<td>4,900</td>
<td>5,000</td>
<td>1.2</td>
</tr>
<tr>
<td>Poly-8</td>
<td>CDCl$_3$</td>
<td>45</td>
<td>3,200</td>
<td>3,000</td>
<td>5,400</td>
<td>1.4</td>
</tr>
<tr>
<td>Poly-7</td>
<td>THF-d$_8$</td>
<td>94</td>
<td>4,700</td>
<td>5,600</td>
<td>5,500</td>
<td>1.2</td>
</tr>
<tr>
<td>Poly-7</td>
<td>CDCl$_3$</td>
<td>80</td>
<td>4,000</td>
<td>4,200</td>
<td>6,700</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Figures 4a and 4c show the linear part of the polymerization kinetics curves ln(Mo/M) vs t which corresponds to the windows in which the radical polymerization can be considered occurring normally with a constant concentration of radical species with time. The polymerization rate of monomer 8 in THF-d$_8$ is lower than the one found for monomer 7. This result demonstrates the significant effect of the acid thiophenic proton on the polymerization rate, retarding the polymerization by transfer reactions. A reduced difference in the polymerization rate between the two monomers is observed when CDCl$_3$ is used as polymerization solvent. This acidic solvent does affect strongly the polymerization rate too by solvent transfer reaction.$^{23}$

Polymers poly-7 and poly-8 obtained by RAFT polymerization were post-modified by Stille cross-coupling with stannylated-EDOT to lead to the awaited poly-5 and poly-9. The powders obtained became insoluble whatever the solvent used probably due to EDOT-EDOT interactions and a too high molar mass of the modified polymers.
Figure 4. a, b: Kinetics of RAFT polymerization of 7; c, d: Kinetics of RAFT polymerization of 8. Operating conditions: $M_{n}^{th} = 5,000 \text{ g mol}^{-1}$; [Monomer] = 0.4 M; [CTA] / [AIBN] = 3; $T = 65^\circ \text{ C}$. 

Nevertheless, as poly-5, prepared by conventional polymerization with a lower molar mass compared to poly-7 or poly-8, was soluble in dichloromethane, the later was studied by cyclic voltammetry. Application of recurrent potential scans on poly-5 in CH$_2$Cl$_2$ led to the electrodeposition of polymers (either on ITO plates or on platinum, Figure 5, Top) with the progressive emergence of a new redox system at lower potential associated to the cross-linking of poly-5. The CV of the polymer recorded in a monomer-free electrolytic medium presents a broad reversible oxidation wave with $E_{pa}$ of 0.5 V vs SCE (Figure 5, bottom).
Figure 5. Top: Electropolymerization of poly-5 on platinum at 5×10^-3 M in 0.10 M n-Bu₄NPF₆/CH₂Cl₂, ref SCE, v = 50 mV s⁻¹. Down: CV of the resulting electrodeposited materials in 0.10 M n-Bu₄NPF₆/CH₂Cl₂, ref SCE, v = 100 mV s⁻¹.

CONCLUSION
After a first attempt to polymerize acrylic systems bearing oligothiophene moieties, we have demonstrated that the presence of exchangeable protons on species inhibits the radical process. In contrary, the use of protected thiophene groups allows RAFT polymerization in good conditions and furthermore the post-functionalization of obtained brominated polymers leads to targeted compounds. Nevertheless, if the methodology appears promising the molar mass of polymers has to be tuned to allow a sufficient solubility of materials. Moreover, we also envision the synthesis of diblock copolymers from poly-6 to increase the solubility and processability of resulting materials.

ASSOCIATED CONTENT
Supporting Information. NMR spectra of 2, 3, 4, 5, 6, 7, 8, 9, poly-5, poly-8 and poly-9. This material is available free of charge via the Internet at http://pubs.acs.org.

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