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Polymer 48 (2007) 4996–5004
polymer
www.elsevier.com/locate/polymer

Thiophene-based dendronized macromonomers and polymers

Prashant Sonar [a], Hadjar Benmansour [b], Thomas Geiger [b], A. Dieter Schlüter [a,*]

[a] Laboratory of Polymer Chemistry, Department of Materials, ETH-Zürich, Wolfgang-Pauli Strasse 10, HCI J 541, CH-8093, Zürich-Hönggerberg, Switzerland
[b] Laboratory for Functional Polymers, Empa – Materials Science & Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

Received 13 April 2007; received in revised form 6 June 2007; accepted 11 June 2007
Available online 16 June 2007

Abstract

The synthesis of thiophene-containing second (G2) and third generation (G3) dendronized macromonomers with methacrylate polymerizable units as well as their corresponding dendronized polymers is reported. The dendrons are prepared from branched thiophene oligomers and are decorated with straight alkyl chains for solubility reasons. The polymerization reactions were done with AIBN as initiator and the polymers were characterized by NMR spectroscopy, elemental analysis and GPC. Molar masses are in the range of $2.2–5.4 \times 10^5$ g mol^{-1} (G2) and $1.3–3.0 \times 10^4$ g mol^{-1} (G3) for different runs. These polymers are investigated by cyclic voltammetry and optical spectroscopy.

Keywords: Dendrons; Free radical polymerization; Oligothiophenes

1. Introduction

Linear [1,2], dendritically branched [3], and cyclic [4] thiophene-based, π-conjugated materials are currently being intensely explored for their potential in optoelectronic devices [5]. This includes polymers with linear oligothiophene side chains [6] as well as dendronized polymers constituted of an oligothiophene backbone shielded and solubilized by aliphatic ether dendrons densely attached to it [7]. While numerous reports have focused on optical and electrochemical characterization of thiophene dendrimers, only few report on charge transport in thin solid films [8]. For optoelectronic applications and in particular for photovoltaic devices, it would be interesting to have conducting molecular columns with diameters in the nanometer range which self-organize into parallel arrays so as to allow the photochemically generated charges to be transported into opposite directions throughout the entire bulk phase. Such nanoscopic order can potentially be achieved with dendronized polymers [9], which were found to give highly ordered structures by self-assembly both on surfaces [10] and in the bulk [11]. Additionally, they can be equipped with optically or electrically active backbones [9] which make dendronized polymers interesting candidates for applications where energy or electron transfers matter. In this respect the fact that the ‘‘surfaces’’ of these macromolecules can be widely engineered is an additional plus [12]. We report here the synthesis and characterization of high molar mass second (G2) and third generation (G3) dendronized polymers whose dendrons consist mostly of branched thiophenes.

2. Experimental part

2.1. Materials

Thiophene dendrons and their stannyl derivatives **1** and **6** were synthesized according to literature methods [3a]. All chemicals were purchased from Aldrich or Acros and used without further purification. Methacryloyl chloride (MAC) was freshly distilled before use. Triethylamine (TEA) and tetrahydrofuran (THF) were refluxed over Na with benzophenone as indicator. 2,2′-Azoisobutyronitrile (AIBN) was purified by recrystallization from methanol. Anhydrous dimethyl formamide

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* Corresponding author.
E-mail addresses: hadjar.benmansour@empa.ch (H. Benmansour), dieter.schluter@mat.ethz.ch (A.D. Schlüter).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.06.024

(DMF) and 4-dimethylaminopyridine (DMAP) were used as received.

2.2. Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) and AV 500 (^{1}H: 500 MHz) spectrometers at room temperature using deuterated chloroform as solvent. High resolution mass spectra and MALDI-MS were recorded on Ionspec Ultrima spectrometer. GPC measurements were carried out using a PL-GPC 220 (Polymer Laboratories Ltd., UK) instrument with a 2× PL-Gel Mix-B LS column set equipped with light scattering detector (7° and 90°). Universal calibration was done using PMMA standards having $M_\mathrm{p} = 2680–3\,900\,000$ g mol^{-1} (Polymer Laboratories Ltd., UK).

High resolution thermogravimetric analysis (TGA) was performed on a Q500 thermogravimetry analyzer (TA Instruments, New Castle, Delaware) in air. Differential scanning calorimetry (DSC) was carried out under nitrogen at a heating or cooling rate of 10 °C/min on a DSC 7 instrument (Perkin–Elmer, Norwalk, Connecticut). Two heating runs and one cooling run were consecutively carried out in a cycle.

Absorbance spectra were measured on a Varian (Cary 50) Spectrophotometer. Fluorescence spectra were measured with a Jobin Yvon Horiba FL311 Fluorolog. The solvents were of spectroscopic grade (99.9%) and were stirred over molecular sieves before use. The solutions were degassed by argon bubbling before each measurement. The solution quantum yields were estimated according to the following formula:

$$\phi_\mathrm{x} = \phi_\mathrm{ref}\left[\frac{I_\mathrm{x}}{I_\mathrm{ref}}\right]\left[\frac{\eta_\mathrm{x}^2}{\eta_\mathrm{ref}^2}\right]$$

where x and ref denote sample and reference (here quinine sulphate having a quantum yield of 54% was used [13]), respectively, and ϕ_x and ϕ_ref the corresponding quantum efficiencies. I is the integrated fluorescence intensity and η the refractive index of the solvent. The samples were excited at a wavelength where both the reference and the sample have the same absorbance.

Cyclic voltammetric measurements were recorded on an Autolab potentiostat using a three cell electrode system with a glassy carbon working electrode, a platinum counter electrode and an Ag/AgCl (3 M KCl) double-junction reference electrode (Metrohm). Tetrabutylammonium perchlorate (0.1 M Puriss electrochemical grade, Aldrich) was used as the electrolyte. Ferrocene was recrystallised from pentane and used as internal standard. For the monomers **5** and **9**, 10^{-4} M solutions in dichloromethane were used. In the case of the polymers, thin films were drop cast (from 5 μL of a 2% solution in chlorobenzene) on custom made 0.7 cm^2 glassy carbon electrodes. Cyclic voltammetric measurements of the films were performed in acetonitrile solution, in which the films were insoluble.

2.3. Synthetic procedure

All reactions were performed under nitrogen atmosphere. Silica gel 60 M (Macherey–Nagel) was used for column chromatography, and reactions were monitored by thin layer chromatography (TLC) using TLC silica gel coated aluminium plates (Merck).

2.3.1. Ethyl-3,5-bis[4,5-bis(5-hexylthiophen-2-yl)thiophen-2-yl]benzoate (3)

A single necked flask was charged with **1** (15 g, 22.19 mmol), 3,5-dibromobenzoic ethyl ester **2** (2.05 g, 6.68 mmol), Pd(PPh$_3$)$_4$ (0.170 g, 0.146 mmol) and DMF (40 mL). After three freeze–pump–thaw cycles, the mixture was heated to 100 °C for 20 h under nitrogen. After cooling to room temperature, it was poured into water, extracted with methylene chloride and washed thoroughly with KF solution to remove excess tributyltin bromide. The organic layer was then dried over magnesium sulphate and the solvent was evaporated. The residue was purified by column chromatography using hexane/ethyl acetate (10:1) as eluent to give **3** as yellow oil (5.23 g, yield 78%).

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.20$ (s, 2H, Ph), 7.96 (s, 1H, Ph), 7.47 (s, 2H, Th), 7.00–6.99 (two dd, d, 4H, Th), 6.73 (s, 4H, Th), 4.49 (q, 2H, OCH$_2$CH$_3$), 2.86–2.80 (t, 8H, ThCH$_2$), 1.73–1.70 (t, 8H, CH$_2$CH$_2$), 1.49–1.32 (m, 27H, 12 CH$_2$ + 1CH$_3$), 0.94 (s, 12H; 4CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 167.32$, 147.62, 147.47, 146.24, 145.91, 145.26, 143.92, 140.00, 134.99, 134.81, 134.52, 132.66, 132.31, 132.16, 131.97, 131.30, 129.54, 127.59, 127.44, 126.84, 126.41, 125.90, 125.40, 124.64, 124.30, 124.11, 124.03, 123.92, 123.62, 123.31, 122.90, 61.38, 31.51, 30.15, 28.77, 22.55, 14.08.

HRMS-MALDI calcd. for $C_{57}H_{70}O_2S_6$: 978.370. Found: 978.363.

Elemental analysis calcd. (%) for $C_{57}H_{70}O_2S_6$: C, 69.89; H, 7.20; O, 3.27; S, 19.64. Found: C, 69.40; H, 7.23; O, 3.17; S, 20.73.

2.3.2. 3,5-Bis[4,5-bis(5-hexylthiophen-2-yl)thiophen-2-yl]benzyl alcohol (4)

A solution of **3** (12.50 g, 12.76 mmol) in THF (100 mL) was added dropwise to a slurry of LiAlH$_4$ (0.73 g, 19.1 mmol) in THF (100 mL) over 1 h at 0 °C. The reaction mixture was then warmed to room temperature, stirred for 16 h and then quenched by dropwise addition of water (3 mL), 15% NaOH (6 mL), and water (2 mL). The resulting precipitate was filtered and the THF evaporated off. The crude product was purified by column chromatography using hexane/ethyl acetate (10:2) as eluent to give **4** as viscous yellow oil (10.2 g, yield 85%).

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.74$ (s, 1H, Ph), 7.54 (s, 2H, Ph), 7.41 (s, 2H, Th), 7.02–6.96 (two dd, d, 4H, Th), 6.72 (s, 4H, Th), 4.80 (s, 2H, CH$_2$OH), 2.85–2.78 (t, 8H, ThCH$_2$), 1.72–1.70 (t, 8H, CH$_2$CH$_2$), 1.36 (m, 24H, 12CH$_2$), 0.92 (s, 12H, 4CH$_3$).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.44$, 146.20, 143.96, 142.50, 141.84, 141.58, 140.98, 137.54, 134.81, 133.88, 132.54, 132.34, 131.13, 129.98, 127.24, 126.31, 124.07, 123.00, 122.70, 121.44, 64.75, 60.42, 41.90, 31.45, 30.14, 29.84, 22.59, 14.09.

HRMS-MALDI calcd. for $C_{55}H_{68}OS_6$: 936.359. Found: 937.363.

Elemental analysis calcd. (%) for $C_{55}H_{68}OS_6$: C, 70.46; H, 7.31; O, 1.71; S, 20.52. Found: C, 70.49; H, 7.43; O, 1.91; S, 20.32.

*2.3.3. 3,5-Bis[4,5-bis(5-hexylthiophene-2-yl)thiophen-2-yl]benzyl methacrylate (**5**)*

A solution of MAC (1.85 g, 17.70 mmol) in THF (50 mL) was added dropwise to a mixture of **4** (11 g, 11.73 mmol), TEA (5.55 g, 54.8 mmol) DMAP (0.05 g) in dry THF (100 mL) at 0 °C over 30 min. The mixture was stirred for 12 h at room temperature and then washed with aqueous $NaHCO_3$ and brine. The organic phase was dried with magnesium sulphate and the solvents were evaporated under vacuum at room temperature. Chromatographic separation was performed thrice using an hexane:ethyl acetate (10:2) mixture to give the macromonomer **5** as a yellow-reddish oil (9.68 g, yield 82%).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.82$ (s, 1H, Ph), 7.59 (s, 2H, Ph), 7.48 (s, 2H, Th), 7.00–6.90 (two dd, d, 4H, Th), 6.74 (s, 4H, Th), 6.26 (s, 1H, $C{=}CH_2$) 5.67 (s, 1H, $C{=}CH_2$), 5.29 (s, 2H, OCH_2Ph), 2.87–2.80 (t, 8H, $ThCH_2$), 2.06 (s, 3H, CH_3), 1.74–1.72 (t, 8H, CH_2CH_2), 1.38–1.33 (m, 24H, $12CH_2$), 0.90 (s, 12H; $4CH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.06$, 147.53, 146.28, 140.68, 137.69, 136.08, 134.84, 134.65, 132.61, 132.28, 131.80, 127.41, 126.46, 126.40, 126.10, 124.83, 124.31, 124.23, 124.09, 123.76, 123.47, 123.30, 65.92, 31.60, 30.15, 29.09, 22.67, 18.40, 14.10.

HRMS-MALDI calcd. for $C_{59}H_{72}O_2S_6$: 1004.386. Found: 1004.0.

Elemental analysis calcd. (%) for $C_{59}H_{72}O_2S_6$: C, 70.47; H, 7.22; O, 3.18; S, 19.13. Found: C, 70.76; H, 7.27; O, 3.08; S, 19.16.

*2.3.4. Ethyl-3,5-bis{4,5-bis[4,5-bis(5-hexylthiophen-2-yl)thiophen-2-yl]thiophen-2-yl}benzoate (**7**)*

The procedure was analogous to that of compound **3**: thiophene dendron **6** (16 g, 13.30 mmol), 3,5-dibromobenzoic ester **2** (1.23 g, 4.00 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.086 mmol), DMF (30 mL). Column chromatography using hexane/ethyl acetate (10:2) as the eluent gave the G3 dendron **7** as a red oil (5.91 g, yield 75%).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.24$ (s, 2H, Ph), 7.99 (s, 1H, Ph), 7.53 (s, 2H, Th), 7.29 (d, 4H, Th), 7.00–6.92 (two dd, d, 8H, Th), 6.70 (s, 8H, Th), 4.48 (s, 2H, OCH_2CH_3), 2.81–2.80 (t, 16H, $ThCH_2$), 1.69–1.67 (t, 16H, CH_2CH_2), 1.47–1.35 (m, 51H, $24CH_2 + 1CH_3$), 0.90 (s, 24H; $8CH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.76$, 147.74, 147.52, 146.35, 146.19, 140.93, 134.73, 134.63, 134.39, 133.14, 132.32, 132.11, 131.95, 131.83, 130.38, 129.85, 127.63, 127.53, 126.88, 126.43, 126.27, 125.82, 124.18, 124.00, 61.50, 34.66, 31.55, 30.13, 28.77, 26.91, 25.27, 22.62, 14.09.

HRMS-MALDI calcd. for $C_{113}H_{134}O_2S_{14}$: 1970.647. Found: 1970.653.

Elemental analysis calcd. (%) for $C_{113}H_{134}O_2S_{14}$: C, 68.78; H, 6.84; O, 1.62; S, 22.75. Found: C, 68.82; H, 6.87; O, 1.70; S, 22.79.

*2.3.5. 3,5-Bis{4,5-bis[4,5-bis(5-hexylthiophen-2-yl)thiophen-2-yl)]thiophen-2-yl}benzyl alcohol (**8**)*

The reaction was carried out as described for the synthesis of compound **4**: compound **7** (7 g, 3.54 mmol), $LiAlH_4$ (0.203 g, 5.32 mmol), THF (200 mL). The reaction was quenched by using 4 mL of water and 5 mL of 15% NaOH solution. The residue was purified by column chromatography using hexane/ethyl acetate (10:1) as eluent to give alcohol **8** as a red oil (5.46 g, yield 80%).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.77$ (s, 1H, Ph), 7.60 (d, 2H, Ph), 7.48 (d, 2H, Th), 7.30 (d, 4H, Th), 7.00–6.91 (two dd, 8H, Th), 6.69 (s, 8H, Th), 4.83 (s, 2H, CH_2OH), 2.83–2.78 (t, 16H, $ThCH_2$), 1.71–1.64 (t, 16H, CH_2CH_2), 1.39–1.33 (m, 48H, $24CH_2$), 0.90 (t, 24H; $8CH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.70$, 147.49, 146.32, 146.16, 142.66, 141.89, 134.82, 134.58, 134.45, 132.99, 132.22, 132.03, 131.94, 131.29, 130.28, 129.75, 127.62, 127.51, 126.41, 126.25, 124.18, 124.02, 123.50, 64.86, 34.67, 31.57, 30.17, 28.75, 26.92, 25.28, 22.58, 14.06.

HRMS-MALDI calcd. for $C_{111}H_{132}OS_{14}$: 1928.637. Found: 1928.641.

Elemental analysis calcd. (%) for $C_{111}H_{132}OS_{14}$: C, 69.04; H, 6.89; O, 0.83; S, 23.25. Found: C, 69.31; H, 6.88; O, 0.78; S, 23.06.

*2.3.6. 3,5-Bis{4,5-bis[4,5-bis(5-hexylthiophen-2-yl)thiophen-2-yl]thiophen-2-yl}benzyl methacrylate (**9**)*

The synthesis was conducted as described for compound **5**: compound **8** (4.75 g, 2.45 mmol), MAC (0.307 g, 2.94 mmol), TEA (1.16 g, 11.46 mmol), DMAP (0.02 g), THF (100 mL). The residue was purified by column chromatography using hexane/ethyl acetate (10:1) as eluent to give macromonomer **9** as a red oil (3.41 g, yield 70%).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.80$ (s, 1H, Ph), 7.60 (d, 2H, Ph), 7.47 (s, 2H, Th), 7.30 (s, 4H, Th), 7.00–6.90 (two dd, 8H, Th), 6.72 (br s, 8H, Th), 6.26 (s, 1H, $C{=}CH_2$), 5.67(s, 1H, $C{=}CH_2$), 5.29 (s, 2H, OCH_2Ph), 2.85–2.77 (t, 16H, $ThCH_2$), 2.04 (s, 3H, CH_3), 1.72–1.61 (t, 16H, CH_2CH_2), 1.40–1.34 (m, 48H; $24CH_2$), 0.90 (t, 24H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.44$, 146.20, 143.96, 142.50, 141.84, 141.58, 140.98, 137.54, 134.81, 133.88, 132.54, 132.34, 131.13, 129.98, 127.24, 126.31, 124.07, 123.00, 122.70, 121.44, 64.75, 60.42, 41.90, 31.45, 30.14, 29.84, 22.59, 14.09.

HRMS-MALDI calcd. for $C_{115}H_{136}O_2S_{14}$: 1996.663. Found: 1999.0.

Elemental analysis calcd. (%) for $C_{115}H_{136}O_2S_{14}$: C, 69.09; H, 6.86; O, 1.60; S, 22.45. Found: C, 69.57; H, 6.85; O, 1.69; S, 22.23.

*2.3.7. Poly[3,5-bis(4,5-bis(5-hexylthiophene-2-yl)thiophen-2-yl)benzylmethacrylate] (**10**)*

To monomer **5** (0.550 g, 0.54 mmol) and AIBN (1.34 mg, 1.5 mol%) in a Schlenk tube was added benzene (0.5 mL) and the mixture was stirred under nitrogen for 30 min until total dissolution of reagents, followed by three freeze–pump–thaw cycles. The homogeneous highly concentrated solution was placed into a 65 °C preheated oil bath. After stirring overnight, the viscosity increased to the point so that the mass had completely solidified. Heating was continued for another day so as to get higher yields. After cooling, the polymeric material was dissolved in the minimum amount of dichloromethane and the resulting solution was precipitated into methanol. This procedure was repeated a couple of times to give **10** as yellow precipitate (400 mg, 73%) which was collected and dried under high vacuum.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.70-7.40$ (br, 3H, Ph), 7.20–6.20 (br, 10H, Th), 5.30 (s, 2H, OCH_2Ph), 2.90–2.40 (br, 8H, $ThCH_2$), 2.06 (s, 3H, CH_3), 1.80–1.20 (br, 32H, CH_2CH_2), 0.99–0.80 (br, 12H, $4CH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.09$, 134.79, 126.10, 123.71, 60.36, 31.58, 30.05, 28.88, 22.37, 18.74, 14.18.

Elemental analysis calcd. (%) for $[C_{59}H_{72}O_2S_6]_n$: C, 70.47; H, 7.22; O, 3.18; S, 19.13. Found: C, 70.57; H, 7.30; O, 3.40; S, 19.16.

*2.3.8. Poly{3,5-bis{4,5-bis[4,5-bis(5-hexylthiophen-2-yl)thiophen-2-yl]thiophen-2-yl}benzyl methacrylate} (**11**)*

The synthesis was analogous to that of polymer **10**: monomer **9** (0.500 g, 0.250 mmol), AIBN (0.53 mg, 1.3 mol%), benzene (0.5 mL). Similar work-up gave polymer **11** as a reddish-brown material (0.350 g, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.90-7.40$ (br, 3H, Ph), 6.97–6.20 (br, 22H, Th), 5.30 (br, 2H, OCH_2Ph), 2.80–2.22 (br, t, 16H, $ThCH_2$), 1.90–0.70 (br, t, 91H, $CH_2CH_2 + CH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.73$, 146.35, 134.80, 134.74, 132.08, 129.78, 127.65, 126.41, 125.83, 124.18, 31.50, 30.16, 28.77, 22.58, 14.07.

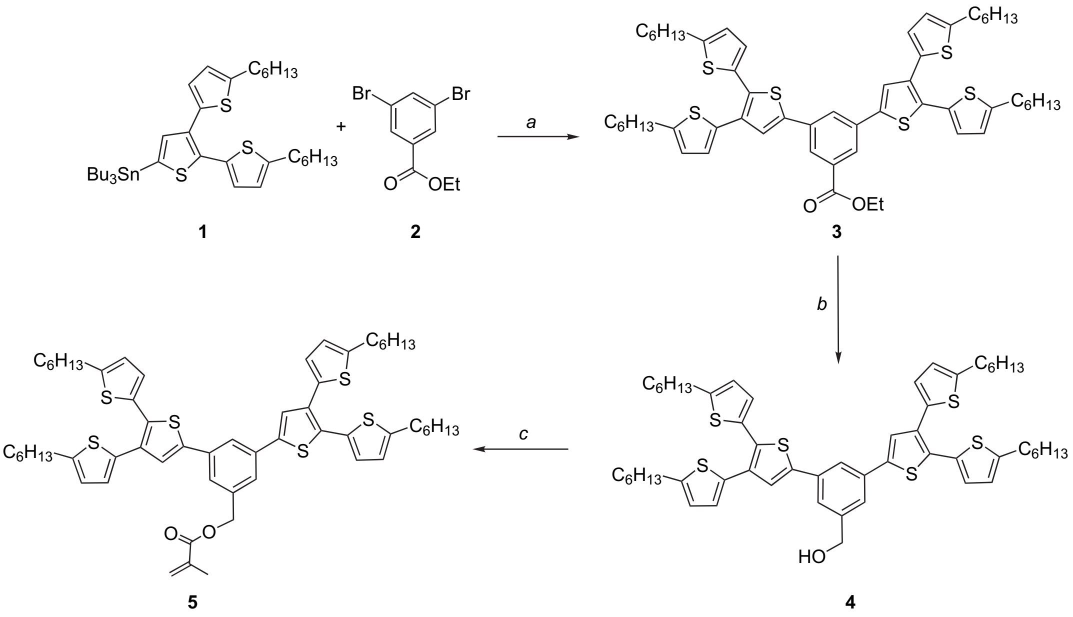
Elemental analysis calcd. (%) for $[C_{115}H_{136}O_2S_{14}]_n$: C, 69.09; H, 6.86; O, 1.60; S, 22.45. Found: C, 69.57; H, 6.85; O, 1.69; S, 22.23.

3. Results and discussion

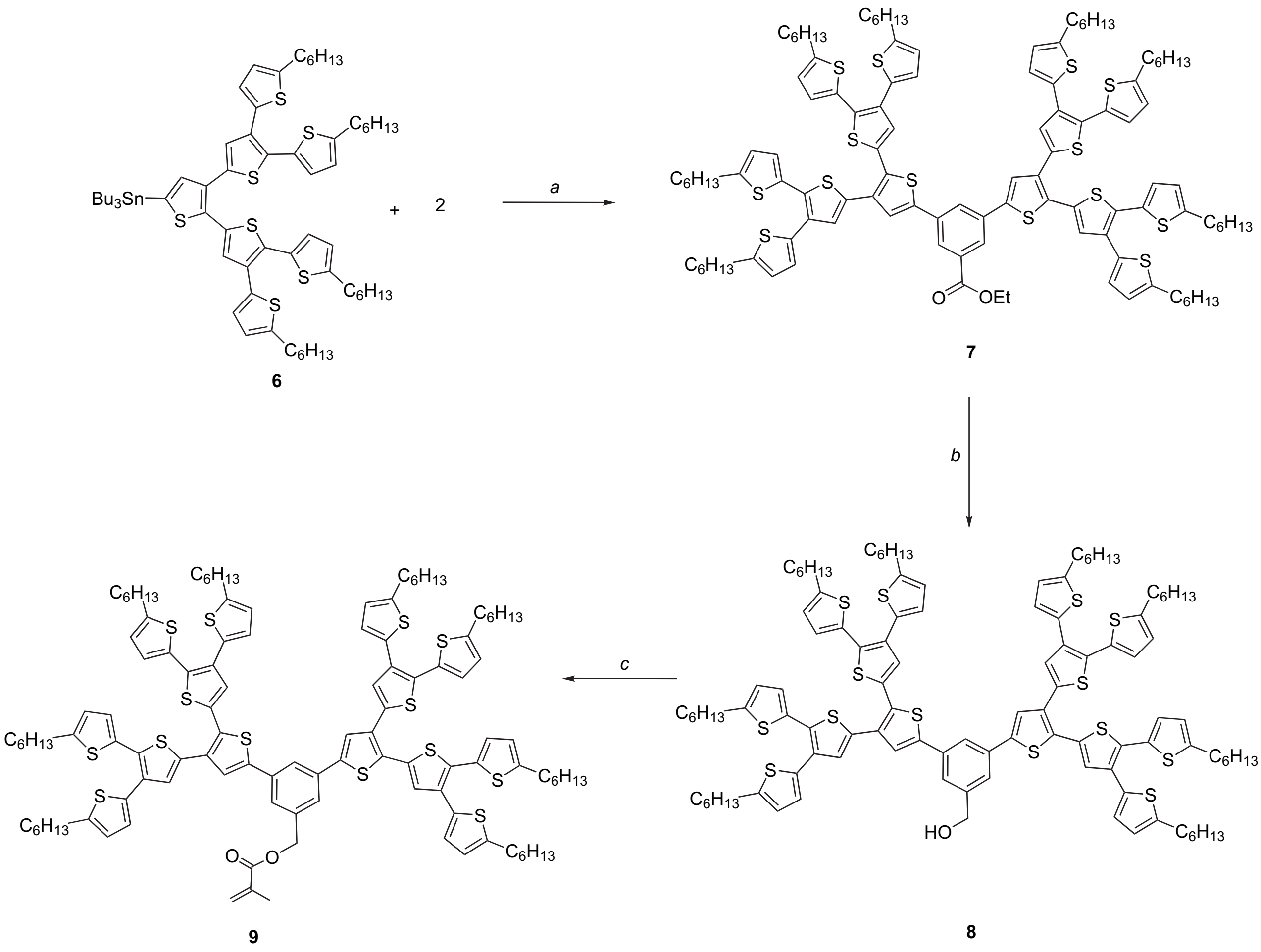
The synthesis of the G2 and G3 macromonomers **5** and **9** started from the thiophene dendrons **1** and **6** which were synthesized according to previously reported procedures (Schemes 1 and 2) [3]. The tributylstannyl groups of **1** and **6** were used to attach these dendrons to the brominated carbon atoms of the branching unit **2** [14] by Stille cross-coupling. An excess of the stannyl derivative was used to ensure completion of the coupling reaction. Yields of 78% (**3**) and 75% (**7**) were achieved for the coupling products after purification by column chromatography. In the next step, the focal point esters were smoothly reduced to the corresponding benzylic alcohols **4** and **8**, respectively, which were then coupled to freshly distilled methacryloyl chloride. Purifications were performed by gradient column chromatography from pure hexane to hexane/ethyl acetate [(10:2) or (10:1)].

The purities were determined by ^{1}H and ^{13}C NMR spectroscopies and confirmed by mass spectrometry. The corresponding ^{1}H NMR spectra are shown in Fig. 1.

Both macromonomers are viscous reddish oils, soluble in common organic solvents. Macromonomers **5** and **9** were polymerized in dry benzene using 1–1.5 mol% AIBN as radical initiator precursor under a nitrogen atmosphere after three freeze–pump–thaw cycles (Scheme 3). The reactions were done in concentrated media to ensure high molecular weight products [15]. Polymers **10** and **11** were recovered as yellowish and reddish-brown materials, respectively, by precipitation



Scheme 1. Reagents and conditions: (a) $Pd(PPh_3)_4$, DMF, 100 °C, 24 h (78%); (b) $LiAlH_4$, THF, rt, 24 h (85%); (c) MAC, DMAP, THF, rt, 16 h (82%).



Scheme 2. Reagents and conditions: (a) Pd(PPh$_3$)$_4$, DMF, 100 °C, 24 h (75%); (b) LiAlH$_4$, THF, rt, 24 h (80%); (c) MAC, DMAP, THF, rt, 16 h (70%).

of concentrated dichloromethane solutions into methanol. This process was repeated to eliminate residual monomer, initiator and other impurities. The polymers were soluble in benzene, THF, and dichloromethane, and characterized by ^{1}H and ^{13}C NMR spectroscopies (see Supplementary data). Elemental analysis gave the expected values.

The molecular weights were determined by gel permeation chromatography (GPC) using PMMA as a standard and two angle light scattering detection. Due to aggregation issues in chloroform, these measurements were carried out in THF (0.5 wt% LiBr); all the elution curves obtained were monomodal (Fig. 2).

Table 1 lists the conditions, molecular weights and yields achieved in several independent runs. Entries 1–4 refer to polymer **10** and entries 5–7 to polymer **11**. The highest molecular weight was obtained for the G2 dendronized polymer **10**, which is within the range of values published for other second generation dendronized polymers [16] and superior to linear polymers containing oligothiophene fragments in the side chains [6,17]. As observed for other dendronized polymers, the average chain lengths of polymers **10** and **11** decrease with increasing dendron generation. This is commonly observed when the macromonomer instead of the synthetically more laborious attach-to route is chosen for synthesis of dendronized polymers [16a,18]. For the specific cases described here, this amounts to a factor of two, approximately. Differential scanning calorimetric investigations on polymers **10** and **11** did not show any sizeable glass transition within the temperature range −50 to +250 °C (see Supplementary data). The thermogravimetric analyses show the main decompositions to set in at approximately 390 and 370 °C for **10** and **11**, respectively (see Supplementary data).

Dendritic thiophene structures are expected to display different spectroscopic properties as compared to their linear counterparts. Their active unit is composed of α–α and α–β linked thiophenes, whereby the former contributes the most to the π–π conjugation. Fig. 2 shows the normalised absorbance spectra of the monomers **5** and **9** and that of the corresponding polymers **10** and **11** in dichloromethane. Low concentrations were used to avoid aggregation. Monomer **5** displays well defined structure with maximum peak absorbance at $\lambda = 296$ and 360 nm, which can be ascribed to localized electronic excitations [3], whereas for **9** a broad, tailing peak with a shoulder at $\lambda = 404$ nm is observed, which is similarly obtained for the dendrimer analogue [8b]. For comparison, the linear α-oligothiophenes [19] with three and four rings display maxima at $\lambda = 354$ and 390 nm, respectively.

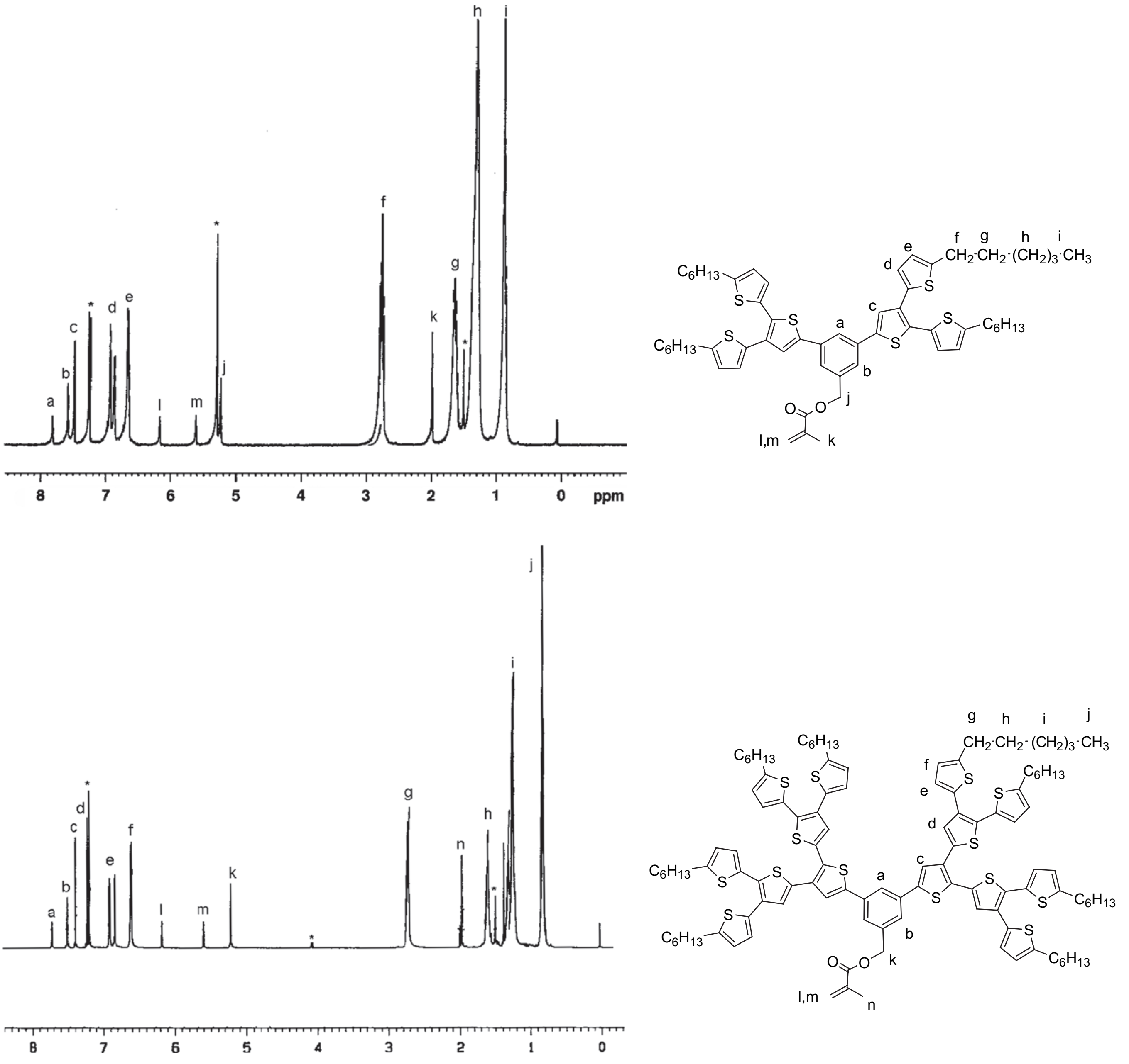
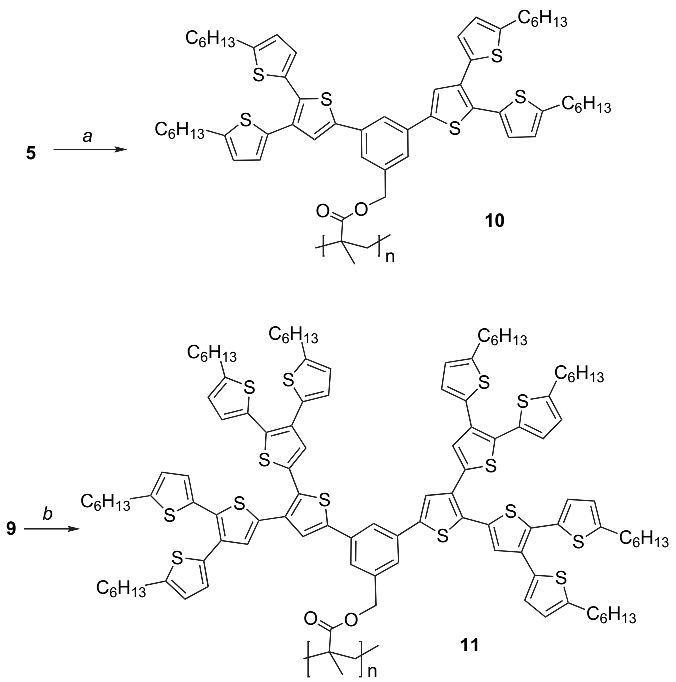


Fig. 1. ^{1}H NMR spectrum of G2 macromonomer **5** (300 MHz) (top) and G3 macromonomer **9** (500 MHz) (bottom) in $CDCl_3$. Solvent signals ($CDCl_3$ peak and residual water and DCM) are marked (*). The peak assignment is based on model compounds and NMR shift prediction programs.

Our dendrimers absorb at higher energies due to their reduced conjugation at the α–β linkage. The onset absorbance of the higher generation dendron is red shifted by 47 nm relative to **5**, and there is virtually no difference between the absorbance of both monomers and the corresponding dendronized polymer.

On the other hand, the fluorescence measurements of the polymers in solution show a clear red shift (55 nm) as the generation increases from two to three, which can be rationalized on the basis of a more extended π-system. However, a relatively small shift (5–15 nm) between the emissions of monomer **5** and its polymer **10** is observed, and for **9** and **11** there is virtually no such shift. This observation points to a conservation of the dendrons' intrinsic properties when connected to polymer backbone.

Solution quantum yields were measured from degassed solutions (Table 2) using a quinine sulphate standard as the reference. The values obtained are modest for all compounds (below 3%). The quantum efficiencies of both polymers are quite similar, which again points towards a limited interaction between adjacent dendrons. The optical band gaps for all compounds were inferred from the cross-point of the normalised absorbance and emission spectra and show a difference of 0.35 eV between G2 and G3, which is of the magnitude of that observed for the linear counterparts.



Scheme 3. Reagents and conditions: (a) AIBN, benzene, 65–70 °C, 48 h, (70–74%); (b) AIBN, benzene, 65–70 °C, 48 h, (69–72%).

The electrochemical properties of monomers and polymers were investigated by cyclic voltammetry. The monomers were measured in a 10^{-4} M dichloromethane solution, while the polymers were investigated as thin films on a glassy carbon electrode using acetonitrile as the solvent, due to their limited solubility in dichloromethane. The cyclic voltammetry curves of the monomers showed three anodic peaks, and no cathodic wave was observed (Figs. 3 and 4). The peaks are irreversible, rather ill-defined and are shifted to lower oxidation potentials as the conjugation of the dendron increases, similarly to other thiophene-based dendrimers [19]. For the polymers **10** and **11**, the oxidation onset is shifted to lower values as the generation increases (from 1.30 to 1.12 V). The oxidation processes of the polymers occurred at higher potentials than those of the monomers. This shift is partly due to the different measurement conditions used for polymers and monomers.

Since there were no significant changes in the luminescence or absorbance spectra when going from monomer to polymer, it is unlikely that orbital energy levels are shifted in the solid state. Knowing both the reduction (about 1.8 V) and the oxidation potentials allowed determining the electrochemical band gap as 3.10 eV for **10** and 2.92 eV for **11**. These gaps are different from those extracted from the optical data of drop cast films, which were 2.94 and 2.62 eV for **10** and **11**, respectively (Table 2). In this case, the optical band gap is smaller than the electrochemical one, which has also been observed for their linear dendritic counterparts [3b].

The cyclic voltammetry data show that these polymers are good donors due to their favourable lowest unoccupied molecular orbital; and to enhance its acceptors properties we envisage introducing acceptor moieties in the structure, by substitution of a number of solubilizing chains. The charge transport properties are currently being investigated and will be reported elsewhere.

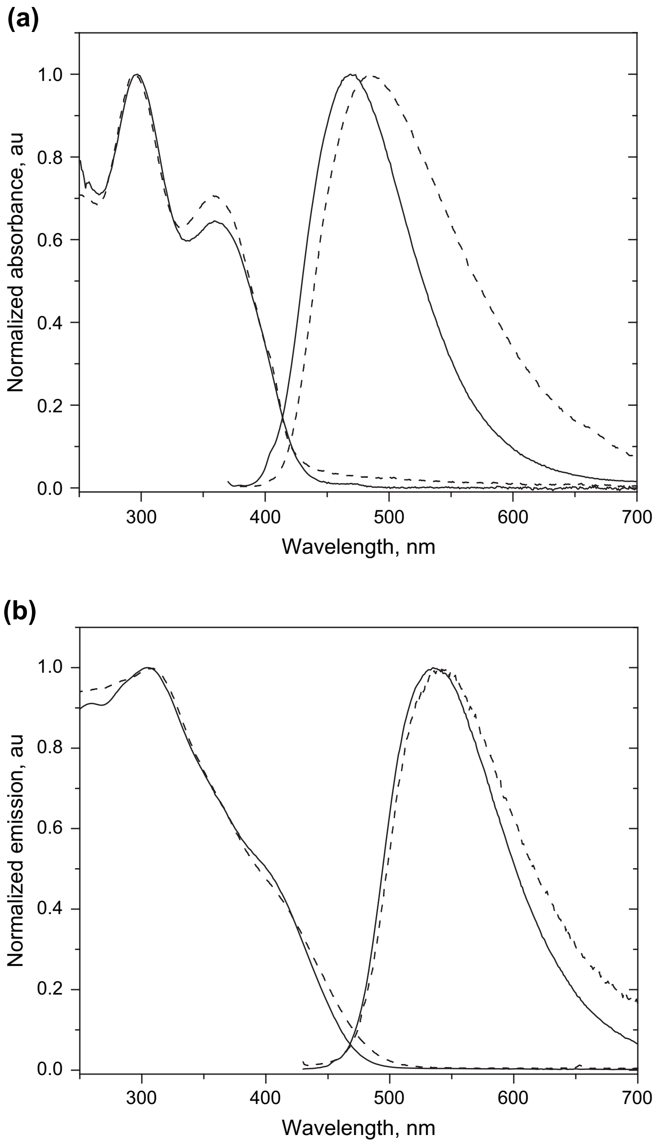


Fig. 2. Normalised absorbance and emission spectra of G2 monomer **5** and polymer **10** (a), G3 monomer **9** and polymer **11** (b) in dichloromethane. Solid and dashed lines correspond to monomers and polymers, respectively.

Table 1
Polymerization conditions, molecular weights and yields achieved in the AIBN initiated polymerization reactions of macromonomers **5** and **9** to give polymers **10** (entries 1–4) and **11** (entries 5–7), respectively

Entry	Solvent	Temp. (°C)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	P_n	P_w	Yield (%)
1	DMF	65	2.2	3.5	219	348	70
2	Benzene	65	2.8	7.1	278	707	72
3	Benzene	70	3.8	11	378	1095	74
4	Benzene	70	5.4	16	537	1593	73
5	Benzene	65	2.8	8.0	40	140	72
6	Benzene	70	1.3	2.9	65	145	69
7	Benzene	70	3.0	7.5	150	375	70

Table 2
Absorbance, fluorescence, quantum yields, oxidation and reduction potentials and optical band gaps for compounds **5**, **9–11**

	Absorbance max[a] (nm)	Fluorescence max (nm)	Quantum yield[b] (%)	First oxidation (V)	First reduction (V)	Band gap[e] (eV)
5	296, 360	470	2.21	1.05[c]	–	3.00
9	307, 404	535	3.71	0.80[c]	–	2.65
10	297, 360	485	2.74	1.31[d]	−1.85	2.94
11	307, 404	540	1.40	1.20[d]	−1.81	2.62

[a] Dichloromethane solution.

[b] Quinine sulphate standard (in 0.1 N H_2SO_4), quantum yield: 54%.

[c] Versus Ag/AgCl (3 M KCl) double-junction, glassy carbon working electrode and Pt counter electrode, in 0.1 M TBAP, using ferrocene as internal standard; dichloromethane solution (3×10^{-5} M), scan rate: 150 mV/s, onset oxidation.

[d] Drop cast solutions (5 μL of a 2% solution) on glassy carbon electrode (0.7 cm^2) dried in vacuum oven for 10 h, scan rate 20 mV/s in acetonitrile, measured at the oxidation onset.

[e] From cross-point between normalised absorbance and emission.

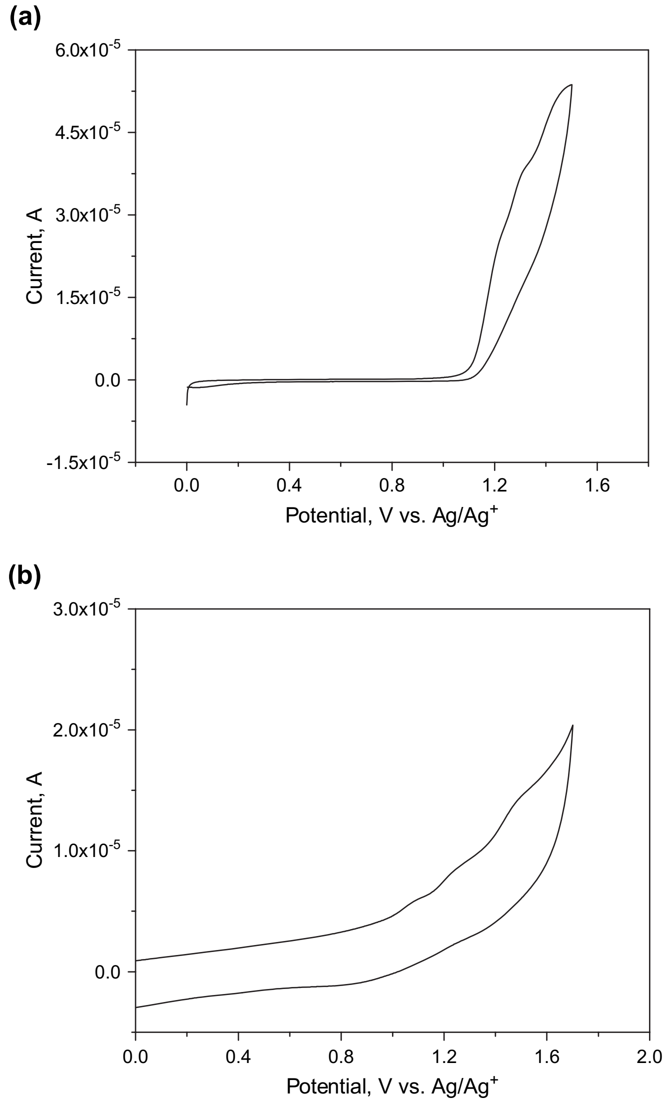


Fig. 3. Cyclic voltammograms of monomers **5** (a) and **9** (b) in dry dichloromethane (10^{-4} M) with 0.1 M tetrabutylammonium perchlorate (TBAP) electrolyte. Ag/AgCl (3 M KCl) double-junction reference electrode, glassy carbon working electrode and platinum counter electrode; scan rate 150 mV/s.

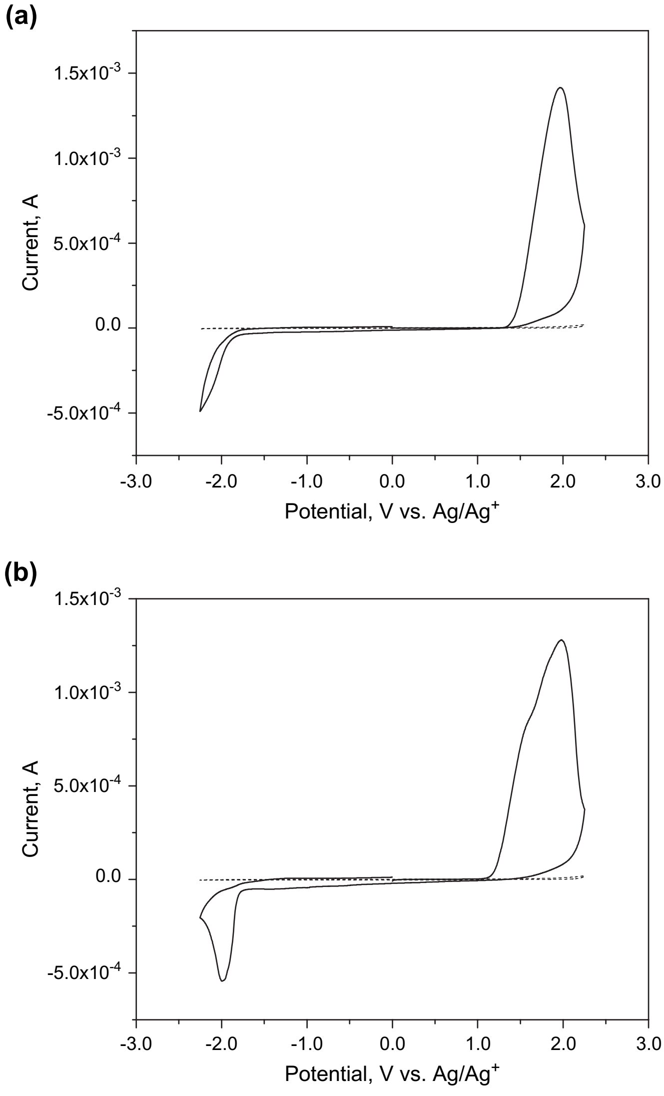


Fig. 4. Cyclic voltammograms of polymers films of **10** (a) and **11** (b) measured in dry acetonitrile (10^{-4} M) with 0.1 M tetrabutylammonium perchlorate (TBAP) electrolyte. Ag/AgCl (3 M KCl) double-junction reference electrode, glassy carbon working electrode, and platinum counter electrode; scan rate 20 mV/s.

4. Conclusion

Thiophene-based second (G2) and third (G3) generation dendronized polymers can be prepared in a straightforward manner to afford high molecular weight products in useful quantities. First photophysical investigations on these novel materials show that the conjugated thiophene dendrons conserve their optical and electrochemical properties when tightly bound to a polymer chain.

The present work is the first step of a project aiming at the synthesis of organic cylindrical semiconductors with nanoscopic dimensions by covalently attaching oligothiophene dendrons with tight spacings to a polymer backbone and, thus, forcing them into close proximity to one another. From earlier atomic force microscopic investigations on individualized high generation dendronized polymers on solid substrates

[9] it is known that macromolecules constructed in this way can in fact be considered as cylindrically shaped nanoobjects. This paper shows that dendronized polymers with oligothiophene dendron side chains can actually be synthesized but more extended substituents are required in order to enforce cross-talking between the latter. Structural polymers of the described kind could find use in thin film optoelectronic devices.

Acknowledgements

We cordially thank M. Colussi for the GPC measurements and Dr. W. Amrein for the high resolution MALDI measurements (both ETH-Zürich). This work was supported by the EMPA internal grant (Series 5-EN3), which is gratefully acknowledged.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2007.06.024.

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