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# Solution processable alternating oligothiophene-PEO-block-co-polymers: synthesis and evidence for solvent dependent aggregation

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A new route to oligothiophene–PEO-block-co-polymers has been developed, in which well-defined α-oligothiophene blocks (from bithiophene to sexithiophene) alternate with poly(ethylene oxide) blocks. These materials show high solubility in common organic solvents. UV/visible and fluorescence studies in solution indicate that the oligothiophene segments are molecularly dissolved in good solvents like chloroform. Aggregation of the oligothiophenes occurs in dioxane–water mixtures, which is manifest by shifts of the UV/visible absorption maxima towards the blue and quenching of the fluorescence. An oligothiophene length of three thiophenes (terthiophene) is necessary to observe this aggregation phenomenon.

## Introduction

There is considerable interest in exploiting the semiconducting properties of solution processable conjugated organic compounds in electronic device structures with the aim of cost reduction and ease of fabrication in the area of disposable electronics.[1] The first generation of conjugated polymers had poor structural definition and very limited processability.[2,3] Generally such materials had large distributions of conjugation lengths and structural defects. Progress in the field of electronics based on organic materials demanded the synthesis of well-defined processable materials and the importance of well-controlled organic synthesis to this field is now widely acknowledged. The synthesis and study of truly monodisperse high purity oligomers has proved a fruitful area. Among the series of thiophene oligomers, the hexamer, sexithiophene, was found to be a very promising material for use in organic field effect transistors (FET).[4] The FET has been envisioned as the key component for the development of displays in portable computers, pagers, memory elements in transaction cards and disposable electronics in general.[5,6] From the commercial interest viewpoint, organic conjugated materials that are processable from solution have an advantage. The higher oligothiophenes (⩾quaterthiophene) have interesting solid state properties but suffer from low solubilities and cannot be processed at room temperature. Solubilising substituents have been attached to the oligothiophene units in both the α- and the β-positions. Whereas α-substituted sexithiophenes did not show very high solubilities,[7–10] highly soluble derivatives with β-side chains have been prepared.[11–15] Alternating oligothiophene main chain polymers with oligothiophenes of various lengths have been reported[16–24] but in all cases β-substituents were employed to ensure solubility. It has been suggested that substitution anywhere other than at the 4- or 5-carbons of the terminal rings of the oligothiophene leads to distortions of conformation and decreased π-overlap.[25] The electronic and optical properties of π-conjugated oligomers and polymers are highly dependent on the conformation of the conjugated segment and the interaction between different polymer chains. It is known that π-conjugated polymers aggregate in poor solvents or upon cooling solutions in good solvents.[26–29] These aggregates exhibit properties which are similar to those observed in the solid state. For various β-substituted polythiophenes these phenomena have been extensively studied but very little data has been reported on the aggregation and stacking of α-substituted oligothiophenes or α-substituted oligothiophene main chain polymers. If α-substituted oligothiophenes or oligothiophene main chain polymers are to be of use in electronic devices, such as FETs, a high degree of order will be necessary in order to obtain high carrier mobilities.

Here we report the first synthetic route to solution processable alternating oligothiophene–PEO-block-co-polymers in which the oligothiophene blocks can be varied from bithiophene to sexithiophene and are exclusively α-substituted. Also UV/visible spectroscopic evidence for aggregation of the oligothiophene segments in these polymers in aqueous solution is presented.

## Experimental

Melting points were obtained using an Electrothermal IA9200 series digital melting point apparatus. Elemental analysis data were recorded on an Exeter Analytical Elemental Analyser CE-440. Mass spectra were recorded on either a Micromass AutoSpec mass spectrometer or using a Hewlett Packard Series II gas chromatograph with a HP1 GC column, attached to a Fisons Trio 1000 mass spectrometer. NMR-spectra were recorded using either a Varian VXR400S ($^1$H at 399.95 MHz and $^{13}$C at 100.58 MHz), a Varian Unity ($^1$H at 299.91 MHz and $^{13}$C at 75.41 MHz) or a Varian Inova ($^1$H at 500 MHz and $^{13}$C at 125 MHz). Chemical shifts are reported in parts per million with respect to the internal reference tetramethylsilane (TMS). Deuterated solvents were used as supplied (Goss). Calculated molecular weights are reported in g mol$^{-1}$. GPC analyses were performed using an ERC 7515A refractive index detector, three 5 μm Polymer Laboratories gel columns (exclusion limits 100, $10^3$, $10^5$ Å) and chloroform as eluent. Columns were calibrated using polystyrene standards (Polymer Labs). *n*-Butyllithium was purchased from Acros (Fisher Scientific), all other reagents were purchased from Aldrich Chemicals and used without further purification. UV/visible-spectra were recorded on a ATI Unicam UV2 spectrometer in quartz cuvettes. Stock solutions for UV/visible-spectroscopy were prepared in dioxane (Aldrich, spectrophotometric grade) and diluted with distilled water to give the following solvent mixtures: 20% water (v/v) (2 ml dioxane stock solution, 0.5 ml water), 50% water (v/v) (1.5 ml dioxane stock solution, 1.5 ml

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water), 83% water (v/v) (0.5 ml dioxane stock solution, 2.5 ml water).

GPC analysis of commercial PEO (Aldrich, average $M_n$ *ca.* 2000) in chloroform using polystyrene calibration gave values of $M_n = 3700$, $M_w = 3900$, PDI (polydispersity index, $M_w/M_n) = 1.05$ whereas MALDI TOF mass spectroscopic analysis confirmed the $M_n$ of *ca.* 2000 as reported by Aldrich. The high molecular weights of the functionalised PEO derivatives **3** and **8** are probably due to the same effect.

### 2-Bromothiophene-5-carboxylic acid, 1

Compound **1** was prepared using the reported route[30] and obtained as a white crystalline solid (49%, lit.[30] 47%), mp 132 °C (lit.[30] 135–136 °C). Found C, 28.31; H, 1.31%; M(MS,EI) 206 ($M^+$ [$^{79}$Br]), 208 ($M^+$ [$^{81}$Br]). Calculated for $C_5H_3BrO_2S$, C, 29.01; H, 1.46%; M 207.05. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.11 (d, $J = 3.9$ Hz, 1H), 7.64 (d, $J = 3.9$ Hz, 1H), 11.4 (broad, COOH); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 122.28, 131.34, 133.81, 135.34, 166.66.

### 2-Bromothiophene-5-carbonyl chloride, 2

Compound **2** was prepared using the reported route[31] and obtained as colourless needles (92%, lit.[31] 100%), mp 36–38 °C (lit.[31] 41–42 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.18 (d, $J = 4.2$ Hz, 1H), 7.73 (d, $J = 4.2$ Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 126.55, 131.89, 138.00, 139.24, 158.46. Due to the rapid hydrolysis of the material no satisfying mass spectrum and elemental analysis data could be recorded for this compound.

### α-(5-Bromo-2-thenoyl)-ω-(5-bromo-2-thenoyloxy)poly(oxyethylene), 3

Poly(oxyethylene) (Aldrich, average $M_n$ *ca.* 2000, 50 g, *ca.* 25 mmol) was melted in a round-bottomed single-necked flask and stirred in the melt under vacuum ($10^{-3}$ mmHg) for 1/2 h. Toluene (100 ml) and pyridine (6 g, 75 mmol) were added to the degassed polymer melt and the mixture stirred until a clear solution was obtained (*ca.* 1/2 h). A solution of 2-bromothiophene-5-carbonyl chloride, **2** (18.1 g, 75 mmol) in toluene (50 ml) was added slowly to the polymer solution at rt. After complete addition the mixture was stirred at rt for 48 h, filtered through Celite (Aldrich) and the product precipitated by addition of the clear solution to hexane. The crude polymer was recovered by filtration, dried under vacuum, re-dissolved in toluene and precipitated in hexane. The white waxy solid was recovered by filtration, washed with hexane and dried under vacuum for 1 d to give α-(5-bromo-2-thenoyl)-ω-(5-bromo-2-thenoyloxy)poly(oxyethylene) (50 g, 84%). GPC ($CHCl_3$): $M_n = 4300$ g mol$^{-1}$; $M_w = 4500$ g mol$^{-1}$; PDI = 1.05. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.54 (m, 175H), 3.69 (m, 4H), 4.32 (m, 4H), 6.98 (d, $J = 3.9$ Hz, 2H), 7.46 (d, $J = 3.9$ Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 64.16, 68.64, 70.21, 70.28, 70.37, 119.93, 130.62, 133.51, 134.33, 160.56.

### 2,2′-Bithiophene, 4

Magnesium turnings (22 g, 192 mmol) were heated with a hot air gun under a dry nitrogen flow and rapid stirring. After cooling, THF (300 ml) was added to the magnesium and 2-bromothiophene (120 g, 0.74 mol) was added slowly *via* a dropping funnel. After complete addition the mixture was refluxed for 1 h, cooled to rt and transferred into a dropping funnel by decanting the solution from excess magnesium. 2-Bromothiophene (100 g, 0.61 mol) was dissolved in THF (300 ml), the catalyst Ni(dppp)$Cl_2$ (1.5 g, 3.6 mmol) was suspended in the THF mixture and the Grignard reagent was added slowly *via* a dropping funnel. During addition of the Grignard reagent the reaction mixture had to be cooled (rt) with a water bath. After complete addition the mixture was stirred for another 5 h at 70 °C and then at rt overnight. A solid precipitated. Excess Grignard reagent was quenched with water and the remaining suspension extracted with diethyl ether. The combined organic extracts were washed with brine, dried ($MgSO_4$) and the solvent removed under vacuum. The residual black oil was distilled under reduced pressure (1 mmHg, 84 °C) to give pure 2,2′-bithiophene (56.6 g, 46%) which crystallised in the receiver flask, mp 32–33 °C (lit.[32] 34 °C). Found C, 57.49; H, 3.54%; M(MS,EI) 166 ($M^+$). Calculated for $C_8H_6S_2$, C, 57.79; H, 3.64%; M 166.27. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.04 (dd, $J = 4.8$ Hz, $J = 3.6$ Hz, 2H), 7.22 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 123.71, 124.30, 127.72, 137.34.

### 2,2′-Bithiophene-5-carboxylic acid, 5, 5-bromo-2,2′-bithiophene-5′-carboxylic acid, 6 and 5-bromo-2,2′-bithiophene-5′-carbonyl chloride, 7

Compounds **5**–**7**were prepared as previously reported.[33]

### α-(5-Bromo-2,2′-bithiophen-5′-ylcarbonyl)-ω-(5-bromo-2,2′-bithiophen-5′-ylcarbonyloxy)poly(oxyethylene), 8

Poly(oxyethylene) (Aldrich, average $M_n$ *ca.* 2000, 10.8 g, *ca.* 5.4 mmol) was heated (90 °C) in a round-bottomed single-necked flask and the melt stirred under vacuum for 1/2 h. Toluene (50 ml) and pyridine (1.3 g, 16.3 mmol) were added to the degassed polymer melt and the mixture stirred until a clear solution was obtained (*ca.* 1/2 h). 5-Bromo-2,2′-bithiophene-5′-carbonyl chloride, **7** (5 g, 16.3 mmol) was added as a solid to the hot (90 °C) polymer solution. After complete addition the mixture was stirred at 90 °C for 3 h then at rt for 3 d. The mixture was filtered through Celite (Aldrich) and the product precipitated by addition of the clear solution to hexane. The crude polymer was recovered by filtration, dried under vacuum, re-dissolved in toluene and precipitated in hexane. The pale yellow waxy solid was recovered by filtration, washed with hexane and dried under vacuum for 1 d to give α-(5-bromo-2,2′-bithiophen-5′-ylcarbonyl)-ω-(5-bromo-2,2′-bithiophen-5′-ylcarbonyloxy)poly(oxyethylene) (10 g, 73%). GPC ($CHCl_3$): $M_n = 4380$ g mol$^{-1}$; $M_w = 4660$ g mol$^{-1}$; PDI = 1.06. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.59 (m, 175H), 3.75 (m, 4H), 4.39 (m, 4H), 6.96 (m, 4H), 7.02 (d, $J = 3.9$ Hz, 2H), 7.64 (d, $J = 3.9$ Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 64.22, 68.89, 70.36, 70.42, 70.44, 70.52, 112.73, 123.91, 125.16, 130.80, 131.56, 134.17, 137.49, 142.81, 161.56.

### 2,5-Bis(trimethylstannyl)thiophene, 9

*n*-Butyllithium (1.6 M, 19.8 ml, 31.6 mmol) was added dropwise to a solution of thiophene (1.33 g, 15.8 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (3.67 g, 31.6 mmol) in hexane (8 ml) at rt. The mixture was refluxed for 1/2 h then cooled to −60 °C and a solution of trimethyltin chloride (6.29 g, 31.6 mmol) in THF (30 ml) added quickly. The mixture was stirred at −60 °C for 10 min before the dry ice–acetone bath was removed and the reaction mixture allowed to warm to rt. The clear solution was stirred at rt for 12 h. The reaction mixture was poured into water and extracted with diethyl ether (2 × 50 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude solid was recrystallised from ethanol to give 2,5-bis(trimethylstannyl)thiophene (3.9 g, 60%) as light brown crystals, mp 99.5 °C (lit.[34] 100–101.6 °C). Found C, 29.47; H, 4.93%; M(MS,EI) 408, 410, 412 ($M^+$, three most intense peaks of the isotope pattern). Calculated for $C_{10}H_{20}SSn_2$, C, 29.31; H, 4.92%; M 409.75. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.39 (s, 18H), 7.40 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ −8.18, 135.78, 142.99.

### 5,5′-Bis(trimethylstannyl)-2,2′-bithiophene, 10

Compound **10** was prepared using the reported route[35] and obtained as colourless needles (85%, lit.[35] 85%), mp 99.5 °C (lit.[35] 95.5–96.5 °C). Found C, 34.48; H, 4.51%; M(MS,EI) 490 (8.96%), 492 (9.05%), 494 (5.74%) ($M^+$, three most intense peaks of the isotope pattern). Calculated for $C_{14}H_{22}S_2Sn_2$, C, 34.19; H, 4.51%; M 491.88. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 0.42 (s, 18H), 7.12 (d, $J = 3.3$ Hz, 2H), 7.31 (d, $J = 3.3$ Hz, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ −8.22, 124.80, 135.81, 135.97, 142.96.

### Dilithium 2,2′-bithiophene-5,5′-dicarboxylate, 11

*n*-Butyllithium (1.6 M, 12.5 ml, 20 mmol) was added slowly dropwise to a stirred solution of 2,2′-bithiophene, **4** (1.52 g, 9.1 mmol) in THF (30 ml). The mixture was heated to 50 °C for 1/2 h, cooled to rt and $CO_2$ gas introduced for 1/2 h while stirring vigorously. The solvent was removed under reduced pressure and the residue stirred in hexane for 1 h. The solid was recovered by filtration and washed with hexane to give dilithium 2,2′-bithiophene-5,5′-dicarboxylate (0.8 g, 34%) which was used without further purification in the next reaction step. No analyses were performed at this stage of the reaction sequence.

### 2,2′-Bithiophene-5,5′-dicarbonyl dichloride, 12

$SOCl_2$ (40 ml) was added slowly to dilithium 2,2′-bithiophene-5,5′-dicarboxylate, **11** (2 g, 7.5 mmol) and the resulting suspension refluxed for 1 h. The $SOCl_2$ was removed under reduced pressure and the residue recrystallised twice from $CHCl_3$–hexane mixture (v/v = 4 : 1) to give pure *2,2′-bithiophene-5,5′-dicarbonyl dichloride* (700 mg, 32%) in the form of orange needles, mp 172 °C. Found C, 41.74; H, 1.50%; M(MS,EI) 289.6 ($M^+$). $C_{10}H_4Cl_2O_2S_2$ requires C, 41.25; H, 1.38%; M 289.9. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta = 7.39$ (broad, 2H), 7.93 (broad, 2H).

### Poly[oxycarbonyl-2,2′-bithiophen-5,5′-ylenecarbonyl-*block*-poly(oxyethylene)], 13

Poly(oxyethylene) (Aldrich, average $M_n$ *ca.* 2000, 3.67 g, *ca.* 1.84 mmol) was melted and stirred under vacuum for 1/2 h before toluene (10 ml) was added to give a clear solution. 2,2′-Bithiophene-5,5′-dicarbonyl dichloride, **12** (535 mg, 1.84 mmol) and pyridine (0.2 ml) were added and the solution stirred at rt for 1/2 h. All solvents were removed under reduced pressure and the melt stirred at 150 °C under high vacuum for 5 h. The viscous melt was dissolved in toluene, filtered through Celite (Aldrich) and the product precipitated by addition of the solution to hexane to give poly[oxycarbonyl-2,2′-bithiophen-5,5′-ylenecarbonyl-*block*-poly(oxyethylene)] (3.5 g) as a white powder. GPC ($CHCl_3$): $M_n = 13\,500$ g $mol^{-1}$, $M_w = 21\,100$ g $mol^{-1}$, PDI = 1.56. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.60 (m, 190H), 3.78 (m, 4H), 4.42 (m, 4H), 7.21 (d, $J = 4.0$ Hz, 2H), 7.69 (d, $J = 4.0$ Hz, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 64.37, 68.93, 70.50 (broad), 125.24, 132.95, 134.25, 142.62, 161.53.

### Poly[oxycarbonyl-2,2′:5′,2″-terthiophen-5,5″-ylenecarbonyl-*block*-poly(oxyethylene)], 14

α-(5-Bromo-2-thenoyl)-ω-(5-bromo-2-thenoyloxy)poly(oxyethylene), **3** (10 g, 4.1 mmol) was heated to 100 °C and the reaction flask purged with nitrogen for 1/2 h while stirring the melt. 2,5-Bis(trimethylstannyl)thiophene, **9**, (1.69 g, 4.1 mmol) and $Pd(PPh_3)_4$ (237 mg, 0.2 mmol) were added to the melt and the mixture heated to 120 °C for 42 h. During the reaction a fraction of the 2,5-bis(trimethylstannyl)thiophene sublimed from the reaction vessel. An $^1H$ NMR spectrum was recorded for a sample taken after 42 h from which the amount of lost 2,5-bis(trimethylstannyl)thiophene was determined. To account for this loss more 2,5-bis(trimethylstannyl)thiophene (200 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.03 mmol) were added after 42 h and the melt stirred at 120 °C for another 12 h. *See general work up procedure for polymers **14–16**.*

The oil was dissolved in more chloroform and the product precipitated by addition of the solution to hexane to give poly[oxycarbonyl-2,2′:5′,2″-terthiophen-5,5″-ylenecarbonyl-*block*-poly(oxyethylene)] which had a higher average molecular weight than the crude product (determined by GPC). Analysis of the higher molecular weight fraction: GPC ($CHCl_3$): $M_n = 14\,360$ g $mol^{-1}$, $M_w = 21\,780$ g $mol^{-1}$, PDI = 1.52. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 3.62 (m, 150H), 3.78 (m, 4H), 4.42 (m, 4H), 7.13 (d, $J = 3.5$ Hz, 2H), 7.19 (s, 2H), 7.68 (d, $J = 3.5$ Hz, 2H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 63.41, 68.10, 69.62 (broad), 123.31, 125.09, 130.91, 133.46, 135.66, 142.31, 160.79.

### Poly[oxycarbonyl-2,2′:5′,2″:5″,2‴-quaterthiophen-5,5‴-ylenecarbonyl-*block*-poly(oxyethylene)], 15

α-(5-Bromo-2-thenoyl)-ω-(5-bromo-2-thenoyloxy)poly(oxyethylene), **3** (10 g, 4.1 mmol) was heated to 100 °C and the reaction flask purged with nitrogen for 1/2 h while stirring the melt. 5,5′-Bis(trimethylstannyl)-2,2′-bithiophene, **10** (2.02 g, 4.1 mmol) and $Pd(PPh_3)_4$ (237 mg, 0.2 mmol) were added to the melt and the mixture heated to 120 °C for 22 h. *See general work up procedure for polymers **14–16**.*

The oil was dissolved in more chloroform and the product precipitated by addition of the solution to hexane to give poly[oxycarbonyl-2,2′:5′,2″:5″,2‴-quaterthiophen-5,5‴-ylenecarbonyl-*block*-poly(oxyethylene)] which had a higher average molecular weight than the crude product (determined by GPC). Analysis of the higher molecular weight fraction: GPC ($CHCl_3$): $M_n = 14\,500$ g $mol^{-1}$, $M_w = 20\,700$ g $mol^{-1}$, PDI = 1.43. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.66 (m, 184H), 3.79 (m, 4H), 4.43 (m, 4H), 7.12 (m, 4H), 7.18 (d, $J = 4.0$ Hz, 2H), 7.69 (d, $J = 4.0$ Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 64.28, 69.01, 70.52 (broad), 123.91, 124.90, 125.97, 131.46, 134.38, 135.45, 137.02, 143.53, 161.75.

### Poly[oxycarbonyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophen-5,5⁗-ylenecarbonyl-*block*-poly(oxyethylene)], 16

α-(5-Bromo-2,2′-bithiophen-5′-ylcarbonyl)-ω-(5-bromo-2,2′-bithiophenyl-5′-ylcarbonyloxy)poly(oxyethylene), **8** (10 g, 3.83 mmol) was heated to 100 °C and the reaction flask purged with nitrogen for 1/2 h while stirring the melt. 2,5-Bis(trimethylstannyl)thiophene, **9** (1.57 g, 3.83 mmol) and $Pd(PPh_3)_4$ (221 mg, 0.2 mmol) were added to the melt and the mixture heated to 120 °C for 4 d. During the reaction a fraction of the 2,5-bis(trimethylstannyl)thiophene sublimed from the reaction vessel. An $^1H$ NMR spectrum of a sample was taken after 4 d from which the amount of lost 2,5-bis(trimethylstannyl)thiophene was determined. To account for this loss more 2,5-bis(trimethylstannyl)thiophene (1.2 g, 2.9 mmol) and $Pd(PPh_3)_4$ (270 mg, 0.03 mmol) were added after 4 d and the melt stirred at 120 °C for another 2 d. *See general work up procedure for polymers **14–16**.*

The oil was dissolved in more chloroform and the product precipitated by addition of the solution to hexane to give poly[oxycarbonyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophen-5,5⁗-ylenecarbonyl-*block*-poly(oxyethylene)] which had a higher average molecular weight than the crude product (determined by GPC). Analysis of the higher molecular weight fraction: GPC ($CHCl_3$): $M_n = 9300$ g $mol^{-1}$, $M_w = 16\,900$ g $mol^{-1}$, PDI = 1.82. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.64 (m, 186H), 3.67 (m, 4H), 4.42 (m, 4H), 7.08 (m, 4H), 7.39 (d, $J = 4.0$ Hz, 2H), 7.14 (d, $J = 3.6$ Hz, 2H), 7.63 (d, $J = 3.6$ Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 64.24, 68.98, 70.48 (broad), 123.77, 124.55, 124.82, 125.92, 131.29, 134.35, 135.08, 135.26, 137.26, 143.60, 161.72.

### General work-up procedure for polymers 14–16

The melt was cooled to rt, dissolved in toluene and the product precipitated by addition of the solution to hexane. The yellow powder was dried under vacuum. The polymer was dissolved in chloroform (100 ml) and hexane added to the stirred solution until the onset of precipitation could be observed. After 12 h of standing without stirring an oil had separated from the solution. The oil was separated from the rest of the solution from which a polymeric product was precipitated by addition to hexane.

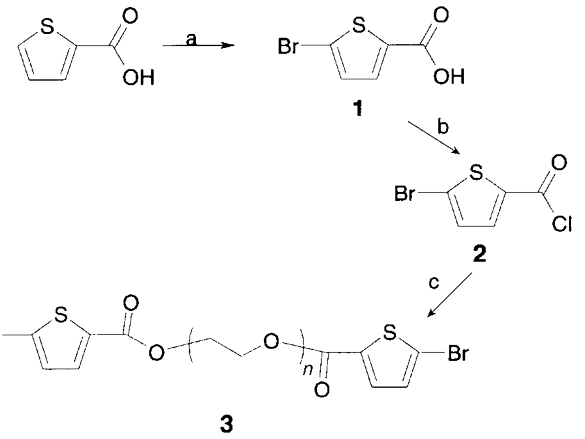
### Poly[oxycarbonyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophen-5,5′′′′′-ylenecarbonyl-*block*-poly(oxyethylene)], 17

α-(5-Bromo-2,2′-bithiophen-5′-ylcarbonyl)-ω-(5-bromo-2,2′-bithiophen-5′-ylcarbonyloxy)poly(oxyethylene), **8**, (12.65 g, 4.85 mmol) was heated to 100 °C and the reaction flask purged with nitrogen for 1/2 h while stirring the melt. 5,5′-Bis(trimethylstannyl)-2,2′-bithiophene, **10** (2.38 g, 4.85 mmol) and $Pd(PPh_3)_4$ (280 mg, 0.2 mmol) were added to the melt and the mixture heated to 120 °C for 3 h. After 3 h the melt had become too viscous to be stirred any more. Toluene (7 ml) was added and the solution stirred for another 12 h at 100 °C. The solution was cooled to rt, dissolved in more toluene and the product precipitated by addition of the solution to hexane. The red powder was dried under vacuum. The polymer was dissolved in chloroform (100 ml) and hexane added to the stirred solution until the onset of precipitation could be observed. After 12 h of standing without stirring an oil had separated from the solution. The oil was separated from the rest of the solution from which a polymeric product was precipitated by addition to hexane. The oil was dissolved in more chloroform and the product precipitated by addition of the solution to hexane to give poly[oxycarbonyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophen-5,5′′′′′-ylenecarbonyl-*block*-poly(oxyethylene)] which had a higher average molecular weight than the crude product (determined by GPC). Analysis of the higher molecular weight fraction: GPC ($CHCl_3$): $M_n = 13\,300$ g mol$^{-1}$, $M_w = 19\,000$ g mol$^{-1}$, PDI = 1.43. $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.61 (m, 192H), 3.79 (m, 4H), 4.42 (m, 4H), 7.07 (m, 6H), 7.10 (d, $J = 4.0$ Hz, 2H), 7.16 (d, $J = 4.0$ Hz, 2H), 7.68 (d, $J = 3.6$ Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 64.25, 69.00, 70.41 (broad), 123.74, 124.45, 124.51, 124.81, 125.93, 131.24, 134.38, 134.97, 135.53, 136.15, 137.39, 143.67, 161.76.

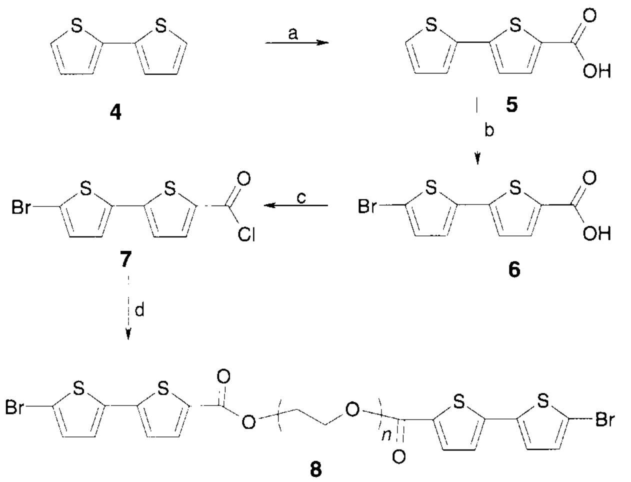
## Results and discussion

### Synthesis

Because of their low solubility the oligothiophene blocks of the co-polymer could not be synthesised and manipulated directly and so they were constructed in the polymer forming step. Two types of monomer, each carrying a segment of the final oligothiophene block were prepared (**3** and **8**, Schemes 1 and 2) and cross-coupled with a 2,5-bis(trimethylstannyl)thiophene (**9**), or 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (**10**, Fig. 1) to give the target polymeric products.



**Scheme 1** Synthesis of the bis-bromo-thiophene macromonomer **3**. a) AcOH, $Br_2$; b) $SOCl_2$; c) toluene, pyridine, PEO ($M_n = 2000$).



**Scheme 2** Synthesis of bis-bromo-bithiophene macromonomer **8**. a) THF, *n*-butyllithium, $CO_2$; b) DMF, NBS; c) $SOCl_2$; d) toluene, pyridine, PEO ($M_n = 2000$).

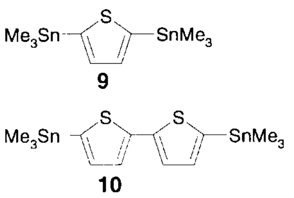
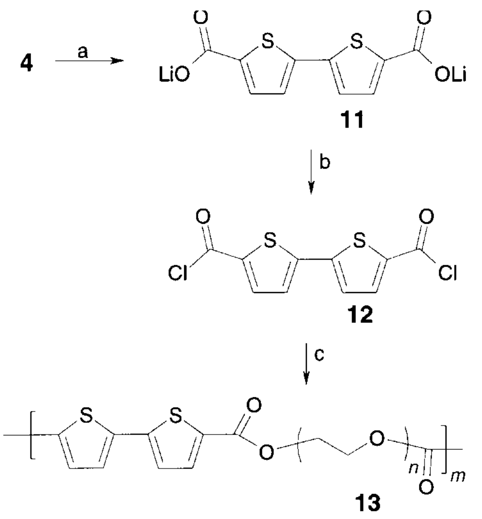


**Fig. 1** 2,5-Bis(trimethylstannyl)thiophene **9** and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene **10** used in a Stille poly-condensation reaction.

α-Bromination of thiophene-2-carboxylic acid and subsequent reaction of the acid **1** with thionyl chloride gave the 2-bromothiophene-5-carbonyl chloride (**2**). Reaction of **2** with commercial PEO gave the di-ester monomer **3** (Scheme 1). Mono-lithiation of 2,2′-bithiophene (**4**) was achieved using *n*-butyllithium in THF at −78 °C. Introduction of $CO_2$ gas into a solution of the anion gave 2,2′-bithiophene-5-carboxylic acid (**5**). Bromination in the 5′-position was carried out using NBS in DMF at −10 °C. The 5-bromo-2,2′-bithiophene-5′-carboxylic acid (**6**) obtained was converted into the acid chloride **7** using thionyl chloride. Reaction with PEO gave the macromonomer **8** (Scheme 2). Bis(trimethyltin) derivatives of thiophene, **9**, and bithiophene, **10** (Fig. 1) were prepared using standard lithiation/nucleophilic substitution chemistry. Preparation of the bithiophene–PEO block co-polymer (**13**) (Scheme 3) was accomplished by di-lithiation of bithiophene followed by reaction with $CO_2$ to give the bis-carboxylate **11**. Reaction with thionyl chloride yielded the di-acid chloride **12** which was subsequently melt polymerised with PEO to give polymer **13**.

Synthesis of the higher oligothiophene polymers **14**–**17** was achieved by cross-coupling of all combinations of the monomers **3**,**8** and **9**,**10** in the melt under Pd(0)-catalysis (Scheme 4).

All polymers prepared by Stille cross-coupling were fractionated to remove lower molecular weight material.



**Scheme 3** Synthesis of the bithiophene polymer **13**. a) THF, *n*-butyllithium, $CO_2$; b) $SOCl_2$; c) PEO ($M_n = 2000$).

Molecular weights were estimated by GPC in chloroform using poly(styrene) standards (Table 1).

All polymeric materials showed very good solubility in various organic solvents like chloroform, dichloromethane, THF and aromatic solvents. Also, dilute solutions in THF or dioxane could be further diluted with water without precipitation of the polymers.

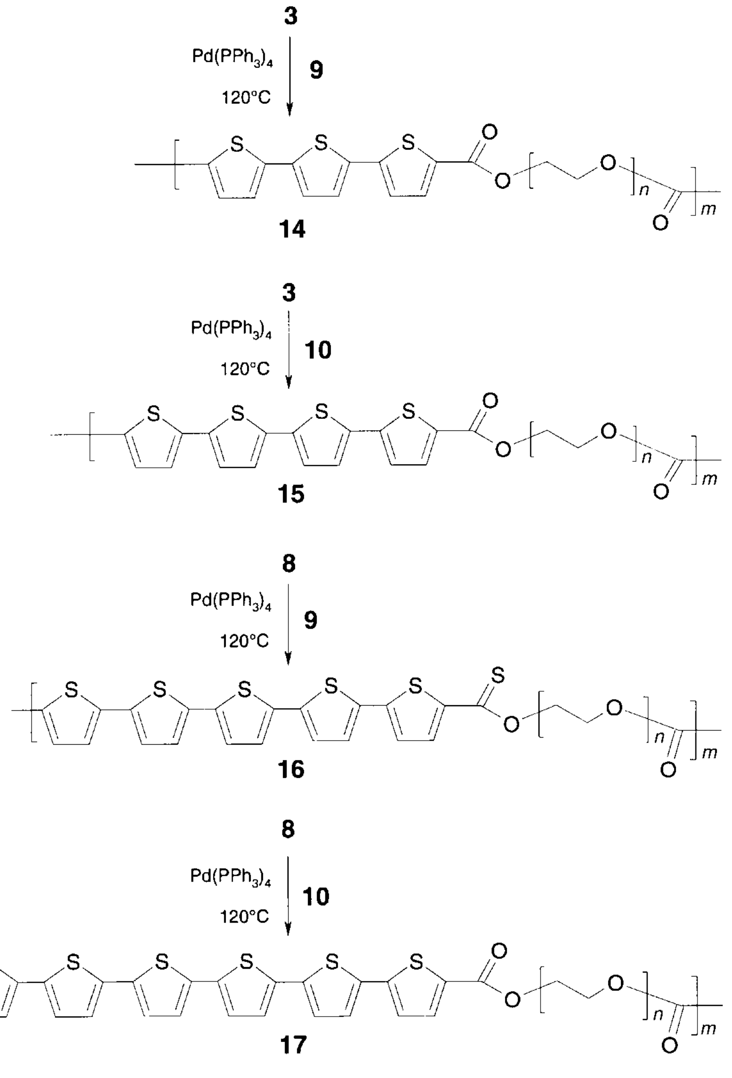
## Mechanical properties

Pure PEO even of high molecular weight is a brittle semi-crystalline material and films made from PEO do not show any significant mechanical strength. Qualitative examination of melt formed films of the above polymers showed markedly different properties with the mechanical strength increasing from the bithiophene polymer **13** to the sexithiophene polymer **17**. While the bithiophene polymer **13** exhibits a behaviour similar to pure PEO, the sexithiophene polymer **17** has properties reminiscent of a cross-linked rubber. This behaviour is consistent with noncovalent crosslinking of disordered PEO caused by aggregation of the oligothiophene blocks within the polymer. The aggregation strength is likely to be lower for shorter and higher for longer oligothiophenes leading to physically cross-linked polymers with a gradation of mechanical properties with the sexithiophene block copolymer **17** displaying the largest effect.

## UV/visible-spectroscopic evidence for aggregation

Chloroform solutions of polymers **13**–**17** with chromophore concentrations of $6.7 \times 10^{-6}$ mol $l^{-1}$ were prepared and their UV/visible spectra recorded (Fig. 2). The absorption spectra show broad bands with little or no resolved vibronic structure as expected for molecularly dissolved chromophores. Due to increasing π-conjugation the absorption maximum shifts progressively towards the red as the thiophene oligomer block length increases.

The fluorescence spectra show more fine structure than the



**Scheme 4** Synthesis of the terthiophene polymer **14**, quaterthiophene polymer **15**, quinquethiophene **16** and sexithiophene **17**.

**Table 1** Molecular weights of polymers **13**–**17**, determined by GPC (chloroform)

| Compound | Low molecular weight fraction | | High molecular weight fraction | |
|---|---|---|---|---|
| | $M_n$ | $M_w$ | $M_n$ | $M_w$ |
| **13** | 13 500 | 21 100 | — | — |
| **14** | 3710 | 9740 | 14 360 | 21 780 |
| **15** | 11 464 | 16 600 | 14 500 | 20 700 |
| **16** | 8150 | 10 900 | 9300 | 16 900 |
| **17** | 12 200 | 17 400 | 13 300 | 19 000 |

absorption spectra (Fig. 3). Each emission spectrum shows two clearly resolved bands and a shoulder which have been identified as the vibronic replicas of the 0–0 transition.[36]

UV/visible-spectra of dioxane solutions of the polymers **13**–**17** with chromophore concentrations of $6.7 \times 10^{-6}$ mol l$^{-1}$ were identical with those recorded for chloroform solutions (Fig. 4–Fig. 8, 0% water traces). Dilution with water gave solutions with 20%, 50% and 83% (v/v) water content. UV/visible spectra of these solutions were recorded and normalised to chromophore concentrations of $6.7 \times 10^{-6}$ mol l$^{-1}$ (Fig. 4–Fig. 8). The absorption maximum of the bithiophene polymer 13 does not shift with varying the water content of the solution, remaining at 350 nm for all four solvent mixtures (Fig. 4).

The absorption maximum of the terthiophene polymer **14** displayed a small shift to shorter wavelength (386 nm) when dissolved in 83% water in dioxane but remained at 396 nm for all other solvent compositions (Fig. 5).

This effect became more pronounced for the quaterthiophene polymer **15** for which the absorption maximum shifts from 422 nm for pure dioxane to 404 nm for 83% water in dioxane (Fig. 6).

For the quinquethiophene polymer **16** the absorption maximum shifted from 436 nm (pure dioxane) to 410 nm (83% water in dioxane, Fig. 7) and for the sexithiophene polymer **17** from 448 nm (pure dioxane) to 410 nm (83% water in dioxane, Fig. 8).

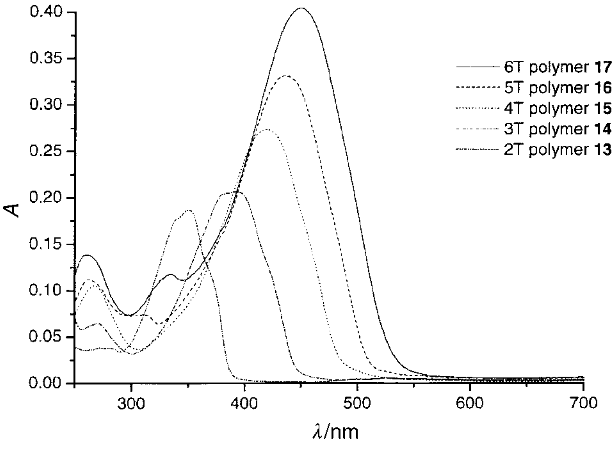


**Fig. 2** UV/visible-spectra of the polymers **13**–**17** in chloroform (chromophore concentration = $6.7 \times 10^{-6}$ mol l$^{-1}$).

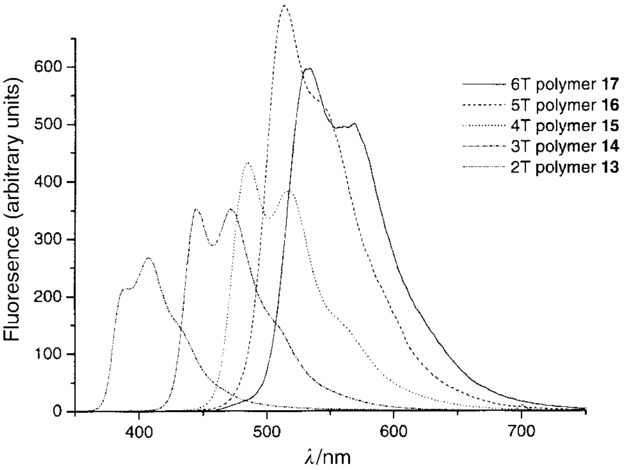


**Fig. 3** Fluorescence spectra of the polymers **13**–**17** in chloroform (chromophore concentration = $6.7 \times 10^{-6}$ mol l$^{-1}$). The excitation wavelengths for the different polymers were: **13**: 350 nm, **14**: 392 nm, **15**: 419 nm, **16**: 436 nm, **17**: 450 nm.

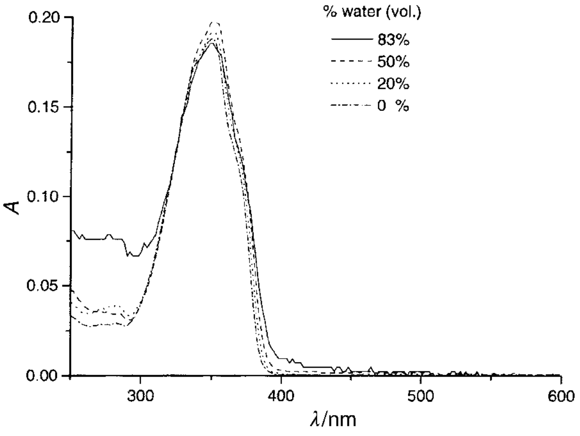


**Fig. 4** UV/visible-spectra of the bithiophene polymer **13** in various dioxane–water mixtures (chromophore concentration = $6.7 \times 10^{-6}$ mol l$^{-1}$).

This phenomenon is well known for oligothiophenes π-stacked in a parallel manner and has been observed in thin solid films.[36] Recently we reported helical π-stacking of a chiral di-substituted sexithiophene derivative in solution.[33] This compound is structurally very similar to the materials described here and can be used as a model system for the sexithiophene polymer **17**. The model system showed the same solvent dependent UV/visible absorption phenomena, independent of the chromophore concentration, while circular dichroism spectroscopy gave evidence for aggregation in polar solvents.[33] Further evidence for parallel face-to-face stacking is the observed quenching of the fluorescence in 83% water in dioxane solutions for all the polymers (**14**–**17**) except the bithiophene polymer **13**. A change of refractive index of the polymer solutions in dioxane–water mixtures compared to pure dioxane or pure chloroform could potentially cause a blue shift in the UV/visible absorption but this phenomenon should be seen for all polymers (**14**–**17**) and be independent of the size of the oligothiophene. However, we did not observe this effect for the bithiophene polymer **14** and therefore conclude that the observed blue shift is not caused by a refractive index change. The model compound described[33] was also used to give mass spectroscopic evidence for aggregation, dependent on the polarity of the solution injected into a Fourier Transform Ion Cyclotron Mass Spectrometer (FTICR).[37] The solvent induced π-stacking might prove useful for the use of these materials in FET devices where a high degree of order enhances carrier

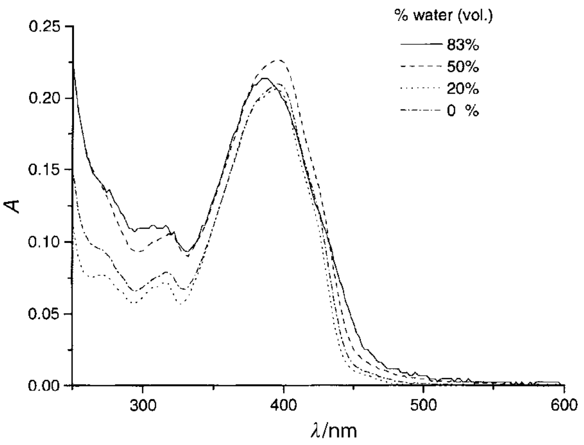


**Fig. 5** UV/visible-spectra of the terthiophene polymer **14** in various dioxane–water mixtures (chromophore concentration $= 6.7 \times 10^{-6}$ mol $l^{-1}$).

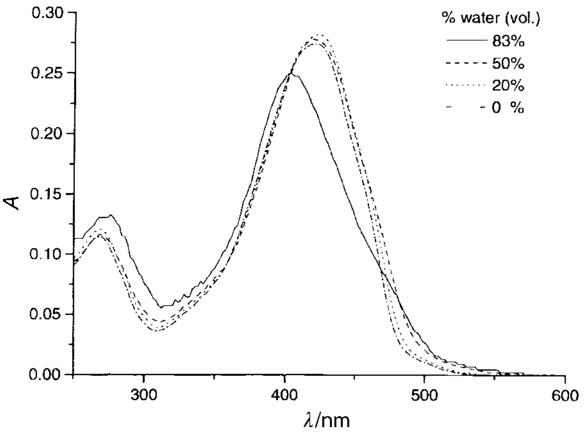


**Fig. 6** UV/visible-spectra of the quaterthiophene polymer **15** in various dioxane–water mixtures (chromophore concentration $= 6.7 \times 10^{-6}$ mol $l^{-1}$).

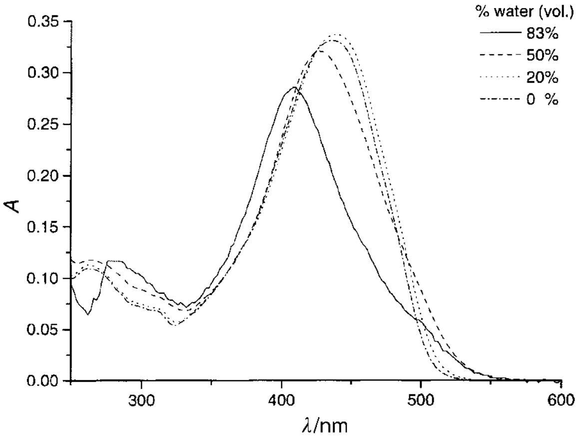


**Fig. 7** UV/visible-spectra of the quinquethiophene polymer **16** in various dioxane–water mixtures (chromophore concentration $= 6.7 \times 10^{-6}$ mol $l^{-1}$).

mobilities.[38] Together with the greatly enhanced solubility compared with that of the unsubstituted oligothiophenes this approach might lead to commercially interesting processable and highly organised materials.

## Conclusions

We have synthesised a new class of solution processable oligothiophene–PEO block co-polymers with variable oligothiophene length. PEO side-chains were shown to have excellent solubilising effects on otherwise insoluble rigid oligothiophenes. The new materials show good solubility in various organic solvents and also mixtures of dioxane–water . In solutions in 83% water in dioxane (v/v) UV/visible-spectra suggest that the oligothiophene rods aggregate in a face-to-face manner.

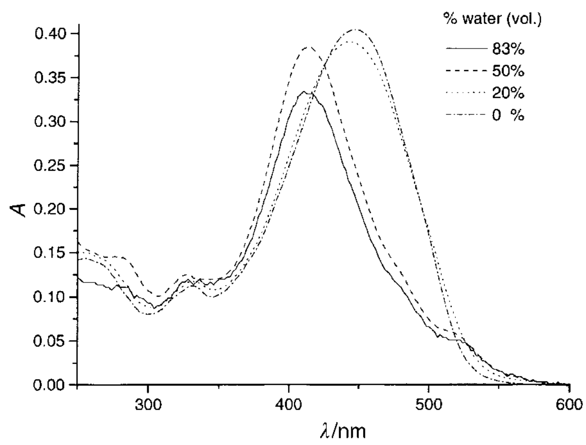


**Fig. 8** UV/visible-spectra of the sexithiophene polymer **17** in various dioxane–water mixtures (chromophore concentration $= 6.7 \times 10^{-6}$ mol $l^{-1}$).

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## References

1 I. D. W. Samuel, *Philos. Trans. R. Soc. London, A*, 2000, **358**, 193.
2 W. J. Feast, 'The Synthesis of Conducting Polymers', in *The Synthesis of Conducting Polymers*, ed. T. A. Skotheim, Marcel Dekker, N.Y., 1986.
3 W. J. Feast, *Chem. Ind. (London)*, 1985, **8**, 263.
4 G. Horowitz, F. Garnier, A. Yassar, R. Hajlaoui and F. Kouki, *Adv. Mater.*, 1996, **8**, 52.
5 H. Stubb, E. Punkka and J. Paloheimo, *J. Mater. Sci. Eng.*, 1993, **10**, 85.
6 C. P. Jarrett, R. H. Friend, A. R. Brown and D. M. de Leeuw, *J. Appl. Phys.*, 1995, **77**, 6289.
7 F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries and P. Alnot, *J. Am. Chem. Soc.*, 1993, **115**, 8716.
8 Y. Wei, Y. Yang and J. M. Yeh, *Chem. Mater.*, 1996, **8**, 2659.
9 H. E. Katz, J. G. Laquindanum and A. J. Lovinger, *Chem. Mater.*, 1998, **10**, 633.
10 H. E. Katz, A. Dodabalapur, L. Torsi and D. Elder, *Chem. Mater.*, 1995, **7**, 2238.
11 G. Barbarella, M. Zambianchi, A. Bongini and L. Antolini, *J. Org. Chem.*, 1996, **61**, 4708.
12 G. Bidan, A. DeNicola, V. Enee and S. Guillerez, *Chem. Mater.*, 1998, **10**, 1052.
13 J. M. Tour and R. L. Wu, *Macromolecules*, 1992, **25**, 1901.
14 F. Goldoni, D. Iarossi, A. Mucci and L. Schenetti, *Chem. Commun.*, 1997, 2175.
15 D. Delabouglise, M. Hmyene, G. Horowitz, A. Yassar and F. Garnier, *Adv. Mater.*, 1992, **4**, 107.
16 H. Ago, T. Kuga, T. Yamabe, K. Tanaka, A. Kunai and M. Ishikawa, *Chem. Mater.*, 1997, **9**, 1159.
17 J. K. Herrema, P. F. Vanhutten, R. E. Gill, J. Wildeman, R. H. Wieringa and G. Hadziioannou, *Macromolecules*, 1995, **28**, 8102.
18 W. C. Chen and S. A. Jenekhe, *Macromolecules*, 1995, **28**, 454.
19 K. Y. Musick, Q. S. Hu and L. Pu, *Macromolecules*, 1998, **31**, 2933.
20 M. Belletete, L. Mazerolle, N. Desrosiers, M. Leclerc and G. Durocher, *Macromolecules*, 1995, **28**, 8587.
21 M. Sato and M. Hiroi, *Chem. Lett.*, 1996, 495.

22 Y. L. Hong and L. L. Miller, *Chem. Mater.*, 1995, **7**, 1999.
23 A. DonatBouillud, L. Mazerolle and M. Leclerc, *Synth. Met.*, 1997, **84**, 235.
24 Y. Kunugi, L. L. Miller, T. Maki and A. Canavesi, *Chem. Mater.*, 1997, **9**, 1061.
25 H. E. Katz, *J. Mater. Chem.*, 1997, **7**, 369.
26 E. Ramos Lermo, B. M. W. Langeveld, R. A. J. Janssen and E. W. Meijer, *Chem. Commun.*, 1999, 791.
27 B. M. W. Langeveld-Voss, M. P. T. Christiaans, R. A. J. Janssen and E. W. Meijer, *Macromolecules*, 1998, **31**, 6702.
28 A. F. Drake, P. Udvarhelyi, D. J. Ando, D. Bloor, J. S. Obhi and S. Mann, *Polymer*, 1989, **30**, 1063.
29 G. Bidan, S. Guillerez and V. Sorokin, *Adv. Mater.*, 1996, **8**, 157.
30 G. Karminskizamola, J. Dogan, M. Bajic, J. Blazevic and M. Malesevic, *Heterocycles*, 1994, **38**, 759.
31 P. Buu-Hoi and N. Hoan, *Recl. Trav. Chim. Pays-Bas*, 1949, **68**, 5.
32 E. Lescot, N. P. Buu-Hoi and N. D. Xuong, *J. Chem. Soc.*, 1959, 3234.
33 A. F. M. Kilbinger, A. P. H. J. Schenning, F. Goldoni, W. J. Feast and E. W. Meijer, *J. Am. Chem. Soc.*, 2000, **122**, 1820.
34 D. E. Seitz, S. H. Lee, R. N. Hanson and J. C. Bottaro, *Synth. Commun.*, 1983, **13**, 121.
35 S. Kotani, K. Shiina and K. Sonogashira, *J. Organomet. Chem.*, 1992, **429**, 403.
36 A. Yassar, G. Horowitz, P. Valat, V. Wintgens, M. Hmyene, F. Deloffre, P. Srivastava, P. Lang and F. Garnier, *J. Phys. Chem.*, 1995, **99**, 9155.
37 A. F. M. Kilbinger, H. J. Cooper, L. A. McDonnell, W. J. Feast, P. J. Derrick, A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2000, 383.
38 F. Garnier, G. Horowitz, D. Fichou and A. Yassar, *Synth. Met.*, 1996, **81**, 163.