JOURNAL OF
Materials
CHEMISTRY

Synthesis, orientation and optical properties of thiophene–dialkoxyphenylene copolymers

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Received 19th November 1999, Accepted 25th January 2000
Published on the Web 29th February 2000

A (thienylene–dialkoxyphenylene) copolymer has been prepared by using an organometallic condensation reaction between a bis(stannyl)thiophene reagent and a substituted dibromobenzene derivative in the presence of a palladium catalyst. The grafting of 2-butoxyethoxy substituents gave the polymer a good solubility in most organic solvents. Moreover, owing to the presence of polar dialkoxy chains along the conjugated skeleton, a material with excellent glass adhesion properties was obtained. It allows the formation of homogeneous thin films coatings. The material is highly fluorescent ($\Phi_{sol} = 0.9$, $\lambda_{sol} = 520$ nm). The polymer was ordered by coating on an oriented Teflon deposit on a glass support and exhibited polarized fluorescence. On the other hand, the material presented a stable reversible blue–red electrochromism associated with a redox transfer at a low potential value (0.5 V *vs.* SCE). Moreover, the electrochromic properties of this material are preserved even in an aqueous electrolytic medium ($LiClO_4$–H_2O). The copolymer with enhanced optical properties compares quite favorably to polythiophene and has good potential for the elaboration of optical devices; for example it seems to be a good candidate for the preparation of electroluminescent diodes with polarized emission.

Conjugated organic polymers constitute an interesting class of materials. Owing to their optical properties which result from the existence of an extended conjugated π system, they are receiving much attention for a variety of applications.[1–4] The electrochromic and electroluminescent properties of the polymers can for example be used for the design of optical devices.[5–12] However, for most applications, polymers exhibiting highly stable optical properties and possessing appropriate glass-adhesion properties are required to process the material.

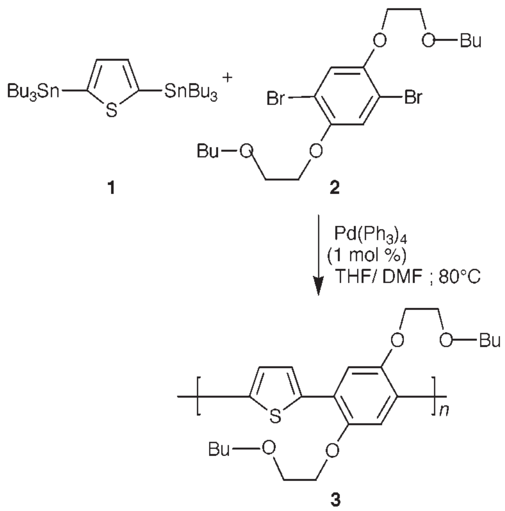
The optical properties of conjugated polymers are not only dependent on the structure of the chain unit, but also on the arrangement of the chain units in the polymer backbone. The mean conjugation length has been shown to be higher in regioregular poly(3-alkylthiophene)s than in similar poly(3-alkylthiophene)s where the chain units are arranged in a random fashion.[13,14] It results in absorption and emission maxima at higher wavelengths. Moreover, the relative arrangement and orientation of the polymer chains with respect to each other play a role in the resulting optical properties of the material. Oriented polymers exhibited electroluminescent properties with polarized emission.[15–20]

The tuning of the polymer properties can therefore result from the control of the synthesis and from the control of the arrangements of the chains in the polymeric material. Whereas the non-selective oxidative polymerization of thienylene, involving $FeCl_3$, led to poorly conjugated material,[21] the use of selective organometallic reagents and the selective formation of carbon–carbon bonds by use of organometallic coupling reactions allow a controlled synthesis and coupling of monomeric units[22–27] to give highly conjugated polymers. Related polycondensation reactions can widely be used to lead to a variety of conjugated chain structures. We for example recently reported the synthesis of highly conjugated thiophene–alkylthiophene copolymers and of ionochromic thiophene–phenylene copolymers.[28–30] We report here an approach to tune the properties of thienylene–phenylene copolymers. We achieved the synthesis of a perfectly alternating thiophene–dialkoxyphenylene copolymer. The presence of polar butoxyethoxy substituents allowed the formation of thin films and the orientation of material. The optical and electroactive properties of the polymer are reported.

Results and discussion

1 Preparation of (thienylene–dialkoxyphenylene) copolymer

A perfectly alternating (thienylene–dialkoxyphenylene) copolymer **3** was prepared by condensation of 2,5-bis(tributylstannyl)thiophene **1** and 1,4-dibromo-2,5-dialkoxyphenylene **2** in the presence of a palladium catalyst, eqn. (1).



(1)

$M_w = 21464$; $M_n = 12049$; DPn = 31

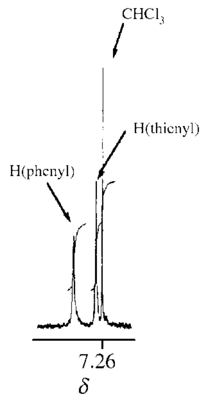


Fig. 1 ^{1}H NMR spectrum of copolymer **3** ($CDCl_3$ solution) in the aromatic region.

The reaction was performed in a 1 : 1 THF and DMF mixture. The catalytic species proved to have a good stability in this solvent mixture and the polymer which formed was soluble in it.[14,31,32] The polymer was isolated by precipitation upon addition of acetone.

The analytical data are consistent with the structure $(C_{22}H_{18}O_4S)_n$ in eqn. (1). The EDAX analysis of the isolated solid material only revealed traces of Sn and Pd. The ^{1}H NMR spectrum of copolymer **3** (Fig. 1) showed only two signals at 7.63 (phenylene protons) and 7.34 ppm (thienylene protons) in the aromatic region. It also showed signals corresponding to the alkoxy substituent at higher field in agreement with the thienylene–phenylene alternating structure in eqn. (1). The polymer was soluble in organic solvents (THF, $CHCl_3$) and characterized using gel permeation chromatography (GPC) on styragel columns using THF as eluent and calibrated with polystyrene standards. Molecular weight $M_w = 21\,464$ and polydispersity $M_w/M_n = 1.78$ were found. This corresponds to an average degree of polymerization, Dpn = 31, indicating that the polymer chain contains on average 62 consecutive alternating aromatic cycles.

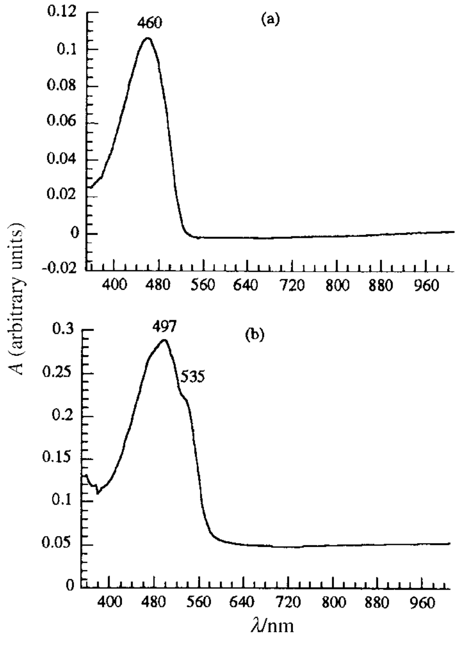


Fig. 2 Absorption spectra of copolymer **3**: (a) in $CHCl_3$ solution; (b) in the solid state (thin film on a glass substrate).

2 Optical properties

2.1 Absorption and fluorescence. The absorption spectrum of (10^{-4} M) $CHCl_3$ solutions of copolymer **3** showed a band at $\lambda_{max} = 460$ nm (Fig. 2a). The relatively high value can be attributed to the presence of the electron donating alkoxy substituent on the phenylene unit.[33,34] The absorption spectrum was also recorded in the solid state. The presence of the polar butoxyethoxy substituent gives the polymer an excellent ability to form a film on a glass support. Very homogeneous thin film coatings (2×10^{-9} mol /mm^{-2}) were formed upon evaporation of a $CHCl_3$ solution of **3**. In the solid state an important bathochromic shift of the absorption maximum was found: $\lambda_{max} = 497$ nm (Fig. 2b). This can be attributed to a higher mean conjugation length in the solid polymer.[35] It probably resulted from more planar conformations of conjugated chains in the solid state than in solution. The intermolecular interactions in the solid state may favor coplanar arrangements of the aromatic rings in the polymer chain and may be responsible for the observed enhanced conjugation.

The emission spectrum of the polymer was also recorded in $CHCl_3$ solution (Fig. 3). An intense absorption at $\lambda_{max} = 520$ nm (2.38 eV) was observed and a high quantum yield ($\Phi = 0.9$) was measured in solution. The room-temperature photoluminescence spectrum recorded on a thick film displayed a strong and well structured profile. A series of defined peaks separated by an optical phonon frequency (0.16 eV) are observed at 2.19 (0-phonon line), 2.03 (1-phonon line) and 1.87 eV (2-phonon line) (Fig. 4a). The shape and the energy of the photoluminescence band is close to that of polythiophene.[36]

Owing to the presence of diether substituents, constituted by a side-chain of eight atoms, along the polymer backbone, the polymer **3** exhibited a high ability to form films. We therefore explored the possibility to prepare oriented thin film according to the method described by Wittmann *et al.*[37–40] Indeed, the orientation of conjugated polymers capable of emitting polarized light is of great interest to fabricate polarized electroluminescent devices.[41] An oriented layer of Teflon was first deposited by rubbing a hot (400 °C) Teflon bar on a glass plate. Then a coating was realized by evaporation of a liquid film of a $CHCl_3$ solution of **3**. As determined by Atomic Force Microscopy (AFM) the thickness of the film varied from 5 to 100 nm. The fluorescence spectra were recorded on a 5 nm thin film and are shown on Fig. 4b. The photoluminescence band is clearly polarized. Indeed the intensity recorded in the VV† configuration is significantly higher than the one measured in the VH configuration (Fig. 4b).

The photoluminescence spectra were recorded for films of different thicknesses (5–100 nm). As shown in Fig. 5 the

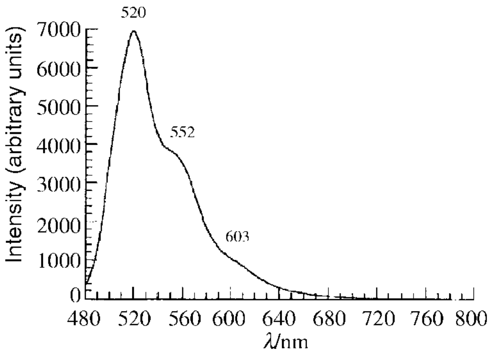


Fig. 3 Emission spectrum of copolymer **3** in $CHCl_3$ solution.

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†VV means that the incident beam and the emitted beam are polarized along the rubbing direction and VH indicates that the polarization of the emitted beam is normal to the incident beam, always polarized in the rubbing direction.

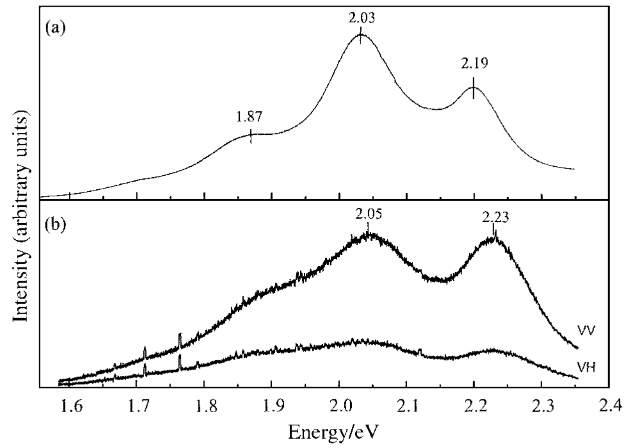

Fig. 4 Photoluminescence spectra at room temperature ($\lambda_{ex} = 514.5$ nm) of a film of copolymer **3** deposited on glass; (a) non-oriented deposited film; (b) thin oriented film (5 nm).

intensity ratio I_{VV}/I_{VH} decreases with increasing thickness of the film. This indicates that the degree of orientation of the polymer chains decreases with the film thickness. This result suggests that only the polymer chains which are in direct interaction with the oriented Teflon deposit are ordered.

It must also be emphasized that the energy of the photoluminescence depends on the film thickness. The energy of the 0-phonon line is about 2.23 eV for thin films (5 nm), at 2.21 eV for films of about 30 nm and shifts to 2.19 eV for thick films (100 nm) (Fig. 5). This dependence can be assigned to the increasing of π stacking of polymer chains with the film thickness which leads, as observed in several examples,[13b] to a red shift of the band gap, and consequently of the photoluminescence band. However, in the thin film, an interaction of the polymeric chain with the Teflon deposit cannot be ruled out. Such an interaction could induce a blue shift of the band gap associated with a lowering of the mean conjugation length. Further studies are necessary to describe precisely the nature of the intermolecular interactions and the mechanism of the orientation of the polymer chains on the Teflon deposit.

2.2 Electrochromic properties

Films of copolymer **3** were also formed on a platinum electrode from a 10^{-3} M solution in $CHCl_3$ and the solid deposit was studied by cyclic voltammetry (Fig. 6). The voltammogram was registered between −2 and +0.8 V (*vs.* SCE). The polymer showed an oxidation peak for a low value of the potential (+0.52 V *vs.* SCE) and the corresponding reduction at 0.44 V. The low value of the oxidation potential can be assigned to the presence of electron donating alkoxy substituents on the phenylene ring in the chain unit.[33,34] In the range of cathodic potentials, the reduction wave of copolymer **3** was observed at −1.96 V (*vs.* SCE): this value of the electron affinity of the polymer which is close to the value of the extraction potential of magnesium $E^0(Mg^{2+}/Mg) = -2$ V indicates a good compatibility of the thienylene–dialkoxyphenylene copolymer and magnesium as electrode material; this property is of interest for electroluminescent diodes.

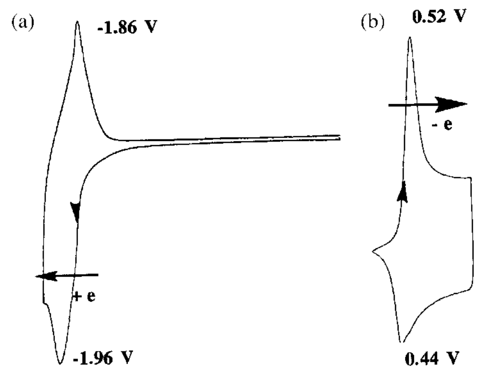

Fig. 6 Cyclic voltammetry of copolymer **3** (thin film on a platinum electrode) in CH_3CN using Bu_4NPF_6 as supporting electrolyte (0.1 M) (reference SCE, sweep rate 50 mV s^{-1}): (a) in the range −2 to 0 V;[6] (b) in the range 0–0.9 V.

A blue–red reversible electrochromism was associated to the redox behavior. The absorption spectra were recorded for a film of copolymer **3** deposited from a 10^{-3} M solution in $CHCl_3$ on an ITO glass support at potentials varying between 0.3 and 0.9 V. The changes in the absorption spectrum as a function of the applied potential are shown in Fig. 7. In its

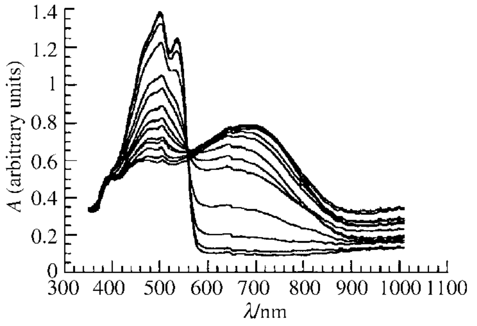

Fig. 7 Variation of the absorption spectrum of a film of copolymer **3** on an ITO support as a function of the applied potential in the range 0–0.75 V by steps of 0.05 V (solvent CH_3CN, supporting electrolyte Bu_4NPF_6).

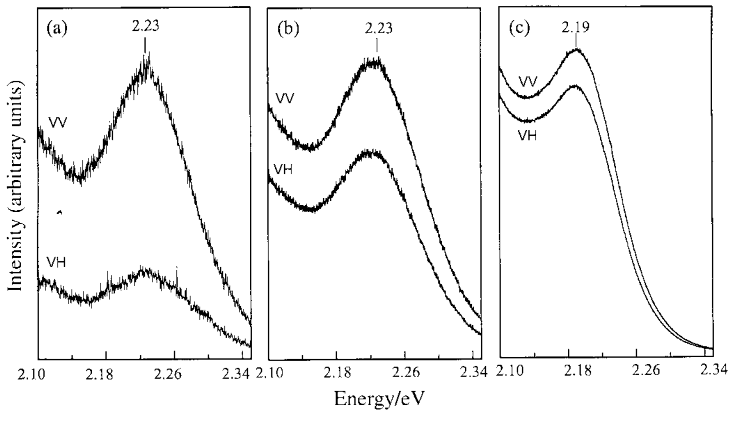

Fig. 5 Photoluminescence spectra of films of copolymer **3** at room temperature ($\lambda_{ex} = 514.5$ nm) with the polarizer parallel (VV curve) and normal (VH curve) to the rubbing direction: (a) thin film (5 nm); (b) 5 nm < thickness film < 100 nm; (c) thick film (100 nm).

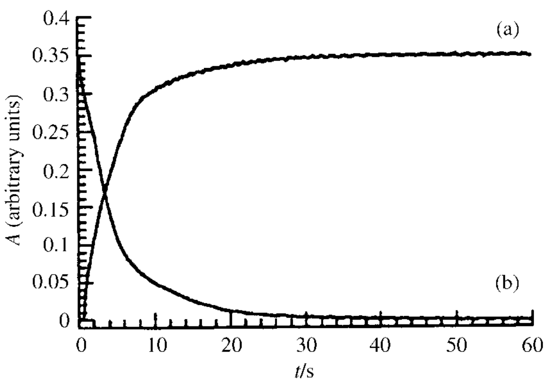

Fig. 8 Variation of the absorbance of copolymer **3** at 700 (a) and at 497 nm (b) at the beginning of the experiment ($t = 0$ s) when the polymer is deposited on a glass electrode at a potential of 0.8 V *vs.* SCE.

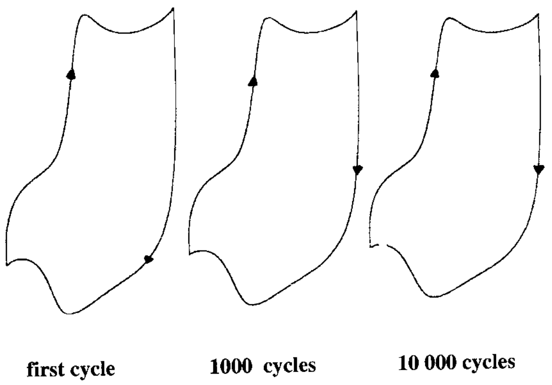

Fig. 10 Cyclic voltammetry evaluation of the red–ox stability in water of a deposit of **3** on a platinum electrode (reference electrode SCE, supporting electrolyte $LiClO_4$; sweep rate 50 mV s^{-1}).

neutral form (before oxidation) the spectrum of the polymer showed a single band at 497 nm associated to an interband transition. Upon oxidation the absorption shifts to 700 nm. This new band is associated to the appearance of bipolaronic states in the gap. The existence of an isosbestic point in the various spectra in Fig. 7 shows that only two absorption bands at 497 and at 700 nm are involved. The variation of the absorbance as a function of time is shown in Fig. 8. The kinetics of the phenomenon are slow and a relatively long coloration time ($t_{1/2} = 3.1$ s) was observed. We also studied for comparison the behavior of polythiophenes in similar experiments which showed a similar electrochromic behavior.[32]

Interestingly the observed reversible electrochromism appeared quite stable with time in the case of copolymer **3**. It was not observed in the case of polythiophene. As shown in Fig. 9(b), the cyclic voltammogram remained unchanged after more than 100 red–ox cycles. The lowering of the electroactive behavior as measured by the $\Delta i/i$ variation in intensity during cyclic voltammetry was only 1% after 2000 red–ox cycles between 0 and 0.8 V (*vs.* SCE). The variation in intensity is shown in Fig. 9(a) and in the case of **3** the $\Delta i/i$ value remained constant with time. The cyclic voltammetry of poly(3-alkylthiophene)s reported in Fig. 9(a) shows a rapid decrease in intensity after a few red–ox cycles. The remarkable stability of **3** is probably associated to its low oxidation potential (0.52 V *vs.* SCE) which avoids degradation of the material at high potential probably by an overoxidation of the organic polymer.[42,43] On the other hand, a reversible swelling of the doping anion occurs during the oxidation–reduction cycles. This can lead to mechanical strain at the interface between the electrode and the polymer. Owing to its high adhesion properties the film of polymer **3** showed a much higher stability than a film of poly(3-alkylthiophene)s. Degradation of the latter occurred rapidly during the red–ox cycles.

Moreover, owing to its low anodic oxidation potential and because of the hydrophilicity brought by the presence of diether substituents on the phenyl ring, the electrochemical and electrochromic properties of polymer **3** have been investigated in an aqueous medium in the presence of $LiClO_4$ as the supporting electrolyte. The electroactivity of polymer **3** was the same in water and in CH_3CN. It remained unchanged even after 10 000 red–ox cycles (Fig. 10). It is quite interesting that the conjugated polymer **3** exhibits such stability and electroactivity in water. The electrochromic behavior of polymer **3** in water is similar to that observed in CH_3CN; a blue–red electrochromism is found at $\lambda = 497$ nm in the neutral form and at $\lambda = 700$ nm in the doped state.

Conclusion

Using a Pd^0 catalysed coupling reaction the preparation of a regularly alternating (thienylene–dialkoxyphenylene) copolymer has been achieved. The introduction of diether side-chains in the copolymer structure provided the material with good ability to form films on a support (glass or electrode). The polymer exhibited interesting optical properties. The fluore-

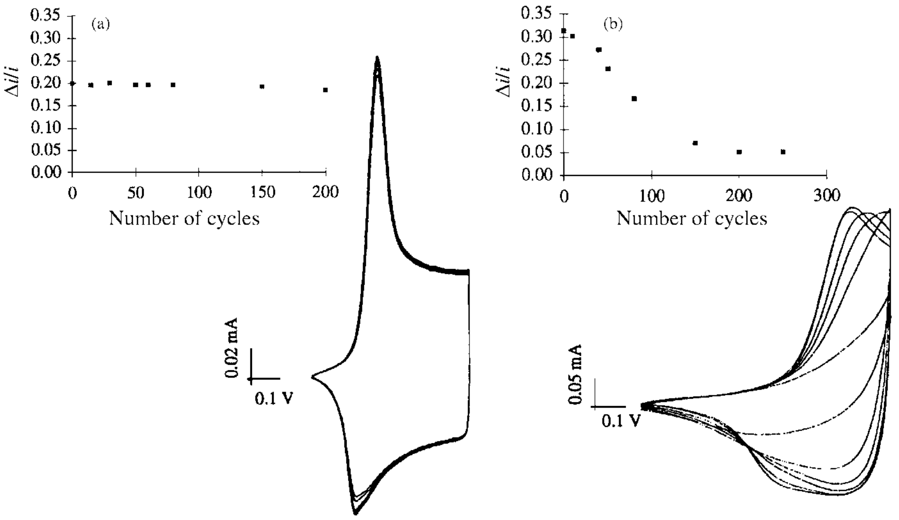

Fig. 9 Compared stabilities by cyclic voltammetry of the electrochromic red–ox system of copolymer **3** (a) and of poly(3-octylthiopene) (b) thin film of polymer on a platinum electrode; reference SCE; solvent CH_3CN; supporting electrolyte Bu_4NPF_6; sweep rate 50 mV s^{-1}).

scence properties of films of polymer **3** were recorded in solution and in the solid state. A high quantum yield of fluorescence is observed in solution. Orientation of the polymer chains was successfully achieved by interaction with a Teflon–glass support in the case of thin films. It resulted in a significant polarization of the emission for the material. Moreover, the thienylene–dialkoxyphenylene copolymer exhibited highly stable electroactive properties. A blue–red reversible and highly stable electrochromism is observed at a low value of the oxidation potential. The electrochromic performance remains unchanged even in an aqueous medium. The optical and electrochemical properties of this new material are improved compared to those of poly(3-alkylthiophene)s. The thienylene–dialkoxyphenylene copolymer could be a good candidate for applications in the field of optical devices.

Experimental

$CHCl_3$, THF, DMF and hexane (SDS) were dried by distillation over phosphorus pentaoxide, sodium–benzophenone and CaH_2 respectively. 2-Butoxyethanol and tributyltin chloride (Aldrich) were used without further purification.

^1H NMR spectra were recorded in $CDCl_3$ at 200 MHz with a Bruker AC 200 spectrometer, using residual $CHCl_3$ (δ 7.27) as the internal standard, ^{13}C NMR spectra at 50.32 MHz with a Bruker AC 200 using $CDCl_3$ (δ 77.70) as the internal standard and IR spectra with a Perkin-Elmer 1000 spectrometer. Melting points were measured with an Electrothermal 9100 apparatus. Absorption spectra were recorded on a MC^2 Safas spectrometer and emission spectra on a SLM-Aminco MC 200 spectrometer. Fluorescence quantum yields were measured by the standard procedure.[44] GPC measurements were made on a Waters device equipped with HR_2 and HR_3 Styragel columns. Cyclic voltammetry was performed on an EGG potentiostat connected to a Kipp & Zonen tracer. Electrochromism measurements were made in a three electrode (ITO, Pt, Ag) spectroelectrochemical cell[45] connected to an EGG 362 potentiostat. Atomic force microscopy (AFM) measurements were made on a Digital Instrument Microscope D3100. EDAX measurements were carried out using a Cambridge 360-stereoscan with an EDS-Link AN 10000 attachment. Raman spectra were recorded using a Jobin-Yvon T64000 spectrometer equipped with a liquid nitrogen cooled CCD detector. The measurements were performed in the back scattering configuration using an Ar-ion laser (Spectra Physics 2000) with 514.5 nm exciting radiation and take into account the dependence of the detection with respect to the fluorescence polarization. All spectra were recorded under vacuum to avoid degradation of the sample.

Preparations

2,5-Bis(tributylstannyl)thiophene (**1**) was obtained as described.[46]

1,4-Bis (butoxyethoxy) benzene(4). To a Schlenk tube containing 50 mL of 2-butoxyethanol were slowly added in small fractions 2.07 g (1.09 mol) of sodium, 7.07 g (0.03 mol) of *p*-dibromobenzene, 2.5 g (0.032 mol) of CuO and 0.1 g (0.3×10^{-3} mol) of KI. The mixture was then heated at 100 °C for 24 hours. After cooling it was filtered over Celite, the solvent evaporated under vacuum and the residue extracted with diethyl ether. After elimination of the ether, the product was recrystallized from ethanol to give colorless crystals in 20% yield. Mp 28–29 °C. Found: C, 69.67; H, 9.76; O, 20.59%. $C_{18}H_{30}O_4$ requires C, 69.64; H, 9.74; O, 20.61%. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.92 (6 H, t, 2 CH_3), 1.37 (4 H, m, 2 CH_2), 1.55 (4 H, m, 2 CH_2), 3.52 (4 H, t, 2 CH_2), 3.74 (4 H, t, 2 OCH_2), 4.06 (4 H, t, 2 OCH_2), 6.84 (4 H, s, 4 CH_{ar}). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 13.93 (2 CH_3), 19.27 , 31.72 (4 CH_2), 68.08, 69.29, 71.37 (6 OCH_2), 115.58 (4 CH), 153.15 (2 C).

1,4-Dibromo-2,5-bis(butoxyethoxy)benzene (2). 1.88 g (0.0060 mol) of compound **4** in solution in 10 mL of carbon tetrachloride were placed in a 100 mL magnetically stirred three-necked flask equipped with a condenser and an isobar dropping funnel. Br_2 (0.62 mL, 0.0121 mol) was added dropwise from the funnel at room temperature. The mixture was stirred for 3 hours at room temperature and then treated with 15 mL of a 20% solution of KOH in water. After three extractions with ether, the organic layers were dried over magnesium sulfate, concentrated *in vacuo* and the residual solid was recrystallized with ethanol to give colorless plates in 61% yield. Mp 42.5–43.8 °C. Found: C, 46.18; H, 6.04; O, 13.64%. $C_{18}H_{28}O_4Br_2$ requires C, 46.17; H, 6.02; O, 13.67%. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.90 (6 H, t, 2 CH_3), 1.37 (4 H, m, 2 CH_2), 1.59 (4 H, m, 2 CH_2), 3.54 (4 H, t, 2 CH_2), 3.77 (4 H, t, 2 OCH_2), 4.10 (4 H, t, 2 OCH_2), 7.15 (2 H, s, 2 CH_{ar}). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 13.93 (2 CH_3), 19.28, 31.79 (4 CH_2), 69.06, 70.23, 71.52 (6 OCH_2), 111.40 (2 C, C1, C4), 119.27 (2 CH, C3, C6), 150.38 (2 C, C2, C5).

Tetrakis(triphenylphosphine)palladium was prepared according to the literature.[47]

Copolymer (3). In a 50 mL Schlenk tube equipped with a condenser were dissolved under a nitrogen atmosphere and at room temperature 0.0115 g (10^{-5} mol) of $Pd(PPh_3)_4$ in 10 mL of THF–DMF (50 : 50). 0.662 g (10^{-3} mol) of **1** and 0.4588 g (10^{-3} mol) of **2** were introduced by a syringe. The reaction mixture was stirred at 80 °C during three days. Heating was then stopped and a red precipitate formed upon adding acetone. The powder was filtered off, washed with acetone and dried *in vacuo* to give 0.427 g of **3** (yield: 90%). The polymer had average molecular weight $M_w = 21\,464$ and $M_n = 12\,049$ with a polydispersity index of 1.78 determined by GPC analysis. Found: C, 66.97; H, 7.69; S, 8.19. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.92 (6 H, t, 2 CH_3), 1.43 (4 H, m, 2 CH_2), 1.63 (4 H, t, 2 CH_2), 3.58 (4 H, t, 2 OCH_2), 3.91 (4 H, t, 2 OCH_2), 4.30 (4 H, t, 2 OCH_2), 7.34 (2 H, s, 2 $CH_{Thienyl}$) and 7.63 (2 H, s, CH_{ar}). ν_{max} (KBr)/cm^{-1}: 3071, 2958, 2928, 2865, 1600, 1537, 1492, 1450, 1405, 1262, 1215, 1119, 1060, 847 and 796. Absorption: λ_{max} ($CHCl_3$) (ε_{max}/l mol^{-1} cm^{-1}) 460 (25 390), (film on glass) 497 nm. Emission: λ_{max} ($CHCl_3$) 521, λ_{max} (film on glass) 569 nm.

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Paper a909155f