

Synthesis, Characterization, and Processing of New Electroactive and Photoactive Polyesters Derived from Oligothiophenes

Anne Donat-Bouillud,[†] Louise Mazerolle,[†] Paul Gagnon,[†] Leonid Goldenberg,[‡]
Michael C. Petty,[‡] and Mario Leclerc^{*,†,‡}

Département de Chimie, Université de Montréal, Montréal, Québec, Canada H3C 3J7, and
School of Engineering and Centre for Molecular Electronics, University of Durham,
Durham, UK DH1 3LE

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Synthesis of various polyesters involving oligothiophene (2–5) units has led to materials exhibiting a good processability together with tunable absorption (from 342 to 428 nm) and fluorescence (from 411 to 558 nm) properties. It has been also found that polyesters with quaterthiophene or pentathiophene units show some electroactivity affording the formation of radical cations and dimerized radical cations, while pentathiophene units even permit the formation of negative charge carriers. The presence of these charge carriers increases dramatically the conductivity to values up to 0.4 S/cm in both oxidized and reduced states. This good electrical transport of both p-type and n-type charge carriers combined with luminescent properties and Langmuir–Blodgett processability could lead to well-organized and efficient light-emitting devices.

Introduction

Conjugated polymers (e.g., polyacetylenes, polypyrroles, polythiophenes, polyanilines, etc.) exhibit interesting properties for the development of lightweight batteries, electrochromic display devices, light-emitting diodes, optical switches, etc.^{1–4} On the other hand, studies on oligothiophenes have revealed that about 6–7 repeat units are necessary to get similar electrical, electrochemical, and optical (linear and nonlinear) properties as those obtained with their corresponding high molecular weight analogues.^{5–9} These features can be related to a saturation of the effective conjugation length. In addition, the characterization of various oligomers has led to a better knowledge, at a molecular level, of the structure–property relationships in this class of materials. For instance, ideal electrochemical and spectroscopic properties of conjugated polymers have been tackled by means of well-defined oligomers as model compounds. In the case of oligothiophenes, it has been clearly shown that these molecules can exhibit multiple redox processes which are related to a stepwise formation of radical cations, dimerized radical cations

(π -stacked radical cations), and dications.^{6–9} In principle, these different charge carriers can lead to paramagnetic or diamagnetic conducting (through interchain transport) materials.

Moreover, the use of oligomers with different conjugation lengths and substituents allows the molecular design of a large variety of materials with tunable linear (absorption and luminescence) and nonlinear optical properties. For instance, the synthesis of well-defined chromophores with controlled absorption bands in the UV–visible range should lead to materials with interesting nonlinear optical properties combined with a low absorption in the near-infrared range. Moreover, it has been also predicted that a sharpening of the absorption band should lead to a large increase of the third-order nonlinear susceptibility.¹⁰ However, it is clear that the mechanical properties and thermal stability of these oligomers are rather poor. It is therefore interesting to incorporate well-defined oligomers in a polymeric chain to yield polymers with isolated electroactive and photoactive moieties. These materials combine the good mechanical properties and processability of high molecular weight polymers to the interesting and tunable electrical, electrochemical, and optical properties of the conjugated moieties.^{11–15} In this regard, we report here the synthesis and characterization of new polyesters derived from oligothiophenes (Chart 1). It is expected

[†] Université de Montréal.

[‡] University of Durham.

* To whom correspondence should be addressed.

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(1) Brédas, J. L., Silbey, R., Eds., *Conjugated Polymers*, Kluwer: Dordrecht, 1990.

(2) Kanatzidis, M. G. *Chem. Eng. News* **1990**, 68, 8 (49), 36.

(3) Miller, J. S. *Adv. Mater.* **1993**, 5, 671.

(4) Burroughes, J. H.; Bradley, D. C. C.; Brown, A. R.; Marks, R. N.; McKay, K.; Friend, R. H.; Burns, P. N.; Holmes, R. B. *Nature* **1990**, 341, 539.

(5) Wynberg, W.; ten Hoeve, Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, 113, 5887.

(6) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, 4, 1106.

(7) Bäuerle, P.; Segelbacher, U.; Maier, A.; Mehring M. *J. Am. Chem. Soc.* **1993**, 115, 10217.

(8) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M. *J. Am. Chem. Soc.* **1993**, 115, 1869.

(9) Sato, M.; Hiroi, M. *Polymer* **1996**, 37, 1685.

(10) Yoshimura, T. *Opt. Commun.* **1988**, 70, 535.

(11) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, 26, 1188.

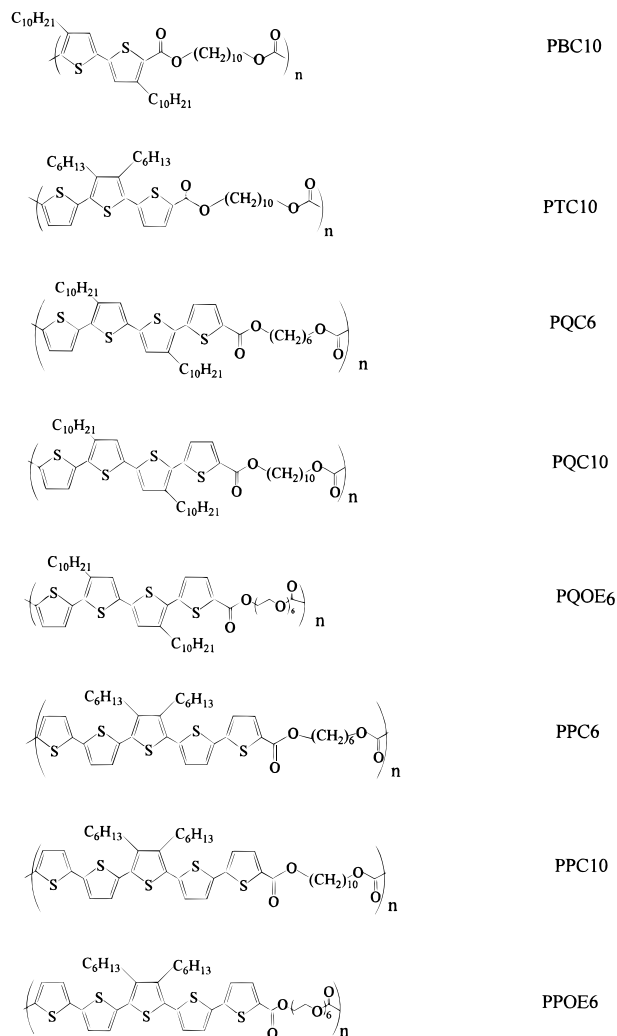
(12) von Seggern, H.; Schmidt-Winkel, P.; Zhang, C.; Schmidt, H. W. *Macromol. Chem. Phys.* **1994**, 195, 2023.

(13) Herrema, J. K.; van Hutten, P. F.; Gill, R. E.; Wildeman, J.; Wieringa, R. H.; Hadziioannou, G. *Macromolecules* **1995**, 28, 8102.

(14) Remmers, M.; Neher, D.; Gruner, J.; Friend, R. H.; Gelinck, G. H.; Warman, J. M.; Quatrocchi, C.; dos Santos, D. A.; Bredas, J. L. *Macromolecules* **1996**, 29, 7432.

(15) Belletête, M.; Mazerolle, L.; Desrosiers, N.; Leclerc, M.; Durocher, G. *Macromolecules* **1995**, 28, 8587.

Chart 1



that the presence of the electron-withdrawing ester groups in the α, α' -positions of the luminescent oligothiophene moieties could enhance their electron affinity and could allow the electrical transport of both p-type and n-type charge carriers.^{15,16} All these properties should also make these polymers good candidates for applications in light-emitting devices.

Results and Discussion

Different polyesters have been obtained, in good yields, from melt polymerization between oligothiophene-dicarbonyl dichlorides and various aliphatic diols. As an example, Scheme 1 describes all the synthetic steps involved in the preparation of PPC10. All resulting polymers are soluble in chloroform and can form free-standing or spin-coated films. NMR analyses revealed a well-defined structure for all polymers. The molecular weight and thermal transitions of the polymers have been also characterized and are reported in Table 1. Most polymers exhibit a relatively high molecular weight with a polydispersity index (M_w/M_n) around 2. These polydispersity indexes are consistent with a polycondensation reaction. These aromatic-aliphatic polyesters show thermal transitions at rela-

Table 1. Molecular Weight and Thermal Properties of the Polymers

polymers	M_w	M_w/M_n	T_g (°C)	T_m (°C)
PBC10	17 500	1.6	-28	34
PTC10	38 600	1.6	-5	<i>a</i>
PQC6	15 000	3.5	-8	<i>a</i>
PQC10	49 000	1.6	-8	65
PQOE6	38 000	1.8	-23	-8
PPOE6	6 200	2.1	-5	<i>a</i>
PPC6	11 000	2.2	20	110
PPC10	16 300	3.1	31	62

^a No melting transition observed.

Table 2. Photophysical Properties of the Polymers in Chloroform Solution

polymer	abs max wavelength (nm)	emission max fluorescence (nm)	quantum yield
PBC10	342	411	0.07
PTC10	378	478	0.07
PQC6	414	527	0.11
PQC10	410	525	0.11
PQOE6	412	527	0.11
PPC6	426	558	0.14
PPC10	428	557	0.10
PPOE6	424	556	0.10

tively low temperatures. In particular, the use of the flexible hexaethylene glycol spacer gives materials with low glass transition temperatures. However, the synthesis of polyamides could be done to get access to materials with higher glass transition and melting temperatures.

As expected, in chloroform, the maximum of absorption in the UV-visible range goes to longer wavelengths as the conjugation length (the number of consecutive thiophene units) increases (Table 2). As mentioned in the introduction, it can be assumed that a saturation effect could take place with 6–7 thiophene units.^{5–9} A similar trend is also observed for the emission properties in chloroform although the quantum yield values remain almost constant. All these photophysical results are consistent with those previously reported by Hadziioannou et al.¹³ for multiblock alternating copolymers derived from poly[(silanylene)thiophene]s. From previous studies on oligothiophenes and polymers derived from thiophenes,¹⁵ these relatively low fluorescence yields could be explained by a radiationless torsional mechanism and intersystem crossing processes. A more complete analysis of the photophysical and light-emitting properties of these materials will be the subject of a separate study. However, all the optical features of these polyesters in solution are in the same range as those obtained with their corresponding oligomeric precursors, indicating that the chromophores are isolated within the polymeric chain.

On the other hand, these chromophores derived from oligothiophenes are also susceptible to showing some electroactivity. The electrochemical properties were not characterized in previous studies on polymers bearing separated oligothiophene units along the main chain,^{13,15} and solid-state cyclic voltammetry has been used in the present work to verify this point (Table 3). Polyesters with bithiophene or terthiophene units can be oxidized, but this redox process is not reversible and these polymers do not show any electroactivity after the first scan. These oxidation potentials observed for PBC10 and PTC10 are relatively high for materials involving bithiophene or terthiophene derivatives but these re-

(16) Demanze, F.; Cornil, J.; Garnier, F.; Horowitz, G.; Valat, P.; Yassar, A.; Lazzaroni, R.; Bredas, J. L. *J. Phys. Chem. B* **1997**, *101*, 4553 and references therein.

Scheme 1

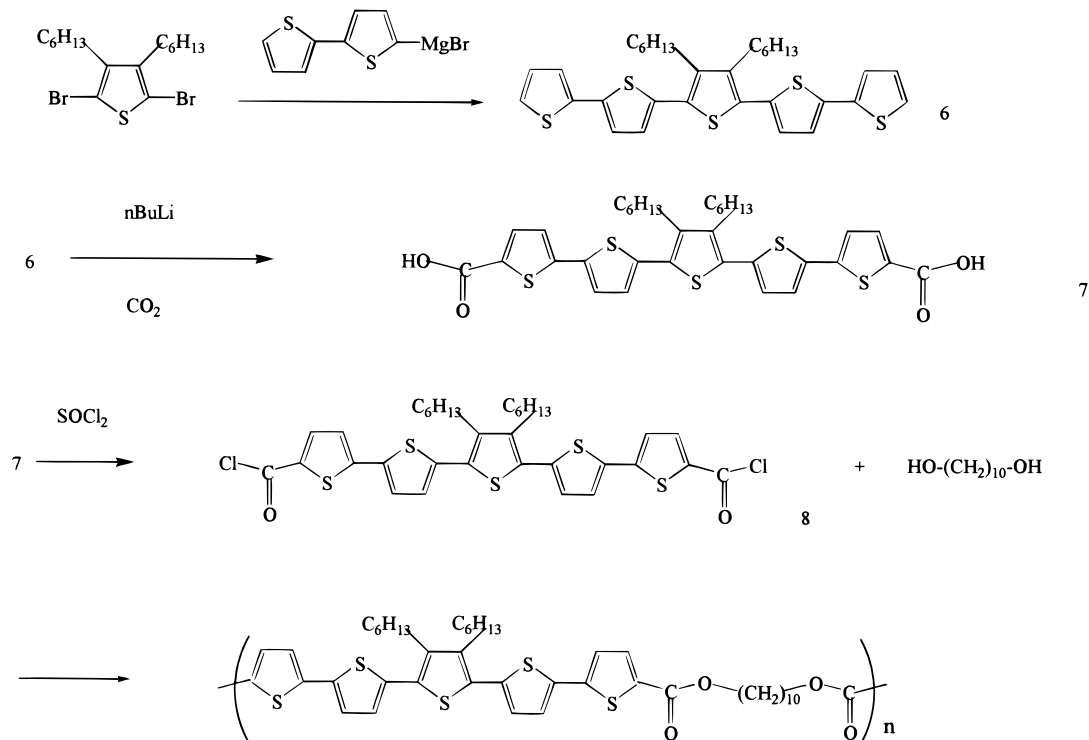


Table 3. Electrochemical Properties of the Polymers in the Solid State

polymer	E_{ox} (V vs SCE)	E_{red} (V vs SCE)
PBC10	1.60 ^a	
PTC10	1.47 ^a	
PQC10	1.26	
PQOE6	1.07	
PPC10	1.06	-1.80
PPOE6	0.96	-1.72

^aIrreversible.

sults can be easily explained by the strong electron-withdrawing effect of the carboxylate units. The high oxidation potentials and small conjugation length can explain the instability of the charge carriers in these polyesters. However, with four conjugated thiophene units, the polyesters can be reversibly oxidized (Figure 1). It is worth noting here that polyesters with hexaethylene glycol spacer groups show lower oxidation potentials which could be related to a better permeability to the counterions. Moreover, upon oxidation, the neutral yellow PQC10 and PQOE6 undergo a strong modification of their electronic structure giving a blue color to the polymer films. This strong electrochromism is related to the formation of stable charge carriers. As shown in Figure 2, at 1.10 V vs SCE, the UV-vis-NIR absorption spectrum of PQC10 shows two new absorption bands around 680 and 1090 nm, while the intensity of the main absorption peak at 420 nm (characteristic of the neutral form) decreases. Around 1.17–1.20 V, two additional absorption bands are then clearly observed near 580 and 1080 nm. All these new optical features could be explained by the formation of radical cations followed by the formation of dimerized radical cations (possibly related to a π -stacking of the electroactive units). These conclusions agree with the results recently reported by Miller et al.¹⁷ for a similar polymer in solution. However, it is clear that in situ solid-state ESR measurements could give more information about

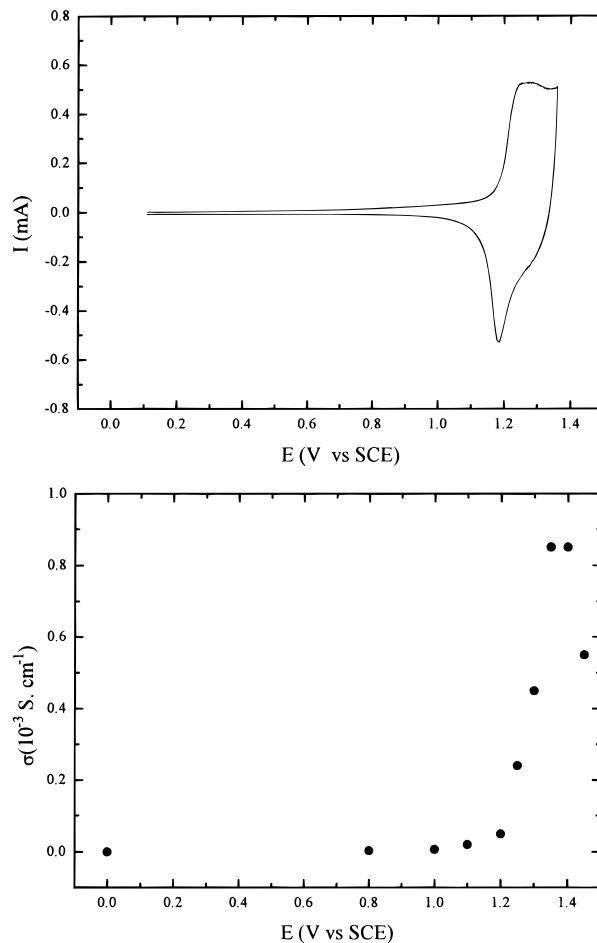


Figure 1. Cyclic voltammogram (solid line) and in situ conductivity of PQC10.

the nature of these charge carriers. The electrochemical generation of these charge carriers leads to conductivity values up to ca. 1×10^{-3} S/cm (Figure 1).

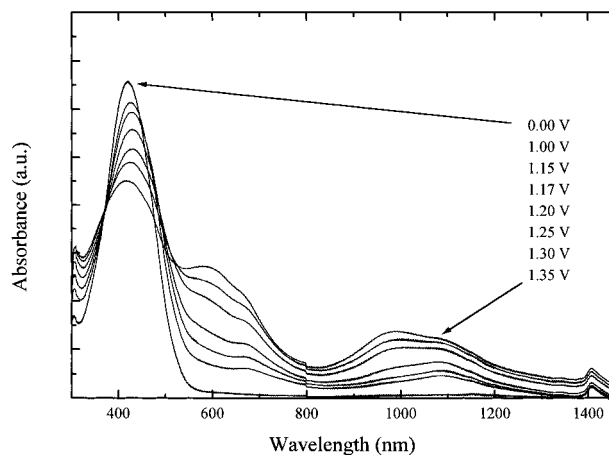


Figure 2. UV-vis-NIR absorption spectra of PQC10 at various electrochemical potentials vs SCE.

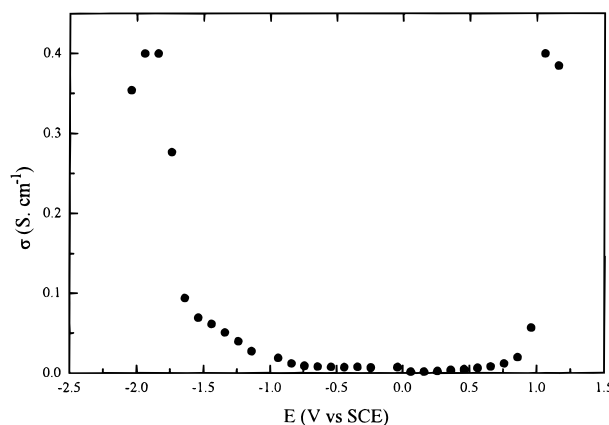
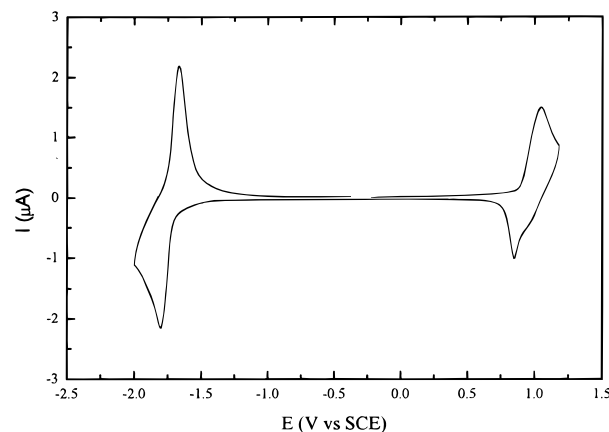


Figure 3. Cyclic voltammogram (solid line) and in situ conductivity of PPC10.

Furthermore, polyesters with five conjugated thiophene units, such as PPC10 (and PPOE6), not only can be reversibly oxidized but also shows some reversible electroactivity upon reduction (Figure 3). Usually, polythiophenes are not easily n-doped,^{18,19} and it seems that the presence of electron-withdrawing carboxylate groups stabilizes the negative charge carriers created upon reduction. As mentioned in the Introduction, the combination of luminescence properties with good electrical transport for both positive and negative charge

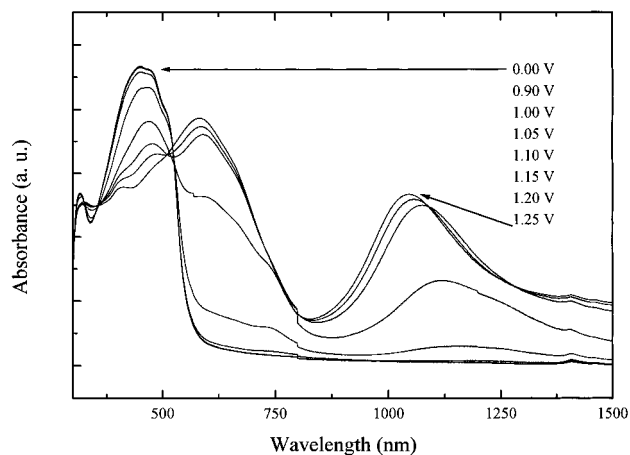


Figure 4. UV-vis-NIR absorption spectra during oxidation of PPC10 at various electrochemical potentials vs SCE.

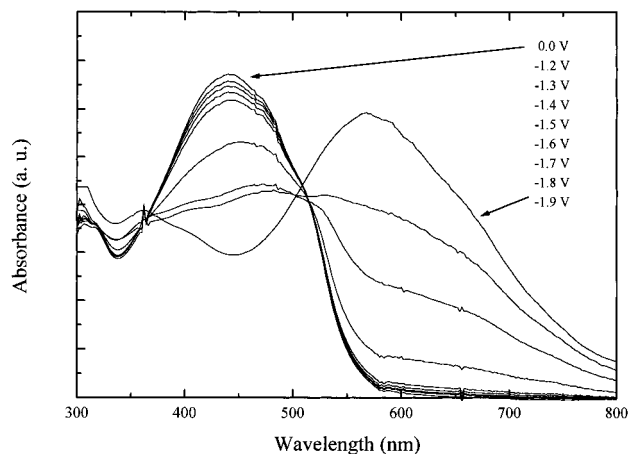


Figure 5. UV-vis-NIR absorption spectra during reduction of PPC10 at various electrochemical potentials vs SCE.

carriers could be particularly useful for the development of efficient light-emitting diodes. In correlation with these redox processes, PPC10 exhibits a strong and reversible electrochromism (from orange to blue). Near 0.9 V vs SCE, this polymer shows two new absorption bands around 740 and 1150 nm (Figure 4). Upon further oxidation, two additional absorption bands appear near 590 and 1040 nm. Once again, these absorption bands could be related to the formation of radical cations and dimerized radical cations. Symmetrically, negative charge carriers (radical anions and/or dimerized radical anions) are created upon reduction with essentially the same absorption features than their positive analogues (Figure 5). In addition to the modification of the UV-vis-NIR absorption features of these polymers, the formation of such charge carriers strongly modifies their electrical properties. For instance, Figure 3 shows the cyclic voltammogram and the correlated in situ conductivity of PPC10. These data clearly indicate that a good electrical transport (conductivities up to 0.4 S/cm) is possible in both oxidized and reduced states. These results as well as those reported above for PQC10 and for a similar polymer by Hong and Miller¹⁷ give clear evidence that a hopping mechanism between localized states can also lead to significant electrical conductivities.

Moreover, in the absence of any electric field, these separated electroactive moieties can be compared to a regular alignment of quantum wells along a back-

(17) Hong, Y.; Miller, L. L. *Chem. Mater.* **1995**, *7*, 1999.

(18) Guerrero, D. J.; Ren, X.; Ferraris, J. P. *Chem. Mater.* **1994**, *6*, 1437.

(19) Zotti, G.; Schiavon, G. *Synth. Met.* **1994**, *63*, 53.

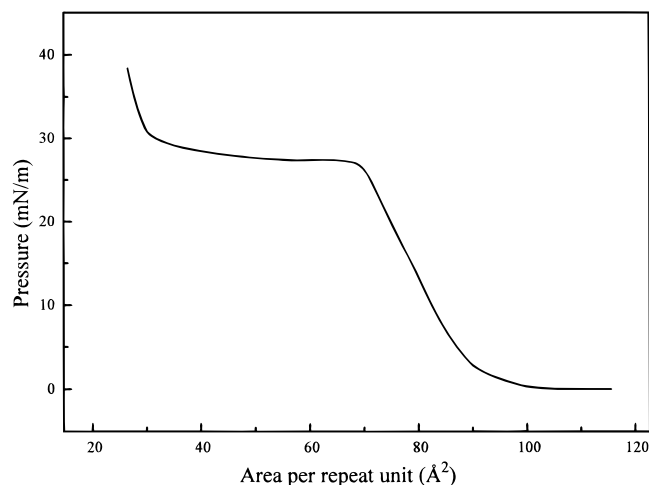


Figure 6. Surface pressure vs area per repeat unit isotherm for PPOE6.

bone.^{20–22} As shown above, the depth and length of these quantum wells are determined by the nature of the oligothiophenes; in the present cases, the finite size of the electroactive moieties allow only the formation of radical cations. The difference between the neutral (0) and the oxidized (1) (or reduced) states can be then used to electrochemically store and read some information at a molecular level. For this purpose, the preparation of well-defined monolayers of the electroactive polyesters was investigated using the Langmuir–Blodgett technique. All electroactive polymers formed monolayers at the air–water interface but, in terms of stability and transfer ratios, best results were obtained with the amphiphilic PPOE6. This polymer exhibits an isotherm with an extrapolated molecular area per repeat unit of 0.90 nm^2 (Figure 6). Monolayer and multilayers (up to 30) have been built on ITO substrates by Y-deposition using a dipping pressure of 25 mN m^{-1} . The transfer ratio was between 0.9 and 1.1 and the thickness of one monolayer is 3 nm with an absorbance of $30\,000 \text{ cm}^{-1}$ at 425 nm. All these results are particularly promising for the development of well-defined electrochemical and electrooptical devices, and these ultrathin films are currently being investigated by AFM and STM techniques.

Conclusion

The incorporation of oligothiophene moieties into polymeric structures has permitted the preparation of tunable electroactive and/or photoactive processable materials with good mechanical properties. Polyesters with bithiophene or terthiophene units show interesting emissive properties in the blue range whereas, in addition to interesting photophysical properties, polymers with quaterthiophene moieties exhibit a reversible redox process which leads to the formation of radical cations. Furthermore, polyesters derived from pentathiophenes show conductivities up to 0.4 S/cm in both the oxidized and reduced states. These results clearly indicate for the first time that both p-type and n-type charge transport hopping (possibly through oligothio-

phene π -stacks) can also lead to interesting electrical conductivity levels. Finally, these polyesters with a regular arrangement of electroactive and photoactive units may lead to the development of well-defined and efficient light-emitting devices.

Experimental Section

Physical Characterization. FTIR measurements were carried out on a Bio-Rad FTS-25 apparatus. NMR measurements were performed with a Varian VXR-400 or -300 spectrometer. Size exclusion chromatography (SEC) measurements were carried out with a Waters apparatus using a series of three Ultrastaygel columns with upper porosity of 10, 50, and 100 nm in tetrahydrofuran. The calibration curve was obtained by running monodisperse polystyrene standards. Thermal characterization of the polymers was obtained with a DSC (TA Instrument, DSC 2910) at a heating rate of $10 \text{ }^\circ\text{C/min}$ under a helium flow. The absorption spectra were recorded on a Hewlett-Packard diode array UV–vis spectrophotometer (Model 8452A) using 1-cm quartz cells from polymer solutions ($(1–3) \times 10^{-5} \text{ M}$) in chloroform. Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrophotometer with an F2T11 special configuration. Each solution was excited at the absorption wavelength maximum using a 1-cm path quartz cell and the concentration used for each polymer was $(1–3) \times 10^{-6} \text{ M}$ in chloroform, giving absorbances always less than 0.06 to avoid any inner filter effect. The quantum yields of fluorescence were determined in argon-saturated solutions at 298 K against 9,10-diphenylanthracene in cyclohexane as standard.¹⁵ All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra. Cyclic voltammetry was carried out in a helium-filled glovebox with an one-compartment cell using an EG&G potentiostat (Model 273) with platinum electrodes (a thin polymer film was cast on the working electrode) at a scan rate of 100 mV/s . The electrolyte was made of 0.1 M tetrabutylammonium hexafluorophosphate or 0.1 M tetraethylammonium tetrafluoroborate in dry acetonitrile. A nonaqueous Ag quasi-reference electrode was used for these experiments and finally corrected to a SCE electrode. In situ spectroelectrochemical measurements were performed using an indium tin oxide (ITO) working electrode and the same electrochemical system. The electrochemical cell was an 1-cm quartz cell put in a Cary 5 UV–vis–NIR spectrophotometer. The spectra were recorded after the stabilization of the desired electrochemical potentials. In situ conductivity measurements were carried out with a two-band microelectrode in solutions of 0.1 M tetrabutylammonium hexafluorophosphate or of 0.1 M tetraethylammonium tetrafluoroborate in acetonitrile according to a procedure described elsewhere.²³ Four-probe (ex situ) conductivity measurements were carried out on FeCl_3 -doped polymers at room temperature in air. Chemical doping was performed by soaking the neutral polyester in a suspension of iron trichloride in chloroform. Plots of conductivity vs the electrochemical potential were calibrated using the conductivity value obtained from the four-probe technique with FeCl_3 -oxidized polymers (ca. 1.10 V vs SCE).²³ This method of calibration is based on the relative independence of the conductivity upon the nature of the counterion (BF_4^- or PF_6^- vs FeCl_4^-) and can give accurate conductivity values within 1 order of magnitude.

For Langmuir–Blodgett studies, all experiments were undertaken in a Class 10 000 microelectronics clean room. The polymers were spread on the surface of ultrapure water (obtained by reverse osmosis, deionization, and ultraviolet sterilisation) from chloroform solutions (1.0 g dm^{-3}). The surface pressure versus molecular area isotherms were measured at $20 \pm 2 \text{ }^\circ\text{C}$, and compression rate ca. $5 \times 10^{-3} \text{ nm}^2 \text{ repeat unit}^{-1} \text{ s}^{-1}$. LB films were deposited onto conducting indium tin oxide (ITO, from Balzers) coated glass slides by

(20) Faïd, K.; Leclerc, M. *Chem. Mater.* **1994**, *6*, 107.

(21) Faïd, K.; Leclerc, M.; Nguyen, M.; Diaz, A. *Macromolecules* **1995**, *28*, 284.

(22) Demanze, F.; Yassar, A.; Garnier, F. *Adv. Mater.* **1995**, *7*, 907.

(23) D'Aprano, G.; Leclerc, M.; Zotti, G. *J. Electroanal. Chem.* **1993**, *351*, 145.

conventional vertical dipping techniques. A dipping speed of 3 mm min⁻¹ was employed, and the first monolayer was dipped on the upstroke when the slide was dipped in the subphase, before compression of the monolayer. To improve the hydrophilic properties of ITO, the slides were treated with saturated Na₂Cr₂O₇-concentrated H₂SO₄ solution for ca. 10 s. Film thicknesses were determined using a surface-profiling Tencor instrument Alpha-Step 200 (stylus force, 11 mg). Force these measurements, a layer of aluminum (thickness, ca. 150 nm) was evaporated over the step between the organic layer and the uncoated substrate.

Synthesis. 4,4'-Didecyl-2,2'-bithiophene-5,5'-dicarbonyl dichloride and 3,4'-dihexyl-2,2':5',2''-terthiophene-5,5''-dicarbonyl dichloride have been prepared following previously published procedures.¹⁵

4,4'-Didecyl-3,5,3',5'-tetrabromo-2,2'-bithiophene (1). To 15 mL of CHCl₃ was added 1.21 g (2.7 mmol) of 4,4'-didecyl-2,2'-bithiophene¹⁵ in a 100 mL flask. Once solubilized, 0.67 mL (13.5 mmol) of bromine (Aldrich) was added in the dark. The mixture was stirred for 3 h and then quenched with 50 mL of an aqueous 1 M NaOH solution. The crude product was washed with water and dried with MgSO₄. The product was purified by flash chromatography with hexanes as eluent (yield 98%). ¹H NMR (400 MHz, CDCl₃, ppm) 0.89 (6H, t), 1.3 (28H, m), 1.6 (4H, m), 2.7 (4H, t). ¹³C NMR (100 MHz, CDCl₃, ppm) 14.13, 22.68, 28.54, 29.34, 29.35, 29.55, 29.60, 30.30, 31.90, 111.0, 114.47, 128.57, 141.39.

4,3''-Dibromo-3',4''-didecyl-2,2';5',2'';5''',2''''-quaterthiophene. To 50 mL of dry diethyl ether was added 0.650 g (26.5 μmol) of magnesium in a 100 mL flask under nitrogen. Then, 5.56 g (26 mmol) of 2-iodothiophene (Aldrich) was added dropwise. The mixture was stirred until all magnesium disappeared. The mixture was then transferred to a 250 mL three-necked flask containing 5.04 g (6.62 mmol) of **1** and 70 mg of PdCl₂(dppf) (PdCl₂-1,1'-bis(diphenylphosphine)ferrocene)²⁴ in 80 mL of dry diethyl ether under nitrogen. The reaction was heated to reflux during 72 h and then quenched with distilled water. The aqueous phase was extracted with ether and the combined organic phase was washed with acidified water and then dried with MgSO₄. The crude product was purified with chromatography on silica gel with hexanes as eluent. After evaporation, a yellow-green solid was obtained with a 43% yield, mp 71–73 °C. ¹H NMR (400 MHz, CDCl₃, ppm) 0.89 (6H, t), 1.28 (28H, m), 1.65 (4H, m), 2.81 (4H, m), 7.1 (2H, t), 7.19 (2H, d), 7.38 (2H, d). ¹³C NMR (100 MHz, CDCl₃, ppm) 14.02, 22.58, 29.17, 29.25, 29.48, 29.50, 29.54, 29.59, 31.81, 116.17, 126.28, 126.59, 127.05, 127.39, 132.40, 134.9, 138.65.

3',4''-Didecyl-2,2';5',2''; 5''',2''''-quaterthiophene (3). To 1.30 g (1.7 mmol) of **2** in 20 mL of dry diethyl ether in a 50 mL three necked flask under nitrogen at 0 °C, 6.5 mL (16.2 mmol) of BuLi (2.5 M) was added dropwise, and then the reaction mixture was allowed to warm to room temperature for 2 h before distilled water was added. The crude product was washed with water and dried with MgSO₄. This gives an orange-brown solid (yield 97%), mp = 56 °C. ¹H NMR (400 MHz, CDCl₃, ppm) 0.86 (6H, t), 1.3 (28 H, m), 1.58 (m, 4H), 2.65 (4H, m), 7.00 (2H, s), 7.08 (2H, m), 7.13 (2H, m), 7.32 (2H, m). ¹³C NMR (100 MHz, CDCl₃, ppm) 14.09, 22.70, 29.32, 29.37, 29.46, 29.54, 29.61, 29.63, 30.46, 31.91, 124.95, 125.46, 126.12, 127.21, 129.49, 134.77, 135.92, 140.01.

3',4''-Didecyl-2,2';5',2'';5''',2''''-quaterthiophene-5,5''-dicarboxylic Acid (4). At -78 °C, 1.03 mL (2.6 mmol) of BuLi (2.5 M) was added dropwise to a solution of 0.70 g (1.15 mmol) of compound **3** in 10 mL of THF. The reaction mixture was allowed to warm to 0 °C for 15 min and then cooled to -78 °C, and dry CO₂ generated by warming dry ice and passing through drying tube (concentrated H₂SO₄) was introduced. CO₂ was bubbled for 30 min at -78 °C and followed by 2 h at room temperature before 3% KOH was added. The aqueous layers was washed three times with diethyl ether. The desired product was precipitated by neutralizing the water phase with

10% HCl and collected by filtration. The filtrate was washed several times with water and dried by vacuum. Orange-red crystals were obtained with a yield of 85% (mp = 244 °C). ¹H NMR (400 MHz, THF-*d*₆, ppm) 0.88 (6H, t), 1.35 (28 H, m), 1.9 (4H, m), 3.05 (4H, t), 7.15 (4H, m), 7.65 (2H, s). ¹³C NMR (100 MHz, THF-*d*₆, ppm) 14.60, 23.70, 30.44, 30.55, 30.68, 30.72, 31.38, 33.01, 127.07, 128.25, 130.36, 134.42, 135.00, 136.65, 142.92, 143.06, 163.05.

3',4''-Didecyl-2,2';5',2'';5''',2''''-quaterthiophene-5,5''-dicarbonyl Chloride (5). In a 25 mL flask, 5 mL of benzene and 500 mg (0.7 mmol) of **4** were heated to reflux before 1.3 mL (18 mmol) of thionyl chloride was added. The mixture was kept under reflux overnight. The crude product was purified with flash chromatography on silica gel (using chloroform as eluent), yield 87%, mp = 103 °C. Elem. Anal. Calcd: %C = 62.05, %H = 6.52, %S = 17.42. Found: %C = 61.80, %H = 6.65, %S = 17.25. ¹H NMR (400 MHz, CDCl₃, ppm) 0.9 (6H, t), 1.35 (28H, m), 1.6 (4H, m), 2.9 (4H, t), 7.0 (2H, s), 7.1 (2H, d), 7.88 (2H, d). ¹³C NMR (100 MHz, CDCl₃, ppm) 14.0, 29.20, 29.28, 29.39, 29.42, 29.46, 30.0, 126.03, 127.61, 128.75, 134.86, 136.49, 138.33, 143.57, 148.12, 159.05.

3'',4''-Dihexyl-2,2';5',2'';5''',2''''-pentathiophene (6). To a three-necked round flask charged with 1.05 g (43 mmol) of magnesium and 90 mL of dry diethyl ether, 7.06 g (29 mmol) of 5-bromo-2,2'-bithiophene²⁵ in 10 mL of dry diethyl ether was added dropwise. The reaction mixture was allowed to reflux until all magnesium disappeared. The Grignard reagent was then added dropwise to a three-necked round-bottom flask charged with 2.95 g (7.2 mmol) of 2,5-dibromo-3,4-dihexylthiophene²⁶ and 287 mg of PdCl₂(dppf) in solution in 200 mL of dry diethyl ether. The reaction was then allowed to reflux during 24 h and let at room temperature during another 48 h. The reaction was quenched with distilled water. The aqueous phase was washed with ether and the organic phase was washed with acidified water and dried with MgSO₄. The crude product was purified with chromatography on silica gel with hexanes followed by recrystallization in ethanol. This gives an orange solid, mp = 76–77 °C (yield 48%). ¹H NMR (300 MHz, CDCl₃, ppm) 0.92 (6H, t), 1.35 (12H, m), 1.5 (4H, m), 2.7 (4H, t), 7.01 (4H, m), 7.11 (2H, m), 7.18 (4H, m). ¹³C NMR (75 MHz, CDCl₃, ppm) 14.03, 22.58, 28.20, 29.54, 30.59, 31.44, 123.57, 123.93, 124.39, 126.29, 127.80, 129.72, 135.07, 137.02, 137.12, 140.29.

3'',4''-Dihexyl-2,2';5',2'';5''',2''''-pentathiophene-5,5''-dicarboxylic Acid (7). Following the procedure used for the synthesis of compound **4**, an orange solid was obtained with a yield of 90% (mp = 260–263 °C). ¹H NMR (300 MHz, THF-*d*₆, ppm) 0.85 (6H, t), 1.4 (12H, m), 1.6 (4H, m), 2.7 (4H, t), 7.11 (2H, d), 7.22 (2H, d), 7.32 (2H, d), 7.60 (2H, d), 10.9 (2H, s). ¹³C NMR (300 MHz, THF-*d*₆, ppm) 17.04, 26.14, 33.04, 34.09, 35.05, 127.42, 129.07, 130.40, 133.38, 136.60, 137.36, 139.78, 139.80, 144.23, 146.46, 165.47.

3'',4''-Dihexyl-2,2';5',2'';5''',2''''-pentathiophene-5,5''-dicarbonyl Dichloride (8). Following the procedure described for the synthesis of compound **5**, a red-bordeaux solid was obtained with a yield of 95%, mp = 92–93 °C. Elem. Anal. Calcd: 57.9% C, 4.8% H. Found: %C = 57.91, %H = 5.12. ¹H NMR (300 MHz, CDCl₃, ppm) 0.85 (6H, m), 1.35 (12H, m), 1.6 (4H, m), 2.75 (4H, t), 7.11 (2H, d), 7.22 (2H, d), 7.32 (2H, d), 7.8 (2H, d). ¹³C NMR (75 MHz, CDCl₃, ppm) 13.96, 22.47, 28.16, 29.44, 30.37, 31.33, 124.07, 126.73, 126.78, 129.74, 134.01, 134.74, 138.26, 138.86, 141.31, 149.08, 158.93.

Poly(1,10-decane-4',4''-didecyl-2,2'-bithiophene-5,5''-dicarboxylate) (PBC10). In a glass tube, 0.1665 g (0.3 mmol) of 4,4'-didecyl-2,2'-bithiophene-5,5''-dicarbonyl dichloride and 0.0507 g (0.3 mmol) of 1,10-decanediol (Aldrich) were mixed under nitrogen. The temperature was raised to 130 °C for 2 h and then to 160 °C for another 2 h. During the last 2 h, the tube was put under reduced pressure to evacuate HCl formed

(25) Barbarella, G.; Bongini, A.; Zambianchi, M. *Macromolecules* **1994**, *27*, 3039.

(26) Wang, C.; Benz, M. E.; LeGoff, E.; Schindler, J. L.; Allbritton-Thomas, J.; Kannerwurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1994**, *6*, 401.

(24) Hayashi, T.; Konishi, M.; Kobori, Y.; Makoto, K.; Higushi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 1.

during the condensation reaction. The crude product was washed with acetone and then dried under reduced pressure for 24 h. The polymer was completely soluble in chloroform. All other polymers were prepared following a similar procedure using hexanediol (Aldrich) or hexaethyleneglycol (Aldrich). All polymerization reactions gave a yield of 75–80%.

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