

# Hydrophilic Oligo(oxyethylene)-Derivatized Poly(3,4-ethylenedioxythiophenes): Cation-Responsive Optoelectroelectrochemical Properties and Solid-State Chromism

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Electroactive  $\pi$ -conjugated polymers have been synthesized by electrochemical polymerization of precursors consisting of two (3,4-ethylenedioxythiophene) (EDOT) groups linked by oligo(oxyethylene) chains of variable length. The analysis of the cyclic voltammetric behavior in the presence of various cations ( $\text{Bu}_4\text{N}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ ) shows that the nature and charge of the electrolyte cation exert a considerable influence on the potential of the anodic peak associated with the oxidation of the polymer, with positive shifts of several hundreds of millivolts in the presence of doubly charged cations. Spectroelectrochemistry shows that complexation of metal cations by the polyether network induces conformational changes in the  $\pi$ -conjugated backbone, which significantly contributes to the observed increase of the oxidation potential and the band gap. The polymers exhibit a high hydrophilicity, and experiments performed in the presence of  $\text{Ba}^{2+}$  show that replacement of acetonitrile by water produces a ca. 500 mV negative shift of the oxidation peak accompanied with a 0.30 eV decrease of the band gap, which reaches a minimal value under these conditions. These phenomena indicative of an enhancement of the effective conjugation in the polymer backbone are attributed to the removal of  $\text{Ba}^{2+}$  cations with concomitant swelling of the polymer by a specific solvation of the oligo(oxyethylene) network by water molecules. As a consequence of this high structural flexibility and environmental stability, the polymers exhibit fast, intense, and reversible ionochromic effects in the solid state.

## Introduction

The interactions between  $\pi$ -conjugated polymers derivatized by linear or macrocyclic polyether and their chemophysical environment have been a focus sustained for more than a decade.<sup>1–16</sup> Cation-dependent electro-

chemical and optical properties were initially observed on poly(thiophenes) (PTs) derivatized with oligo(oxyethylene) side chains.<sup>2</sup> Complexation of lithium cations by the polyether side chains produced a negative shift of the oxidation potential and a bathochromic shift of the absorption maximum resulting from the planarization and rigidification of the polymer by "ionic cross-linking".<sup>2</sup>

Conjugated polymers with improved cationic sensitivity and selectivity were reported almost simultaneously by three groups.<sup>3–5</sup> Bäuerle and Scheib have described the synthesis and electropolymerization of thiophene

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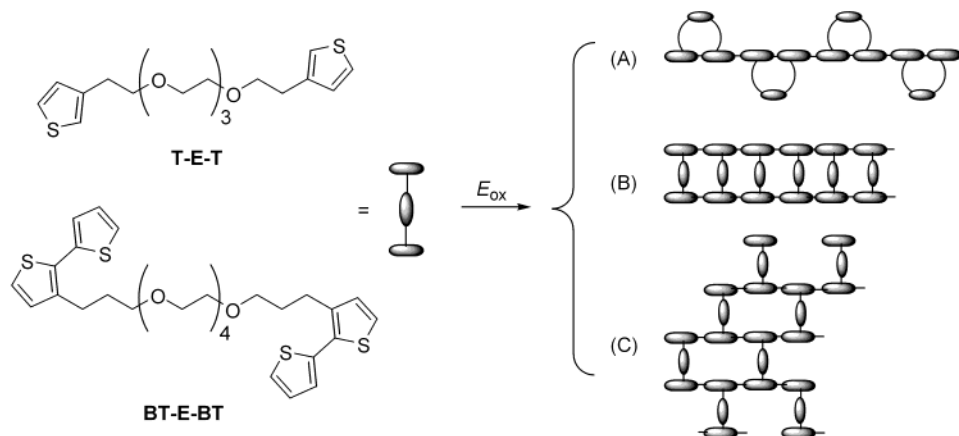
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**Scheme 1. Formation of Different Types of Polymeric Structures from Precursors with Two Electropolymerizable Thiophene Units (Th–Linker–Th)**

precursors with pendent 12C4 crown ethers. The presence of alkali cations leads to a gradual positive shift of the cyclic voltammetric (CV) waves and a decrease of electroactivity, which depend on the size and concentration of the metal cation.<sup>3</sup> Similar results were reported for polypyrrole 3-substituted by monoazacrown ethers.<sup>4</sup> Marsella and Swager have synthesized crown ethers integrating bithiophene units by connecting an oligo(oxyethylene) chain to the 3 and 4' positions of adjacent thiophene rings. Complexation of alkali cations by the macrocyclic cavity produces a twist of the conjugated backbone and thus a blue shift of the absorption maximum correlated to the size of the metal cation.<sup>5</sup> More recently, the same group has described calix[4]arene-functionalized PTs with improved binding constants and highly selective electrochemical and optical responses for Na<sup>+</sup>.<sup>6</sup>

Many functional PTs of the first generation were built by attaching the functional group to the thiophene ring via a flexible linker of appropriate length in order to minimize the distortions of the  $\pi$ -conjugated backbone caused by steric interactions among substituents.<sup>7</sup> Of course, because bulky groups such as macrocyclic crown ethers require rather long linkers, this approach may pose the problem of the electrical communication between the complexing site and the  $\pi$ -conjugated system.

To solve this problem, several groups have developed synthetic approaches aiming at the integration of part of the  $\pi$ -conjugated system in the macrocyclic cavity.<sup>5,8–12</sup> Examples of such strategies involve the attachment of an oligo(oxyethylene) chain on consecutive thiophene rings,<sup>5</sup> at the 3 and 4 positions of the same thiophene unit,<sup>9,10</sup> or at the bridging carbon of poly(cyclopentabithiophene).<sup>11</sup> The resulting polymers generally exhibit better sensitivity and selectivity than systems of the first generation.<sup>1</sup>

In 1990 we proposed a different concept based on the electropolymerization of a precursor involving two electropolymerizable thiophene groups linked by an oligo(oxyethylene) chain (T-E-T, Scheme 1).<sup>13</sup> As shown in Scheme 1, polymerization of such precursors can generate three different types of polymeric structures, namely, (i) a PT chain with lateral macrocyclic cavities (A), (ii) a ladder polymer in which rungs are constituted by the oligo(oxyethylene) segments (B), and (iii) a randomly cross-linked tridimensional polymer (C). While it is clear

that the actual polymer structure is probably an admixture of these various possibilities with a predominance of case C, it is noteworthy that, in any situation, polymerization of such two-site precursors leads to the formation of two- or three-dimensional (2D or 3D) cross-linked polymeric structures containing cavities with two sides constituted by the  $\pi$ -conjugated PT chains and two others by oligo(oxyethylene) segments. Such cavities are, therefore, potentially capable of interacting with guest species.

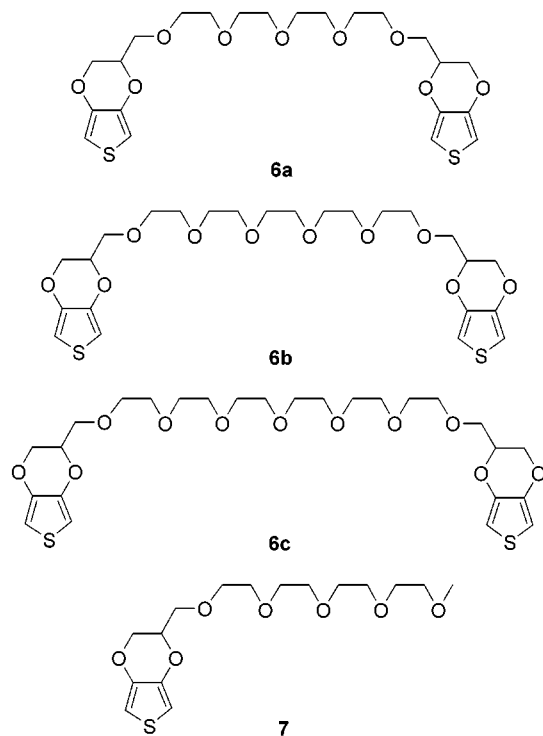
Recently, we have shown that electropolymerization of a precursor consisting of two bithiophene (BT) groups linked by a polyether chain (BT-E-BT, Scheme 1) leads to ion-imprinted polymers because of the occurrence of a template effect during electropolymerization.<sup>14</sup> Compared to monomeric precursors, BT-based precursors present the advantage of electropolymerizing at a potential ca. 500 mV less positive and at lower concentrations of substrate.<sup>1b,14</sup>

As a further extension of this concept, we now report a new series of polymers resulting from the electropolymerization of precursors involving two EDOT groups linked by oligo(oxyethylene) chains of increasing length (**6a–c**, Chart 1). Monomer **7** with a single polyether side chain has been synthesized for comparison.

The cation-dependent electrochemical and optical properties of the new polymers have been analyzed by cyclic voltammetry and spectroelectrochemistry in organic and aqueous media in the presence of various metal cations. The results of these experiments reveal an interesting association of properties involving cation recognition, structural flexibility, and unusual affinity for aqueous media.

## Experimental Section

Cyclic voltammetry was performed in a three-electrode, two-compartment cell equipped with a platinum working micro-electrode ( $\varnothing = 1$  mm) and a platinum wire counter electrode. An Ag/AgCl electrode checked against the ferrocene/ferrocinium couple (Fc/Fc<sup>+</sup>) before and after each experiment was used as the reference. The reference electrode was equipped with a nonaqueous double bridge in order to avoid possible interference with metal cations. The electrolytic medium involved MeCN (HPLC grade) or ultrapure water and 0.10 M tetrabutylammonium or metal perchlorate. All experiments were carried out in solutions deaerated by argon bubbling. Electrochemical experiments were carried out with a PAR 273

**Chart 1. Structures of Synthesized EDOT-Based Precursors 6a–c and 7**

potentiostat with positive feedback compensation. Films for electrochemical characterization were deposited on platinum microelectrodes of  $7.85 \times 10^{-3} \text{ cm}^2$  area at a constant potential of 1.20 V with a constant deposition charge of 400  $\mu\text{C}$ . The electrolytic medium involved 0.01–0.013 M monomers (**6a–c** or **7**) and 0.10 M tetrabutylammonium perchlorate in MeCN. Films for spectroelectrochemical experiments were grown under the same conditions on a platinum electrode ( $\varnothing = 5 \text{ mm}$ ) using a deposition charge of 5 mC. Deposition on indium–tin oxide (ITO;  $9 \times 25 \text{ mm}$ ) was performed under the same conditions with a deposition charge of 20 mC  $\text{cm}^{-2}$ .

UV–vis–NIR experiments were performed on a Perkin-Elmer Lambda 19 NIR spectrometer. Electronic absorption spectra of the undoped polymers were recorded in reflection mode on films electrodeposited on a Pt disk ( $\varnothing = 5 \text{ mm}$ ), using the already described experimental setup for spectroelectrochemistry.<sup>17</sup>

**Tetraethylene Glycol Dimesylate (2a).** Tetraethylene glycol (**1a**; 27.2 g, 0.140 mol) and triethylamine (34.0 g, 0.336 mol) in dry dichloromethane (DCM; 100 mL) under nitrogen were cooled to  $-5^\circ\text{C}$ . Methanesulfonyl chloride (38.4 g, 0.336 mol) in dry DCM (40 mL) was added dropwise to this solution for 1.5 h at  $0^\circ\text{C}$ ; the mixture was allowed to warm to room temperature and stirred at room temperature for 15 h. Triethylamine hydrochloride was filtered off, and the DCM solution was washed with cold water and dried over sodium sulfate. Removing the solvent afforded compound **2a** (49.0 g, 100%) as a light-yellow oil, which was used without further purification:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.38 (4H, m,  $\text{CH}_2\text{OSO}_2$ ), 3.77 (4H, m,  $\text{CH}_2\text{CH}_2\text{OSO}_2$ ), 3.65 [8H, m,  $-(\text{OCH}_2\text{CH}_2)_2-$ ], 3.08 (6H, s,  $\text{SO}_2\text{CH}_3$ ).

**Hexaethylene glycol dimesylate (2c)** was prepared according to the same procedure as that for hexaethylene glycol (**1c**; 2.55 g, 0.903 mmol) and triethylamine (2.56 g, 2.53 mmol) in dry DCM (20 mL): yield 3.95 g (100%) of a yellowish oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.38 (4H, m,  $\text{CH}_2\text{OSO}_2$ ), 3.76 (4H, t,  $^3J = 4.4 \text{ Hz}$ ,  $\text{CH}_2\text{CH}_2\text{OSO}_2$ ), 3.63 [16H, m,  $-(\text{OCH}_2\text{CH}_2)_4-$ ], 3.09 (6H, s,  $\text{SO}_2\text{CH}_3$ ).

**Tetraethylene Glycol Bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-ylmethyl) Ether (6a).** Sodium hydride (60% in mineral oil; 0.36 g, 9.0 mmol) was suspended in dry THF (15 mL) under nitrogen, a catalytic amount of 18-crown-6 (40 mg, 0.15 mmol) was added, and the mixture was cooled to  $-25^\circ\text{C}$ . (2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methanol (**5**;<sup>18</sup> 1.20 g, 6.97 mmol) was added to this mixture in one portion, and the mixture was allowed to warm to room temperature and stirred at room temperature for 1.5 h. It was cooled again to  $-10^\circ\text{C}$ , and tetraethylene glycol dimesylate (**2a**; 1.05 g, 3.00 mmol) in THF (10 mL) was added for 30 min. The mixture was stirred at room temperature under nitrogen for 15 h, diluted with DCM/water (75/75 mL), and acidified to pH 7. The water layer was extracted with a new portion of DCM (75 mL), combined DCM extracts were washed with 5%  $\text{NH}_4\text{Cl}$  ( $2 \times 70 \text{ mL}$ ) and dried with  $\text{MgSO}_4$ , and the solvent was evaporated. The residual yellow oil (ca. 2 g) was subjected to flash chromatography (silica gel), yielding the desired product (1.02 g, 67.7%), which was eluted by ether. After that, a small amount of monoproduct **8** (0.05 g, 3.9%) was eluted by ether/ethanol (20:1, v/v). Repeated column chromatography of the crude product (silica gel, ether) gave pure **6a** (0.77 g, 51.1%) as a yellowish oil.

**6a:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.323 (2H, d,  $^4J_{2,5} = 3.7 \text{ Hz}$ , thiophene-2), 6.316 (2H, d,  $^4J_{2,5} = 3.7 \text{ Hz}$ , thiophene-5), 4.32 [2H, m,  $-\text{OCH}_2^{\text{ab}}\text{CH}^{\text{f}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.25 [2H, dd,  $^2J_{\text{a,b}} = 11.7 \text{ Hz}$ ,  $^3J_{\text{b,c}} = 2.2 \text{ Hz}$ ,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.06 [2H, dd,  $^2J_{\text{a,b}} = 11.7 \text{ Hz}$ ,  $^3J_{\text{a,c}} = 7.5 \text{ Hz}$ ,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 3.76 [2H, dd,  $^2J_{\text{d,e}} = 10.6 \text{ Hz}$ ,  $^3J_{\text{d,c}} = 5.1 \text{ Hz}$ ,  $\text{OCH}_2\text{CH}^{\text{c}}(\text{CH}^{\text{f}}\text{H}^{\text{e}}\text{OR})\text{O}-$ ], 3.67 [2H, m,  $-\text{OCH}_2\text{CH}(\text{CH}^{\text{d}}\text{H}^{\text{f}}\text{OR})\text{O}-$ ], 3.64 [16H, m,  $-(\text{OCH}_2\text{CH}_2)_4-$ ];  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.59, 141.50 (thiophene-3,4), 99.59, 99.51 (thiophene-2,5), 72.61, 71.18, 70.64, 70.58, 70.52, 69.62, 66.10. HRMS (FAB):  $m/z$  502.1321 ( $\text{M}^+$ ). Calcd for  $\text{C}_{22}\text{H}_{30}\text{O}_9\text{S}_2$ : 502.1331. Anal. Calcd for  $\text{C}_{22}\text{H}_{30}\text{O}_9\text{S}_2$ : C, 52.57; H, 6.02; O, 28.65; S, 12.76. Found: C, 52.35; H, 6.24; S, 12.61.

**8:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.328 (1H, d,  $^4J_{2,5} = 3.65 \text{ Hz}$ , thiophene-2), 6.322 (1H, d,  $^4J_{2,5} = 3.65 \text{ Hz}$ , thiophene-5), 4.38 (2H, m,  $\text{CH}_2\text{OSO}_2$ ), 4.31 [1H, m,  $-\text{OCH}_2^{\text{ab}}\text{CH}^{\text{f}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.25 [1H, dd,  $^2J_{\text{a,b}} = 11.7 \text{ Hz}$ ,  $^3J_{\text{b,c}} = 2.2 \text{ Hz}$ ,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.06 [1H, dd,  $^2J_{\text{a,b}} = 11.7 \text{ Hz}$ ,  $^3J_{\text{a,c}} = 7.5 \text{ Hz}$ ,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 3.76 [3H, m,  $-\text{OCH}_2\text{CH}^{\text{c}}(\text{CH}^{\text{f}}\text{H}^{\text{e}}\text{OR})\text{O}-$  +  $\text{CH}_2\text{CH}_2\text{OSO}_2$ ], 3.70 [1H, m,  $-\text{OCH}_2\text{CH}(\text{CH}^{\text{d}}\text{H}^{\text{f}}\text{OR})\text{O}-$ ], 3.66 [12H, m,  $-(\text{OCH}_2\text{CH}_2)_3-$ ], 3.08 (3H, s,  $\text{SO}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.78, 141.71 (thiophene-3,4), 99.90, 99.81 (thiophene-2,5), 72.87, 71.42, 70.86, 70.85, 70.79, 70.74 (2C), 69.85, 69.55, 69.23, 66.33, 37.92 ( $\text{SO}_2\text{CH}_3$ ). HRMS (FAB):  $m/z$  462.1032 ( $\text{M}^+$ ). Calcd for  $\text{C}_{16}\text{H}_{26}\text{O}_9\text{S}_2$ : 462.1018.

**Pentaethylene Glycol Bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-ylmethyl) Ether (6b).** This compound was prepared using the procedure described for **6a**, from compound **5** (1.20 g, 6.97 mmol) and pentaethylene glycol dimesylate (1.60 g, 2.93 mmol): yield 1.32 g (82.5%). Repeated column chromatography of the crude product gave pure compound **6b** (0.96 g, 60.0%) as a yellowish oil:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.323 (2H, d,  $^4J_{2,5} = 3.7 \text{ Hz}$ , thiophene-2), 6.317 (2H, d,  $^4J_{2,5} = 3.7 \text{ Hz}$ , thiophene-5), 4.32 [2H, m,  $-\text{OCH}_2^{\text{ab}}\text{CH}^{\text{f}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.25 [2H, dd,  $^2J_{\text{a,b}} = 11.7 \text{ Hz}$ ,  $^3J_{\text{b,c}} = 2.1 \text{ Hz}$ ,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.06 [2H, dd,  $^2J_{\text{a,b}} = 11.7 \text{ Hz}$ ,  $^3J_{\text{a,c}} = 7.5 \text{ Hz}$ ,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 3.76 [2H, dd,  $^2J_{\text{d,e}} = 10.6 \text{ Hz}$ ,  $^3J_{\text{d,c}} = 5.1 \text{ Hz}$ ,  $-\text{OCH}_2\text{CH}^{\text{c}}(\text{CH}^{\text{f}}\text{H}^{\text{e}}\text{OR})\text{O}-$ ], 3.68 [2H, m,  $-\text{OCH}_2\text{CH}(\text{CH}^{\text{d}}\text{H}^{\text{f}}\text{OR})\text{O}-$ ], 3.64 [20H, m,  $-(\text{OCH}_2\text{CH}_2)_5-$ ];  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.67, 141.57 (thiophene-3,4), 99.57, 99.49 (thiophene-2,5), 72.67, 71.23, 70.68, 70.62, 70.61, 70.55, 69.67, 66.14. HRMS (FAB):  $m/z$  546.1571 ( $\text{M}^+$ ). Calcd for  $\text{C}_{24}\text{H}_{34}\text{O}_{10}\text{S}_2$ : 546.1593. Anal. Calcd for  $\text{C}_{24}\text{H}_{34}\text{O}_{10}\text{S}_2$ : C, 52.73; H, 6.27; O, 29.27; S, 11.73. Found: C, 52.50; H, 6.48; O, 30.06; S, 11.25.

**Hexaethylene Glycol Bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-ylmethyl) Ether (6c).** Prepared according to the

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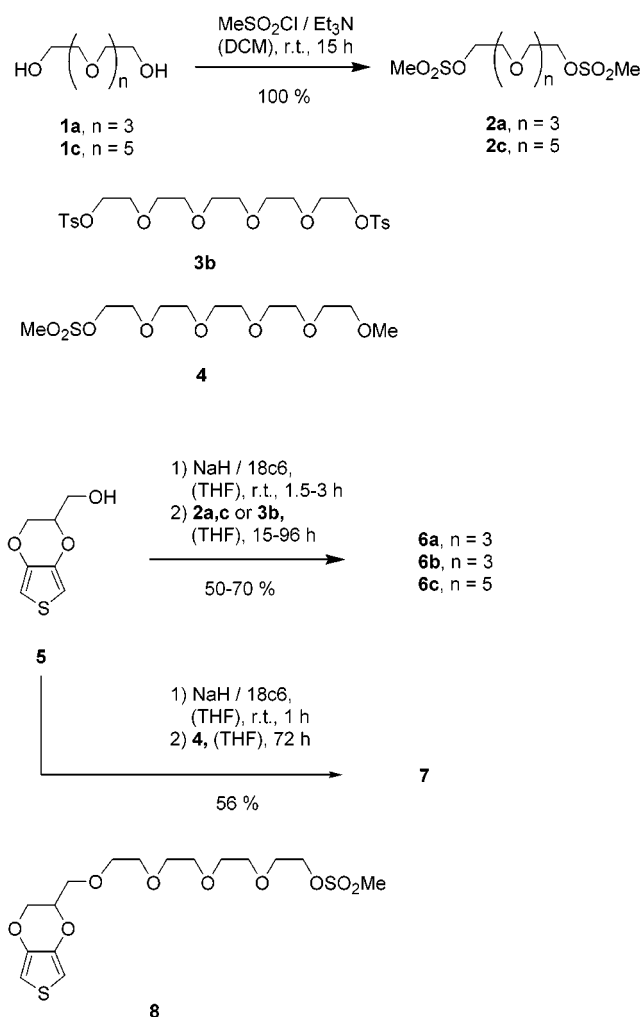
procedure described for **6a**, from (2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-2-yl)methanol (**5**; 1.72 g, 10.0 mmol) and hexaethylene glycol dimesylate (1.76 g, 4.00 mmol): yield 1.62 g (68.3%) of a yellowish oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.324 (2H, d,  $^4J_{2,5} = 3.65$  Hz, thiophene-2), 6.316 (2H, d,  $^4J_{2,5} = 3.65$  Hz, thiophene-5), 4.32 [2H, m,  $-\text{OCH}_2^{\text{ab}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.26 [(2H, dd,  $^2J_{\text{a,b}} = 11.7$  Hz,  $^3J_{\text{b,c}} = 2.2$  Hz,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.06 [2H, dd,  $^2J_{\text{a,b}} = 11.7$  Hz,  $^3J_{\text{a,c}} = 7.5$  Hz,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 3.78 [2H, dd,  $^2J_{\text{d,e}} = 10.6$  Hz,  $^3J_{\text{d,c}} = 5.1$  Hz,  $-\text{OCH}_2\text{CH}^{\text{c}}(\text{CH}_2\text{H}^{\text{d}}\text{OR})\text{O}-$ ], 3.68 [2H, m,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{H}^{\text{d}}\text{OR})\text{O}-$ ], 3.64 [24H, m,  $-(\text{OCH}_2\text{CH}_2)_6-$ ];  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.61, 141.53 (thiophene-3,4), 99.62, 99.53 (thiophene-2,5), 72.64, 71.22, 70.66, 70.59 (2C), 70.55 (2C), 69.65, 66.13. HRMS (FAB):  $m/z$  590.1884 ( $\text{M}^+$ ). Calcd for  $\text{C}_{26}\text{H}_{38}\text{O}_{11}\text{S}_2$ : 590.1856. Anal. Calcd for  $\text{C}_{26}\text{H}_{38}\text{O}_{11}\text{S}_2$ : C, 52.87; H, 6.48; O, 29.79; S, 10.86. Found: C, 53.12; H, 6.70; S, 10.69.

**2-(2,5,8,11,14-Pentaoxapendadecyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (7).** Sodium hydride (60% in mineral oil) (0.40 g; 10.0 mmol) was suspended in dry THF (20 mL) under nitrogen, catalytic amount of 18-crown-6 (50 mg; 0.19 mmol) was added and the mixture was cooled to  $-10^\circ\text{C}$ . (2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methanol **5** (1.00 g; 5.8 mmol) was added to this mixture in one portion, the mixture was allowed to warm to room temperature and stirred at room temperature for 1 h. It was cooled again to  $0^\circ\text{C}$  and tetraethyleneglycol monomethyl ether mesylate (2.86 g; 10.0 mmol) in THF (10 mL) was added for 20 min. The mixture was stirred at room temperature under nitrogen for 3 days, diluted with 5%  $\text{NH}_4\text{Cl}$  (100 mL), and treated with an excess of piperidine to remove tetraethyleneglycol monomethyl ether mesylate. The product was extracted with ether ( $4 \times 50$  mL), washed with water, dried with  $\text{MgSO}_4$ , and the solvent was evaporated yielding brown oil (2.04 g; 87.8%). Crude product was subject of flash chromatography (silica gel; eluents – DCM, then DCM:ethanol = 20:1) affording the desired compound (1.77 g; 76.3%) as light-yellow oil. Repeated column chromatography (silica gel; eluent – ether) afforded pure compound **7** (1.31 g; 56.3%) as light-yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.324 (1H, d,  $^4J_{2,5} = 3.7$  Hz, thiophene-2), 6.318 (1H, d,  $^4J_{2,5} = 3.7$  Hz, thiophene-5), 4.32 [1H, m,  $-\text{OCH}_2^{\text{ab}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.25 [1H, dd,  $^2J_{\text{a,b}} = 11.65$  Hz,  $^3J_{\text{b,c}} = 2.1$  Hz,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 4.06 [1H, dd,  $^2J_{\text{a,b}} = 11.65$  Hz,  $^3J_{\text{a,c}} = 7.45$  Hz,  $-\text{OCH}^{\text{a}}\text{H}^{\text{b}}\text{CH}^{\text{c}}(\text{CH}_2\text{OR})\text{O}-$ ], 3.77 [1H, dd,  $^2J_{\text{d,e}} = 10.6$  Hz,  $^3J_{\text{d,c}} = 5.1$  Hz,  $-\text{OCH}_2\text{CH}^{\text{c}}(\text{CH}_2\text{H}^{\text{d}}\text{OR})\text{O}-$ ], 3.69 [1H, m,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{H}^{\text{d}}\text{OR})\text{O}-$ ], 3.65 [14H, m,  $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_2-$ ], 3.55 (2H, m,  $\text{CH}_2\text{OCH}_3$ ), 3.38 (3H, s,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.62, 141.53 (thiophene-3,4), 99.62, 99.53 (thiophene-2,5), 72.65, 71.95, 71.23, 70.67, 70.60 (2C), 70.55 (2C), 70.51, 69.65, 66.14, 58.98 ( $\text{CH}_3$ ). HRMS (FAB):  $m/z$  362.1404 ( $\text{M}^+$ ). Calcd for  $\text{C}_{16}\text{H}_{26}\text{O}_7\text{S}$ : 362.1399. Anal. Calcd for  $\text{C}_{16}\text{H}_{26}\text{O}_7\text{S}$ : C, 53.02; H, 7.23; O, 30.90; S, 8.85. Found: C, 52.45; H, 7.42; O, 31.48; S, 8.88%.

## Results and Discussion

**Synthesis of the Precursors.** The synthesis of the target compounds **6a–c** and **7** is depicted in Scheme 2. In each case the synthesis basically involves mono- or bis-linking of an oligo(oxyethylene) derivative (mesylates **2a,c** and **4** or ditosylate **3b**) with hydroxymethyl-EDOT (**5**).<sup>15</sup> Tetra- and hexaethylene glycol dimesylates **2a** and **2c** were quantitatively obtained by reacting tetra- and hexaethylene glycol (**1a** and **1c**) with methanesulfonyl chloride in the presence of triethylamine. The target compounds **6a–c** were then obtained in 50–70% yield by reacting hydroxymethyl-EDOT (**5**) with dimesylates **2a** or **2c** or ditosylate **3b**. Compound **7** with a single EDOT ring was prepared in a similar fashion by reaction of mesylate **4** with hydroxymethyl-EDOT. Compound **8** has been isolated as a byproduct of the synthesis of **6a**. All target compounds were satisfactorily characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, elemental analysis, and high-resolution mass spectrometry.

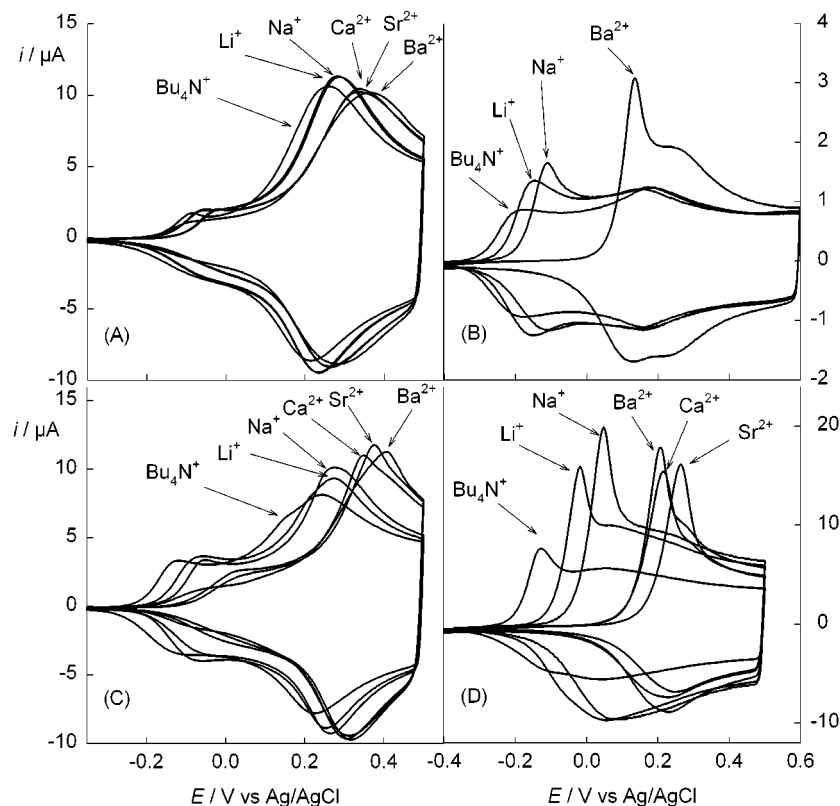
## Scheme 2. Synthesis of Precursors **6a–c** and **7**



**Electrosynthesis of the Polymers.** Compounds **6a–c** and **7** were electropolymerized in MeCN solutions containing 0.10 M  $\text{Bu}_4\text{NClO}_4$  and 0.01–0.013 M precursor. Polymerization was achieved either in potentiostatic conditions or by recurrent potential scans between  $-0.40$  V and the foot of the oxidation wave (1.20 V). Because of the absence of a direct electronic substituent effect, all precursors oxidize at the same potential as EDOT.<sup>15</sup>

Whereas precursors **6a–c** undergo straightforward electropolymerization on platinum or ITO, attempts to electropolymerize compound **7** on ITO remained unsuccessful while electrodeposition on platinum was more difficult than that for compounds **6** and required application of a ca. 100 mV overpotential. This behavior is reminiscent of that of PTs bearing oligo(oxyethylene) side chains for which electropolymerization becomes increasingly difficult as the length of the polyether side chain increases.<sup>16</sup> In this context, the facile electrodeposition of strongly adherent films from all of the two-site precursors **6a–c** underlines an important advantage of this class of precursors probably related to the higher dimensionality of the resulting polymers.

Polymer films for electrochemical and spectroelectrochemical experiments have been grown in potentiostatic conditions. The film thickness was controlled by the deposition charge and kept constant in all experiments.



**Figure 1.** Cyclic voltammograms of electrodeposited polymer films in the presence of various cations: (A) poly(**6a**); (B) poly(**6b**); (C) poly(**6c**); (D) poly(**7**). Electrolytic medium 0.10 M perchlorate/MeCN, 20 °C, and scan rate 100 mV s<sup>-1</sup>. Deposition conditions: Pt disk,  $\varnothing = 1$  mm; MeCN, 0.013 M **6a–c**, 0.10 M Bu<sub>4</sub>NClO<sub>4</sub>;  $E_{\text{dep}} = 1.20$  V;  $Q_{\text{dep}} = 400$   $\mu\text{C}$ .

**Table 1. Anodic Peak Potentials ( $E_{\text{pa}}$ ) in the Presence of Bu<sub>4</sub>N<sup>+</sup> and Shifts of the Current Peak Potentials ( $\Delta E_{\text{p}}$ ) of the Polymers in the Presence of Various Metal Cations<sup>a</sup>**

polymer	Bu <sub>4</sub> N <sup>+</sup>	$\Delta E_{\text{p}}/\text{mV}^b$				
		Li <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
Poly( <b>6a</b> )						
$E_{\text{pa1}}$	−0.118	+52	+54	+88	+89	+32
$E_{\text{pa2}}$	+0.261	19	+23	+71	+69	+93
Poly( <b>6b</b> )						
$E_{\text{pa1}}$	−0.177	+21	+60			+313
$E_{\text{pa2}}$	+0.180	0	0			+77
Poly( <b>6c</b> )						
$E_{\text{pa1}}$	−0.135	+71	+78	+107	+161	+85
$E_{\text{pa2}}$	+0.222	+47	+50	+121	+149	+183
Poly( <b>7</b> )						
$E_{\text{pa1}}$	−0.193	+172	+140	+407	+461	+393

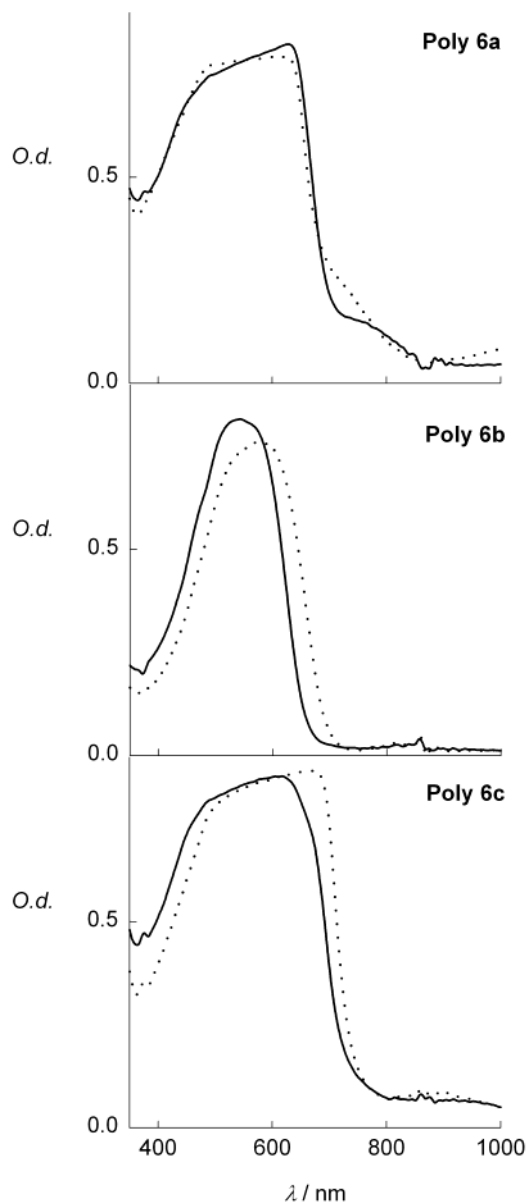
<sup>a</sup> Films electrodeposited on a Pt disk ( $\varnothing = 1$  mm,  $E_{\text{dep}} = 1.20$  V,  $Q_{\text{d}} = 400$   $\mu\text{C}$ ). Data recorded in 0.10 M perchlorate/MeCN at a scan rate of 100 mV s<sup>-1</sup> with reference Ag/AgCl. <sup>b</sup>  $\Delta E_{\text{p}} = E_{\text{pa}}(\text{M}^{n+}) - E_{\text{pa}}(\text{Bu}_4\text{N}^+)$ .

**Effects of Metal Cations on the Electronic Properties of the Polymers.** After polymerization, the polymer films were rinsed with acetonitrile and transferred in a series of MeCN solutions containing different cations for CV analysis. Parts A–D of Figure 1 show the CV recorded in the presence of various cations, while the corresponding data are listed in Table 1. In view of the rather similar effects obtained with the doubly charged cations (Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>) during the initial set of experiments on poly(**6a**), -(**6c**), and -(**7**), barium was used as the representative example of these doubly charged cations for the rest of the work.

In the presence of Bu<sub>4</sub>N<sup>+</sup>, the CV analyses of the various polymers exhibit two successive redox systems centered around -0.10 and +0.20 V with an onset of electroactivity at around -0.300 V. While the second redox system is the most intense for poly(**6a**) and -(**6c**), the CV analyses of poly(**6b**) and -(**7**) reveal a strong intensification of the first redox system with a 50–70 mV negative shift of the first anodic peak potential ( $E_{\text{pa1}}$ ). These differences, which may reflect a more extended effective conjugation, suggest the existence of an optimal length of the oligo(oxyethylene) chain compatible with the preservation of an extended effective conjugation of the PT backbone.

For all polymers, replacement of Bu<sub>4</sub>N<sup>+</sup> by successively Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> produces a gradual positive shift of the two anodic peak potentials ( $E_{\text{pa1}}$  and  $E_{\text{pa2}}$ ). In each case the largest shifts occur with doubly charged cations Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>. However, noticeable differences can be observed among the polymers. Thus, for poly(**6a**) only a moderate shift (less than 100 mV) of  $E_{\text{pa1}}$  and  $E_{\text{pa2}}$  occurs. Qualitatively similar effects are observed for poly(**6c**) with, however, larger positive shifts of  $E_{\text{pa1}}$  and  $E_{\text{pa2}}$  (up to 160–180 mV). On the other hand, poly(**6b**) and -(**7**) exhibit quite different behavior because in both cases  $E_{\text{pa2}}$  is practically unaffected while  $E_{\text{pa1}}$  undergoes the largest shifts observed here ( $\Delta E_{\text{pa1}} > 300$  mV for poly(**6b**) with Ba<sup>2+</sup> and  $\Delta E_{\text{pa1}} > 460$  mV for poly(**7**) with Sr<sup>2+</sup>).

Comparison of these various series of curves shows that poly(**6b**) and -(**7**) lead to the best discrimination of the various cations in terms of potential shifts. This result suggests that flexibility of the polymer structure plays an important role in the recognition process.



**Figure 2.** In situ electronic absorption spectra of undoped films of poly(**6a–c**) in the presence of 0.10 M  $\text{Bu}_4\text{NClO}_4$  (dotted line) and 0.10 M  $\text{Ba}(\text{ClO}_4)_2$  (solid line); applied potential  $-0.50$  V. Deposition conditions: Pt disk,  $\varnothing = 5$  mm; MeCN, 0.010 M **6a–c**, 0.10 M  $\text{Bu}_4\text{NClO}_4$ ;  $E_{\text{dep}} = 1.20$  V;  $Q_{\text{dep}} = 5$  mC.

While these results clearly show that the polymers possess cation recognition properties, the sensitivity remains low and observation of the maximal shifts of the CV peaks requires a rather high concentration (typically 0.10 M)

Previous works on PTs or polypyrrole with pendent crown ethers have shown that the presence of increasing concentrations of alkali cations in the electrolytic medium induces a gradual positive shift of  $E_{\text{pa}}$  accompanied with a broadening of the anodic wave and a decrease of electroactivity.<sup>3,4,8,9</sup>

As shown in Figure 2, these latter effects are not observed here and the positive shifts of  $E_{\text{pa}1}$  and/or  $E_{\text{pa}2}$  occur without loss of electroactivity. Furthermore and contrary to previously reported behaviors, the positive shift of the CV peaks is associated with sharpening of the anodic peak, which might be related to an enhanced mobility of ionic species in the polymer bulk. Finally, it

must be emphasized that all of these changes in the CV are reversible and that the initial CV can be fully restored after a simple redox cycle in the presence of  $\text{Bu}_4\text{N}^+$ . This latter result unequivocally demonstrates that the modification of the CV response is not related to a degradation of the polymers, a point which was not always clearly established in previous works.<sup>3,4,8,9</sup>

The effects of metal cations on the electrochemical behavior of conjugated polymers bearing linear or macrocyclic polyether have been discussed in the frame of different mechanisms.<sup>1–5</sup>

Crown ethers incorporating a large variety of redox probes such as quinones, nitro groups, ferrocene, or tetrathiafulvalene have been extensively investigated in the past 2 decades.<sup>19</sup> In the case of an oxidizable redox probe, like, for example, ferrocene, complexation of a metal cation by the crown ether induces a positive shift of the oxidation potential due to the electron-withdrawing effect of the complexed cation.<sup>19</sup> Such a mechanism also operates in some modified electrodes where the whole crown ether/redox probe couple is attached onto an electrode surface by means of various methods such as self-assembled monolayers,<sup>20</sup> electrogenerated conducting polymers,<sup>21</sup> or electrodeposited dendrimers.<sup>22</sup>

A different mechanism has been proposed to explain the electrochemical behavior of PTs derivatized with crown ethers in the presence of alkali cations. Because in that case the redox probe is constituted by the PT backbone itself, it has been postulated that the complexation of metal cations by the macrocycle modifies the distribution of ionic species within the polymer, resulting in the development of a Donnan potential.<sup>9</sup> This potential barrier contributes to the pinning of the doping anions in the vicinity of the complexing sites, thus hindering or delaying their diffusion and migration toward the positive holes on the  $\pi$ -conjugated backbone.<sup>3,9</sup>

Such an interpretation is consistent with the absence of modification of the optical spectrum, which allows one to rule out the occurrence of cation-induced modification in the geometry of the conjugated PT backbone.

Potential shifts associated with conformational changes have been reported for different series of polyether-derivatized PTs.<sup>2,23</sup> Depending on the structure of the polyether substituents, interactions with metal cations produce either a planarization of the  $\pi$ -conjugated system and hence a negative shift of  $E_{\text{pa}}$  and a red shift of  $\lambda_{\text{max}}$ <sup>2</sup> or a distortion of the conjugated structure, resulting in a blue shift of the absorption.<sup>5,23</sup>

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**Table 2. Electronic Absorption Data for the Undoped States of the Polymers Poly(6a–c) Electrodeposited on a Pt Disk Electrode<sup>a</sup>**

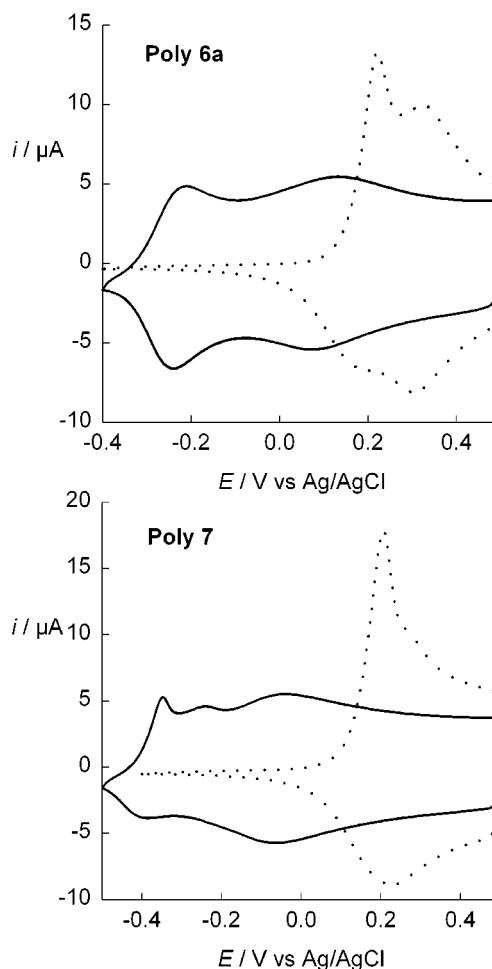
polymer	$\lambda_{\max}/\text{nm}$		$E_g/\text{eV}$	
	Bu <sub>4</sub> N <sup>+</sup>	Ba <sup>2+</sup>	Bu <sub>4</sub> N <sup>+</sup>	Ba <sup>2+</sup>
poly(6a)	629	625	1.74	1.74
poly(6b)	580	535	1.78	1.92
poly(6c)	677	621	1.66	1.69

<sup>a</sup> Data recorded in situ in 0.10 M perchlorate/MeCN at an applied potential of  $-0.50$  V vs Ag/AgCl. Deposition conditions: Pt disk,  $\varnothing = 5$  mm; MeCN, 0.010 M **6a–c**, 0.10 M Bu<sub>4</sub>NClO<sub>4</sub>;  $E_{\text{dep}} = 1.20$  V;  $Q_{\text{dep}} = 5$  mC.

Although the positive shifts of the peak potentials observed here are reminiscent of the behavior of crown ether derivatized PTs,<sup>3,4,8,9</sup> the fact that these shifts are not accompanied by a broadening of the CV waves and a decrease of electroactivity suggests a different mechanism.

To clarify that point, the electronic absorption spectra of the polymers have been recorded by spectroelectrochemistry after electrochemical undoping in the presence of Bu<sub>4</sub>N<sup>+</sup> and Ba<sup>2+</sup>. Despite several attempts under various experimental conditions, homogeneous films of poly(7) of quality good enough for optical measurements could not be deposited on the larger platinum electrode used for spectroelectrochemistry. The spectra of poly(6a–c) (Figure 2) and the data in Table 2 show that, as expected from CV data, the spectrum of poly(6a) is practically unaffected by the replacement of the cation of the electrolytic medium. In contrast, the spectra for poly(6c) show that a simple redox cycle in the presence of Ba<sup>2+</sup> induces a 56 nm hypsochromic shift of  $\lambda_{\max}$ . However, a closer examination of the spectra shows that this shift corresponds, in fact, to a 12–13 nm blue shift of the long-wavelength absorption edge and hence to a 0.03 eV increase of the band gap ( $E_g$ ). This suggests that, besides a moderate decrease of the effective conjugation, the interactions of the polymer with Ba<sup>2+</sup> produce a modification of the rigidity of the  $\pi$ -conjugated backbone and hence a change in the relative intensity of the various vibronic transitions. For poly(6b),  $\lambda_{\max}$  shifts hypsochromically by 45 nm, but in this case, a parallel shift of the absorption edge occurs and  $E_g$  increases by 0.14 eV.

These results thus clearly show that the positive shifts of the peak potentials are correlated to a significant reduction of the effective conjugation of the PT backbone. This suggests that the complexation of the metal cation by the oligo(oxyethylene) network induces a distortion of the  $\pi$ -conjugated system. However, comparison of the energy differences indicated by CV and optical data reveals important discrepancies. Thus, the 0.313 V positive shift of  $E_{\text{pa1}}$  observed for poly(6b) is correlated to an increase of  $E_g$  of only 0.14 eV. For poly(6c),  $E_{\text{pa2}}$  shifts positively by 0.183 V, whereas  $E_g$  increases by only 0.03 eV. Because a parallel shift of the reduction potential of the PT backbone is very unlikely, these large energy differences suggest that cation-induced conformational changes are not the unique cause for the observed positive shifts of the peak potential. Consequently, it may be hypothesized that, as was already proposed for crown ether derivatized PTs,<sup>3,9</sup> complexation of metal cations by the oligo(oxyethylene) network results in the formation of a



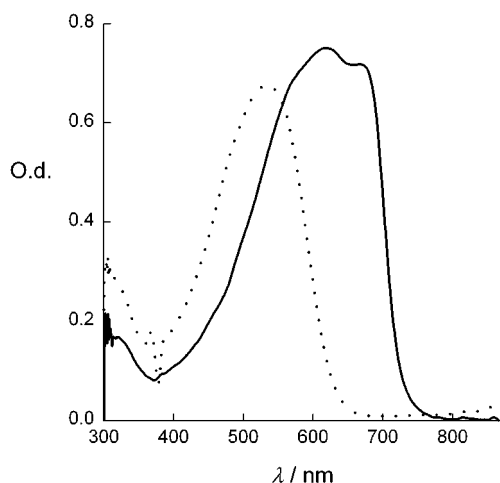
**Figure 3.** Cyclic voltammograms of poly(6b) and -(7) in acetonitrile (dotted line) and in water (solid line) in the presence of 0.10 M Ba(ClO<sub>4</sub>)<sub>2</sub>, 20 °C, and scan rate 100 mV s<sup>-1</sup>. Deposition conditions: Pt disk,  $\varnothing = 1$  mm; MeCN, 0.013 M **6b** or **7**, 0.10 M Bu<sub>4</sub>NClO<sub>4</sub>;  $E_{\text{dep}} = 1.20$  V;  $Q_{\text{dep}} = 400$   $\mu\text{C}$ .

potential barrier which limits the diffusion and migration of ionic species in the polymer during the doping process. The observed cation-induced positive shifts of the peak potential would then result from the cooperative effects of conformational changes and the electrostatic barrier.

**Effect of Aqueous Media on the Electronic Properties of the Polymers.** It has been shown already that the grafting of polyether chains onto the PT backbone considerably increases the hydrophilicity of the polymer and thus its electroactivity in an aqueous medium.<sup>24</sup> More recently, a similar effect was observed for poly(EDOT) substituted by short polyether chains.<sup>15</sup> On this basis, a comparative analysis of the electrochemical behavior of poly(6b) and -(7) in organic and aqueous media has been carried out.

Figure 3 shows the CVs recorded in the two solvents using Ba(ClO<sub>4</sub>)<sub>2</sub> as the electrolyte. Replacement of MeCN by water leads to a dramatic negative shift of  $E_{\text{pa1}}$  from +0.220 to  $-0.210$  V for poly(6b) and from +0.200 to  $-0.357$  V for poly(7). While these results confirm that the polymers are fully electroactive in

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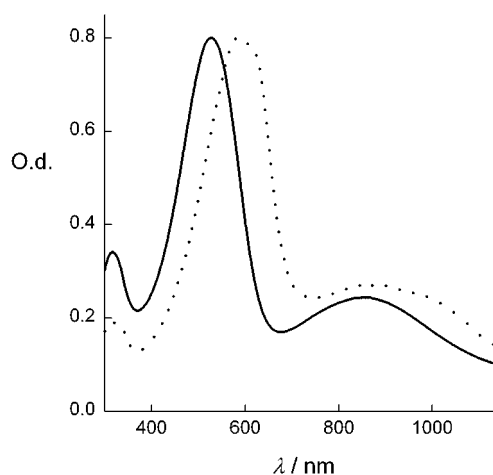
**Figure 4.** Electronic absorption spectra of undoped poly(**6b**) in acetonitrile (dotted line) and in water (solid line); 0.10 M  $\text{Ba}(\text{ClO}_4)_2$ . Deposition conditions: Pt disk,  $\varnothing = 5$  mm; 0.013 M **6b**, 0.10 M  $\text{Ba}(\text{ClO}_4)_2$ ;  $E_{\text{dep}} = 1.20$  V;  $Q_d = 5$  mC.

water, the sign and the magnitude of the potential shifts are astonishing because PTs derivatized by polyether chains are, in general, less electroactive and more difficult to oxidize in water than in an organic medium.<sup>24</sup>

Comparison of the electronic absorption spectra of a film of poly(**6b**) electrochemically undoped in the presence of  $\text{Ba}(\text{ClO}_4)_2$  in MeCN and in  $\text{H}_2\text{O}$  shows that an aqueous medium produces considerable changes in the optical properties of the polymer (Figure 4). The absorption maximum undergoes a 100 nm bathochromic shift to 635 nm, while a vibronic fine structure emerges with a new shoulder at 675 nm. These changes are accompanied by a hyperchromic effect, while the band gap decreases from 1.95 to 1.65 eV. Despite its magnitude (0.30 eV), the decrease of  $E_g$  is noticeably smaller than the negative shift of the oxidation peak (0.43V), suggesting that conformational relaxation might not be the only mechanism responsible for the shift of the peak potential.

These two series of results suggest that in MeCN complexation of  $\text{Ba}^{2+}$  by the polyether network produces simultaneously a distortion of the  $\pi$ -conjugated systems and the formation of a potential barrier that both contribute to an increase of the oxidation potential of the polymer. Immersion of the film in water results in the removal of  $\text{Ba}^{2+}$  cations from the polymer bulk, a process which leads at the same time to the suppression of the electrostatic barrier and to the relaxation of the  $\pi$ -conjugated structure toward a more planar geometry.

In the frame of this interpretation, a film undoped in  $\text{Bu}_4\text{NClO}_4/\text{MeCN}$  where no cation complexation is expected would represent a benchmark and should exhibit optimal effective conjugation. However, comparison of the optical data for poly(**6b**) films undoped in  $\text{Bu}_4\text{NClO}_4/\text{MeCN}$  (Table 2) and in  $\text{Ba}(\text{ClO}_4)_2/\text{H}_2\text{O}$  reveals in this latter case a further red shift of  $\lambda_{\text{max}}$  from 580 to 635 nm associated with a 0.13 eV decrease of  $E_g$  from 1.78 to 1.65 eV. This result shows that, besides the extraction of  $\text{Ba}^{2+}$ , immersion of the polymers in an aqueous medium produces a further enhancement of the effective conjugation length. A possible explanation for this effect could involve specific solvation of the hydrophilic oligo-(oxyethylene) network by water molecules, leading to a



**Figure 5.** Open-circuit electronic absorption spectrum of an electrochemically undoped film of poly(**6b**) on ITO after immersion in 0.10 M  $\text{Bu}_4\text{NClO}_4/\text{MeCN}$  (dotted line) and in 0.10 M  $\text{Ba}(\text{ClO}_4)_2/\text{MeCN}$  (solid line). Deposition conditions: Pt disk,  $\varnothing = 5$  mm; 0.013 M **6b**, 0.10 M  $\text{Ba}(\text{ClO}_4)_2$ ;  $E_{\text{dep}} = 1.20$  V;  $Q_d = 5$  mC.

swelling of the polymer. Such a swelling process would result in the stretching of the  $\pi$ -conjugated chains, thus forcing them to adopt a more planar and more rigid geometry. Of course, further work is needed to confirm this hypothesis.

**Solid-State Chromism.** The ionochromic properties of solutions of conjugated PTs derivatized by linear or macrocyclic polyethers have been reported by several groups.<sup>5,23</sup> However, until now examples of ionochromism in the solid state remained scarce. We have already shown that electrochemical undoping of poly-[3-(3,6-dioxaheptyl)thiophene] in the presence of lithium cations produces a few nanometers red shift of  $\lambda_{\text{max}}$  and an enhancement of the vibronic fine structure.<sup>2</sup>

While the above-discussed optical data provide conclusive evidences for solid-state ionochromism and solvatochromism, the modifications of the optical spectrum of the polymers by the chemical environment have been observed in static conditions on films conditioned by at least one redox cycle in the various electrolytic media.

To gain some qualitative information on the kinetics of the optical changes, the following sequence of experiments has been carried out. A film of poly(**6b**) electrodeposited on ITO from a solution of **6b** in 0.10 M  $\text{Bu}_4\text{NClO}_4/\text{MeCN}$  was electrochemically undoped at  $-0.50$  V, rinsed with acetonitrile, and immersed in a 0.10 M solution of  $\text{Bu}_4\text{NClO}_4$  in MeCN. The electronic absorption spectrum of the film shows an absorption band at 600 nm corresponding to the  $\pi-\pi^*$  transition of the conjugated chain and a less intense broad band with a maximum of around 860 nm, which corresponds to the highest energy transition of the polaron state. The presence of this polaron band results from spontaneous partial redoping of the polymer in open-circuit conditions because of the low redox potential of poly-(EDOTs). Immersion of the film in a MeCN solution containing 0.10 M  $\text{Ba}(\text{ClO}_4)_2$  produces an immediate color change with a hypsochromic shift of  $\lambda_{\text{max}}$  from 600 to 520 nm (Figure 5 and Table 3). This process is fully reversible, and the initial spectrum is instantaneously restored when the film is dipped back in  $\text{Bu}_4\text{NClO}_4/\text{MeCN}$  or even in pure acetonitrile.



**Table 3. Changes in the Electronic Absorption Data for Poly(6b) Films on ITO<sup>a</sup>**

treatment	$\lambda_{\text{max}}/\text{nm}$
dipping in Bu <sub>4</sub> N <sup>+</sup> /MeCN	600
dipping in Ba <sup>2+</sup> /MeCN	520
dry film after Ba <sup>2+</sup> /MeCN	506
dry film after Ba <sup>2+</sup> /H <sub>2</sub> O	506
dry film after sonication in pure MeCN or H <sub>2</sub> O	560

<sup>a</sup> Films electrodeposited on ITO and electrochemically undoped in 0.10 M Bu<sub>4</sub>NClO<sub>4</sub>/MeCN. Deposition conditions: ITO on a glass base (9 × 25 mm); 0.010 M **6b**, 0.10 M Bu<sub>4</sub>NClO<sub>4</sub>;  $E_{\text{dep}} = 1.20$  V;  $Q_{\text{d}} = 20$  mC.

Interestingly, these chromic effects persist in the dry state, and films that have been cycled in the presence of Ba<sup>2+</sup> either in MeCN or in water show, after complete drying, identical absorption spectra with a maximum at 506 nm. On the other hand, sonication of the same films in pure acetonitrile or water followed by complete drying induces a bathochromic shift of  $\lambda_{\text{max}}$  to 560 nm in both cases.

Again, these results indicate that complexation of Ba<sup>2+</sup> by the oligo(oxyethylene) segments induces a distortion of the  $\pi$ -conjugated backbone and a decrease of the effective conjugation, whereas extraction of Ba<sup>2+</sup> cations from the polymer by immersion in a barium-free solvent allows the  $\pi$ -conjugated backbone to relax toward a more planar structure.

On the other hand, comparison of the optical data for metal-free polymer in the dry state (560 nm, Table 3) and wetted by water (635 nm) definitively confirms the existence of specific interactions between the polymer and water molecules.

Finally, these results show that, in addition to its key role in the interactions with the chemical environment of the polymer, the oligo(oxyethylene) network provides an unusual structural flexibility to the  $\pi$ -conjugated PT backbone, thus allowing the polymer to instantaneously respond to external chemical stimuli even in the solid state.

**Stability under Redox Cycling.** As was already discussed, polymers derived from the two-site precursors **6a–c** form strongly adherent films which can only be removed by polishing the electrode. This behavior which emphasizes an inherent advantage of multisite precursors suggests that the stability under redox cycling might also be high. To test this hypothesis, a film of poly(**6b**) has been deposited on a Pt electrode and

submitted to repetitive voltammetric cycles in 0.10 M Bu<sub>4</sub>NClO<sub>4</sub>/MeCN between  $-0.40$  and  $+0.50$  V at a scan rate of  $100 \text{ mV s}^{-1}$ . Measurement of the amount of charge reversibly exchanged by the polymer showed that the film retains at least 94% of its initial electroactivity after 12 000 cycles, thus demonstrating the high stability of this class of polymers.

## Conclusion

Polymerization of precursors involving two EDOT groups linked by an oligo(oxyethylene) chain leads to cross-linked conjugated polymers of higher dimensionality in which oligo(oxyethylene) and PT networks coexist. These polymers exhibit a unique combination of properties such as improved adherence, high stability under redox cycling, and enhanced sensitivity of the electronic properties toward the chemical environment. The analysis of the electrochemical behavior of the polymers in the presence of metal cations has revealed cation recognition properties with potential shifts of several hundred millivolts. As shown by optical data, these potential shifts result in large part from conformational changes. Perhaps the most important findings of this work concern the high affinity of the polymers for aqueous media. Electrochemical and optical experiments provide a coherent picture supporting the existence of specific interactions between water molecules and the oligo(oxyethylene) network. These interactions stabilize the  $\pi$ -conjugated backbone into a privileged conformation corresponding to a considerable enhancement of the effective conjugation length and hence reduction of the band gap.

The environmental sensitivity of these polymers associated with their structural flexibility has allowed one to obtain first evidences for intense, fast, and reversible ionochromism and solvatochromism on solid films of  $\pi$ -conjugated polymers.

This combination of electrochemical and optical sensitivity, structural flexibility, and hydrophilicity thus opens interesting perspectives for a future design of a modified electrode based on functionalized poly(EDOT)s in particular in the field of bioelectronic sensors.

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