

Doping-Induced Ion-Exchange in the Highly Conjugated Self-Doped Polythiophene from Anodic Coupling of 4-(4*H*-Cyclopentadithien-4-yl)butanesulfonate

Gianni Zotti,* Sandro Zecchin, and Gilberto Schiavon

Istituto di Polarografia ed Elettrochimica Preparativa, Consiglio Nazionale delle Ricerche, c.o Stati Uniti 4, 35020 Padova, Italy

Anna Berlin,* Giorgio Pagani, and Augusto Canavesi

Dipartimento di Chimica Organica e Industriale dell'Università e Centro CNR Speciali Sistemi Organici, via C. Golgi 19, 20133 Milano, Italy

Received May 2, 1997. Revised Manuscript Received August 28, 1997[⊗]

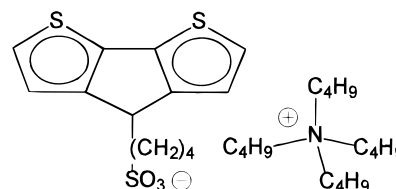
Anodic coupling of tetrabutylammonium 4-(4*H*-cyclopentadithien-4-yl)butanesulfonate in acetonitrile + 0.1 M Bu₄NClO₄ produces self-doped polythiophene films with high conjugation length ($\lambda_{\max} = 540$ nm; $E^\circ = -0.3$ V vs Ag/Ag⁺), conductivity (0.6 S cm⁻¹) and solubility in water (ca. 10 g L⁻¹). Electrochemical quartz crystal microbalance measurements of the ion flux during polymer oxidative doping in acetonitrile + 0.1 M MClO₄ (M = Li, Me₄N, Et₄N, Pr₄N, and Bu₄N) have shown that cation ejection is accompanied by anion injection in 1:1 ratio.

Introduction

Self-doped polyconjugated polymers have been proposed in the past^{1–11} as water-soluble conducting polymers, but in fact the characteristics of the produced materials are far from being optimized. Their solubility is often scarce (e.g., 0.5 g L⁻¹) as well as their conductivity (10⁻²–10⁻³ Scm⁻¹^{9,11}). Also their conjugation length, which measures their rank as conducting materials, is limited, as in the case of poly(thien-3-yl-alkanesulfonate)s for which the maximum absorption is at 420–430 nm,^{6,8} i.e., in the range of thiophene tetramers. In addition their redox potential is high (ca. 0.7 V vs Ag/AgCl²). The most recent work on the synthesis of poly(thien-3-yl-alkanesulfonate)s¹¹ has given products with maximum absorption at 460 nm. Better results are obtained from carboxy-functionalized poly(alkylthiophene)s,⁹ but these polymers cannot be really considered self-doped since their proton dissociation is scarce.

The self-doping ability of this class of polymers has been rarely investigated.^{2,3} In one case only has the

Scheme 1. Formula of Tetrabutylammonium 4-(4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]-dithienyl)butanesulfonate



mass change upon doping been reported, and this concerned a pyrrole copolymer.³ No such report exists to our knowledge for a polythiophene. For this reason and to obtain a regular extensively conjugated sulfonated polythiophene, we have focused our attention to tetrabutylammonium 4-(4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithienyl)butanesulfonate (Scheme 1) as starting monomer. This choice was made since (i) cyclopentadithiophene is a thiophene-based monomer with a low oxidation potential; (ii) the functionalization is remote from the coupling sites, a structural design that has proven to be beneficial;^{12–15} (iii) the sulfonate group is separated by four methylene groups from the cyclopentadithiophene end which is enough to eliminate any inductive effect of the sulfonate group; (iv) the tetrabutylammonium cation gives the monomer high solubility in acetonitrile; (v) we could exploit the carbon acidity of this dithienyl analogue of fluorene by reacting the conjugate anion with sultones, a procedure successfully employed for the N-functionalization of pyrrole-based monomers.^{16–18} Here we report the synthesis of the monomer, its

* Correspondence should be addressed to gzotti@pdadr1.pd.cnr.it.

⊗ Abstract published in *Advance ACS Abstracts*, November 15, 1997.

(1) Havinga, E. E.; ten Hoeve, W.; Meijer, E. W.; Wynberg, H. *Chem. Mater.* **1989**, *1*, 650.

(2) Ikenoue, Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1988**, *110*, 2983.

(3) Reynolds, J. R.; Sundaresan, N. S.; Pomerantz, M.; Basak, S.; Baker, C. K. *J. Electroanal. Chem.* **1988**, *250*, 355.

(4) Qiu, Y. J.; Reynolds, J. R. *J. Electrochem. Soc.* **1990**, *137*, 900.

(5) Havinga, E. E.; van Horssen, L. W.; ten Hoeve, W.; Wynberg, H.; Meijer, E. W. *Polym. Bull. (Berlin)* **1987**, *18*, 277.

(6) Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *20*, 151.

(7) Delabouglise, D.; Garnier, F. *New J. Chem.* **1991**, 233.

(8) Ikenoue, Y.; Saida, Y.; Kita, M.; Tomozawa, H.; Yashima, H.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1694.

(9) Bauerle, P.; Gaudl, K.; Wurthner, F.; Sariciftci, N.; Negelbauer, H.; Mehring, M.; Zhong, C.; Doblhofer, K. *Adv. Mater.* **1990**, *2*, 490.

(10) Havinga, E. E.; Van Horssen, L. W. *Makromol. Chem. Macromol. Symp.* **1989**, *24*, 67.

(11) Arroy-Villan, M. I.; Diaz-Quijado, G. A.; Abdou, M. S. A.; Holdcroft, S. *Macromolecules* **1995**, *28*, 975.

(12) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Macromolecules* **1994**, *27*, 1938.

(13) Zotti, G.; Schiavon, G.; Zecchin, S.; Berlin, A.; Pagani, G. *Synth. Met.* **1994**, *66*, 149.

(14) Zotti, G.; Berlin, A.; Pagani, G.; Schiavon, G.; Zecchin, S. *Adv. Mater.* **1995**, *7*, 48.

(15) Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G.; Canavesi, A. *Chem. Mater.* **1995**, *7*, 2309.

electrochemical polymerization by anodic coupling in acetonitrile and the characterization of the resulting polymer. In particular we describe the electrochemical quartz crystal microbalance evaluation of the polymer cation exchange properties with positive doping in acetonitrile.

Experimental Section

Chemicals and Reagents. The monomer lithium 4-(4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithienyl)butanesulfonate was synthesized as described below; the corresponding tetrabutylammonium salt was prepared from aqueous solution of the lithium salt by ion exchange with H⁺-exchange resin (Dowex HCR-W'' by Sigma) followed by neutralization with tetrabutylammonium hydroxide and evaporation to dryness. 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene was prepared according to the literature.^{19–21} Acetonitrile (AN) was reagent grade (Merck) with a water content <0.01%. All other chemicals were reagent grade and used as received.

Lithium 4-(4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithienyl)butanesulfonate. *n*-BuLi (1.6 N) in hexane (0.70 mL, 1.1 mmol) was added dropwise to a stirred solution of 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (200 mg, 1.1 mmol) in THF (8 mL), under nitrogen and maintaining the temperature at 0 °C. After 1.0 h of stirring at room temperature, the resulting solution was cooled at 0 °C and added dropwise to a solution of 1,4-butanediol (153 mg, 1.1 mmol) in THF (5 mL) at 0 °C. After stirring at room temperature for 1.5 h, the reaction mixture was treated with water and extracted with ether. The aqueous phase was evaporated at reduced pressure and the residue treated with petrol ether/2-propanol (volume ratio 7:3) to give the title compound as a white solid (290 mg, 80% yield), mp >250 °C.

Anal. Calcd for C₁₃H₁₃LiO₃S₃: C, 48.72; H, 4.06%. Found: C, 48.57; H, 4.09%. ¹H NMR (D₂O, 300 MHz) δ 1.50 (2H, m, CH₂), 1.75 (2H, m, CH₂), 1.90 (2H, m, CHCH₂), 4.80 (1H, t, H⁴), 4.81 (2H, t, CH₂SO₃Li), 7.23–7.36 (4H, AB system, thiophene protons).

Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three-electrode cells. Unless otherwise stated the supporting electrolyte was tetrabutylammonium perchlorate (Bu₄NClO₄) 0.1 M in AN. The counter-electrode was platinum; reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The working electrode for cyclic voltammetry was a platinum minidisk electrode (0.003 cm²). For electronic spectroscopy a 0.8 × 2.5 cm indium-tin-oxide (ITO) sheet (ca. 80% transmittance, ca. 20 Ω/sq resistance, from Balzers, Liechtenstein) was used. A platinum sheet (15 cm²) was used in preparative electrolyses.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer; IR spectra in reflection-absorption on a Perkin-Elmer 2000 FTIR spectrometer.

Ex situ conductivity measurements were performed at room temperature with the four-probe technique using a Keithley 220 programmable current source and a Keithley 195A digital multimeter. The apparatus and procedures used in the in situ conductivity experiments were previously described in detail.²² The relevant working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with interband

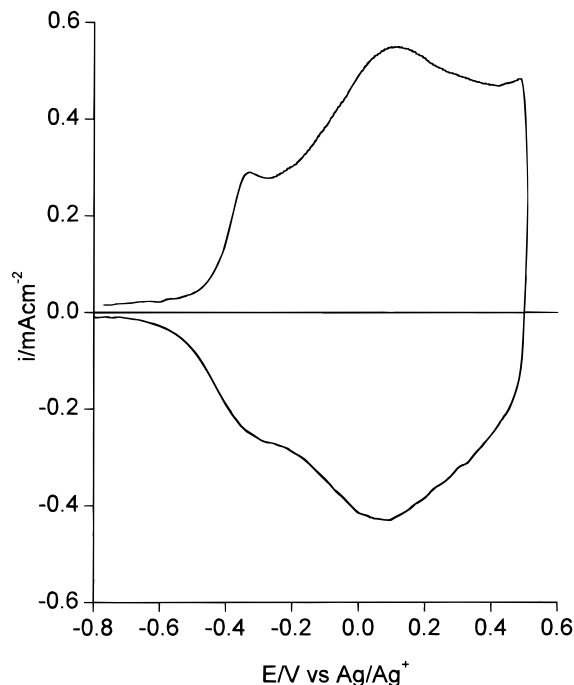


Figure 1. Cyclic voltammetry for poly(4-(4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithienyl)butanesulfonate) in AN + 0.1 M Bu₄NClO₄. Scan rate: 0.1 V s⁻¹; reversible charge: 4 mC cm⁻².

spacing of 6 μm, typically polymer-coated with the passage of 20 mC, which ensured the attainment of limiting resistance conditions. Poly(3-methylthiophene) (60 S cm⁻¹) was used as conductivity standard.

Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a platinum-coated AT-cut quartz electrode (0.2 cm²), resonating at 9 MHz, onto which the polymers were deposited. The oscillator circuit was homemade and the frequency counter was a Hewlett-Packard Model 5316B. Calibration of the quartz crystal microbalance was performed with silver deposition from a 10⁻² M solution of AgNO₃ in AN + 0.1 M Bu₄NClO₄. Data were collected by a microcomputer with a homemade analyzing software by which frequency changes Δν were monitored as mass changes Δ*m*.

Results and Discussion

Monomer Synthesis. The functionalization in position 4 of 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene with the butanesulfonate group has been readily achieved by reaction of the conjugate carbanion lithium salt with 1,4-butanediol, in analogy with previously reported *N*-functionalization of pyrrole derivatives.^{16–18}

Polymer Electrodeposition and Characterization. The lithium salt of the monomer is so sparingly soluble in AN + 0.1 M Bu₄NClO₄ (ca. 10⁻⁴ M), that polymerization is prevented. Addition of water, which dissociates the lithium salt, in 1% v/v concentration increases the solubility to ca. 10⁻³ M. Under these conditions cyclic voltammetry (CV) displays the oxidation peak of the monomer at 0.6 V, i.e., the same value of 4-alkyl-substituted cyclopentadithiophene,¹² indicating that the sulfonate substituent does not affect the electronic properties of the monomer. Continuous cycling of the potential over the oxidation peak results in the progressive buildup of the polymer. The CV of the deposits is shown as a twin set of redox processes at *E*^o = -0.3 and 0.1 V (Figure 1), i.e., the same values for the analogous polymer bearing a butyl chain at position 4,¹² providing evidence that the substituent does not influence the redox properties of the polymer chain. The

(16) Reynolds, J. R.; Ruiz, J. P.; Wang, F.; Jolly, C. A.; Nayak, K.; Marynick, D. S. *Synth. Met.* **1989**, *28*, C621.

(17) Sundaresan, N. S.; Basak, S.; Pomerantz, M.; Reynolds, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 621.

(18) Collard, D. M.; Fox, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 9414.

(19) Jeffries, A. T.; Moore, Ondeyka, D. M.; Sprinsteen, A. W.; MacDowell, D. W. H. *J. Org. Chem.* **1981**, *46*, 2885.

(20) Kraak, E.; Wiersema, A. K.; Jordens, P.; Wynberg, H. *Tetrahedron* **1968**, *24*, 3381.

(21) Brenna, E. Ph.D. Thesis, University of Milan, 1993.

(22) Schiavon, G.; Sitran, S.; Zotti, G. *Synth. Met.* **1989**, *32*, 209.

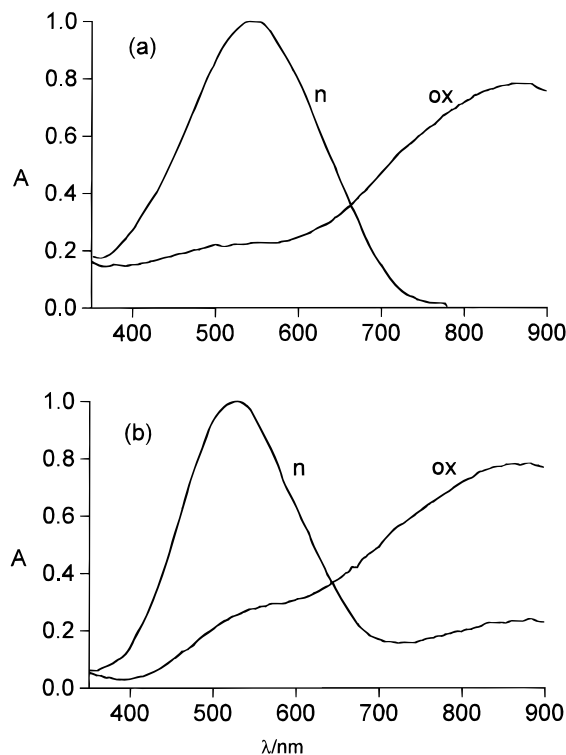


Figure 2. Spectra of neutral (n) and oxidized (ox) poly(4-(4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithienyl)butanesulfonate) (a) as film in AN + 0.1 M Bu₄NClO₄ and (b) in water solution.

polymer is produced with a charge yield (ratio of reversible charge, measured at 0.6 V, over deposition charge, measured in the neutral state) of ca. 15%. As a film it displays a maximum adsorption at 550 nm, indicating an extensive conjugation length, comparable with that of the alkyl-substituted analogues.¹²

A higher monomer concentration, useful for a fast bulk polymer production and for in situ conductivity measurements, can be attained with a higher water contents but in this case both the CV and the electronic spectrum indicate clearly that the oxidized polymer undergoes degradation by nucleophilic attack of water. For this reason we prepared the tetrabutylammonium salt of the monomer which instead is very soluble in AN. Electropolymerization is possible starting from 10⁻² M solution also in the absence of supporting electrolyte. The polymer is produced with a higher charge yield (25%) without any appreciable coloring of the solution. This result rules out losses by oligomer dissolution and therefore allows to evaluate from the charge yield the doping level of the oxidized (at 0.6 V) polymer as 1 electron/2 cyclopentadithiophene moieties or 0.25 electron/thiophene unit, i.e., the level usually met in polythiophenes. The film is also reduced at ca. -2.2 V, but the process is irreversible, due to dissolution of the reduced material, as shown by the coloring of the solution nearby the filmed surface, rather than to reactions following the electron transfer.

The neutral polymer film displays a maximum absorption at 525 nm, which is hypsochromically displaced in comparison with that produced from the less concentrated lithium salt, a fact attributable to the presence of lower oligomers. In any case potential cycling causes the maximum absorption to shift to 540 nm (Figure 2a) due to further polymerization of the oligomeric deposit

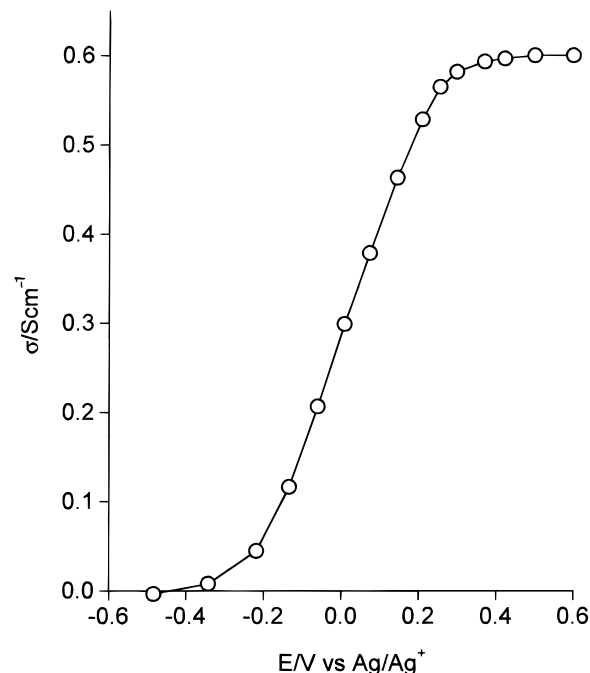


Figure 3. In situ conductivity of poly(4-(4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithienyl)butanesulfonate) in AN + 0.1 M Bu₄NClO₄.

as previously observed for other polythiophenes.²³ The oxidized film shows the maximum absorption at 870 nm.

The maximum absorption of the neutral polymers before and after CV cycling has allowed to evaluate its average degree of polymerization DP. Interpolating the well-known linear relationship between the optical energy gap and the inverse of DP, built from the maximum absorption of cyclopentadithiophenes and some of their oligomers,¹² has given DP values of 5 and 7 for the pristine and the potential cycled polymers, respectively. DP was determined also by analysis of the IR reflection-absorption spectrum using the intensity ratio of the CH out-of-plane deformation bands at 810 cm⁻¹, due to backbone rings, and at 650 cm⁻¹, due to the terminal rings.¹² The results are essentially the same obtained by the UV-vis analysis. Thus the polymer chains are constituted by 10–15 thiophene rings, and the polymer is in fact oligomeric.

The maximum in situ conductivity of the polymer, shown in Figure 3, in dependence of the applied potential, is 0.6 S cm⁻¹, i.e., considerably higher than those reported for other self-doped polymers.^{9,10} It is in any case lower than that of the corresponding alkyl-substituted analogue poly(4-*n*-butyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene) (80 S cm⁻¹¹²). This is due to the presence of the sulfonate-tetrabutylammonium ion pair, which increases the interchain distance. According to some authors¹¹ the lower conductivity of the alkyl-sulfonated polymers vs their alkylated counterparts is due to ion aggregation (ion pairing among chains) which introduces disorder in the structure associated with decoplanarization of the thiophene rings. This does not seem to be our case since the conjugation length of the polymer chains is essentially the same in both the alkylsulfonated and the alkylated polymers.

The pristine neutral material is moderately soluble in water producing a violet solution ($\lambda_{\max} = 528$ nm,

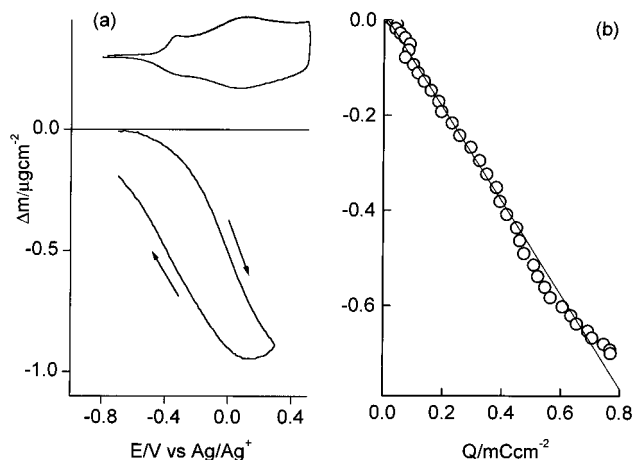


Figure 4. Mass change Δm vs (a) potential E and (b) redox charge Q for poly(4-(4H-cyclopenta[2,1-b:3,4-b']dithienyl)butanesulfonate) in AN + 0.1 M Bu₄NClO₄. Upper (a): CV for comparison.

Figure 2b) accompanied by an absorption at ca. 900 nm, due to partial aerial oxidation. It is remarkable that the maximum absorption of the solution is essentially the same of the solid film. The absence of any solvatochromic effect is due to the long distance of the sulfonate functionalization from the coupling sites. The material becomes water-insoluble after potential cycling, responsible for coupling oligomers to long polymer chains.

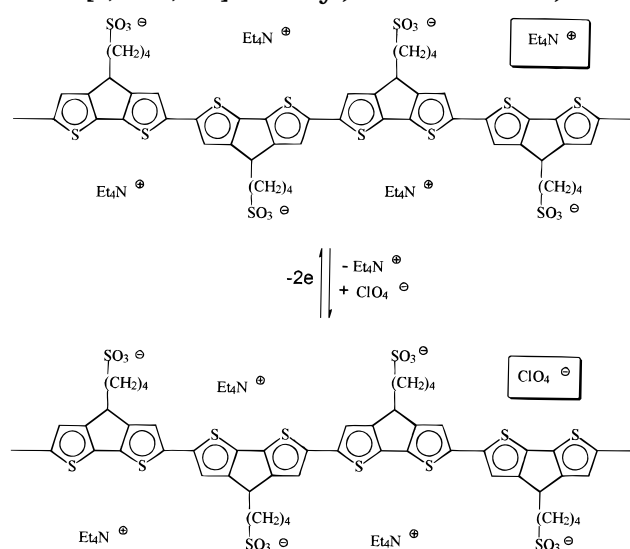
The bulk oxidized polymer produced by oxidative electrolysis at 0.7 V is a dark blue material extensively soluble in water (ca. 10 g L⁻¹). The blue solution shows the maximum absorption at 870 nm accompanied by a weak signal at ca. 500 nm due to partial reduction by water (Figure 2b).

Conductive films have been cast on glass plates from water solution of the oxidized polymer. Typical spots of 3 cm² area were produced from 0.1 mL of solutions containing 10 g L⁻¹ of the polymer; the average thickness of the spots was ca. 2 μm. Four-probe measurements have indicated a good conductivity (ca. 0.03 S cm⁻¹), however 20 times lower than that of in situ produced samples. This result may be ascribed to the concurrence of partial dedoping by water, relatively low molecular weight, and possibly morphological differences from the pristine material due to the water treatment.

Ion Exchange during Polymer Doping–Dedoping. During the oxidative process the polymer is expected to eject cations, therefore exerting its ability as self-dopable polymer. In the past this behavior has not been clarified satisfactorily since the measured negative mass changes were not correlated with the applied charge.³

We have checked the EQCM response of the polymer films upon CV in AN containing perchlorate salts of various cations in 0.1 M concentration (Figure 4). The mass change during the CV in the presence of Bu₄N⁺ (Figure 4a) shows clearly that cations are ejected during positive doping. The relationship of mass change Δm and charge Q (Figure 4b) is linear but the slope, corresponding to $F\Delta m/Q = 100$ g mol⁻¹, is much lower than that expected from the cation mass ($F\Delta m/Q = 240$ g mol⁻¹). At the opposite side the lithium cation produces a mass increase of $F\Delta m/Q = 50$ g mol⁻¹. Slopes intermediate between these values are obtained

Scheme 2. Cation–Anion Flux during Positive Doping of Poly(4-(4H-cyclopenta[2,1-b:3,4-b']dithienyl)butanesulfonate)



with the other investigated cations (Me₄N⁺, Et₄N⁺, and Pr₄N⁺).

The data indicate that cation ejection is not the only process of ion exchange but that it is accompanied by a pronounced anion injection. This suggestion has been confirmed by IR analysis of the polymer film before and after oxidation showing the appearance of the perchlorate bands at 1100 and 620 cm⁻¹ after oxidation. We have estimated the contribution of the cation flux for the various cations making the assumption that the solvent exchange is negligible, a particularly likely hypothesis for the tetraalkylammonium salts. The molar fraction of cation flux X_c and anion flux $(1 - X_c)$ to the mass change have been evaluated by the charge and the relevant mass change according to the following equation:

$$\Delta m = -X_c(Q/F)W_c + (1 - X_c)(Q/F)W_a$$

where W_c and W_a are the cation and anion molecular weights.

The X_c values for the investigated set of cations were found to be 0.5 ± 0.1 , so that a rather undifferentiated behavior is clearly evidenced. It is remarkable that the cation flux is the same for the alkylammonium and the lithium cation, which is more strongly bound to the sulfonate groups²⁴ as confirmed by the observation that the polymer E° value in 0.1 M lithium perchlorate is shifted positively by 0.1 V from the value in 0.1 M tetraalkylammonium perchlorate. From the high cation flux it appears that the self-doping ability of the polymer is noticeable but is kept within the limits of 50% of its total capability. Moreover the X_c values were found to be the same in 0.05 and 0.5 M electrolyte concentration and in other solvents (e.g., water) which rules out environmental effects and points to the material structure as responsible for this result.

On the basis of these results we believe that the equal partitioning of the cation and anion fluxes is due to the requirement of keeping the polymer structure unchanged. The simple cation ejection would require a

(24) Hojo, M.; Hasegawa, H.; Miyauchi, Y.; Moriyama, H.; Yoneda, H.; Arisawa, S. *Electrochim. Acta* **1994**, *39*, 629.

consistent and probably energetically demanding shrinking of the structure which is avoided by the replacement of a cation with an anion, as illustrated in Scheme 2. It is possible that these structural requirements are not present in a polymer with a lower content of self-dopant pending anions. This reasoning is supported by the elemental analysis of the doped form of a copolymer of pyrrole and 3-(pyrrolyl)propanesulfonate (2:1 ratio), a material almost devoid of (perchlorate) anion.³

Conclusions

The anodic coupling of a functionalized bithiophene bearing an alkylsulfonate group remote from the coupling site has allowed the production of a self-doped polythiophene of unprecedented characteristics such as high conjugation length, conductivity, and solubility.

These properties allow an easy casting of conductive films from water solutions. Moreover these deposits are oligomeric so that they may be subsequently insolubilized by electrochemical cross-linking.

The regular structure of the polymer, dictated from the monomer structure, and its low content of defects,

indicated by its high conjugation length, have been used for the investigation of the ion exchange properties accompanying the oxidative doping. In acetonitrile the polymer oxidation is accompanied by both cation ejection and anion injection in an equal flux. This quite unexpected behavior appears to be related to polymer structural requirements.

The presence in a regular and defect-free polythiophene structure of the sulfonate group, which has been shown to promote selectively the anodic coupling of dipyrrole to polypyrrole,²⁵ will be useful for the template polymerization of polypyrrole over and within polythiophene structures which we are actually exploiting.

Acknowledgment. The authors would like to thank R. Salmaso and S. Sitran of the CNR for their technical assistance.

CM970301G

(25) Zotti, G.; Schiavon, G.; Zecchin, S.; Sannicolo', F.; Brenna, E. *Chem. Mater.* **1995**, 7, 1464.