Localization Effects in Asymmetrically Substituted Polythiophenes: Controlled Generation of Polarons, Dimerized Polarons, and Bipolarons

Karim Faïd and Mario Leclerc*

Département de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7 Canada

My Nguyen and Art Diaz

IBM Almaden Research Center, San Jose, California 95120-6099

Received May 25, 1994; Revised Manuscript Received October 12, 1994®

ABSTRACT: The attachment to polythiophenes of substituents with different electronic properties produces polymeric materials with unusual electrical and optical properties. Controlled generation of polarons, dimerized polarons, and bipolarons was achieved through the formation of moieties of high and low band gap energy along the polythiophene backbone. The occurrence of such *quantum wells* decreased the recombination of the polarons in bipolarons as would be observed in symmetrically substituted polythiophenes. One of the most interesting consequences of this band-gap engineering is the ability of tuning the transport properties of these polymers. These novel characteristics make possible the formation of paramagnetic and diamagnetic conducting states through the control of the redox state. They may also enhance the polaron population available for singlet exciton conversion in electroluminescent devices.

Introduction

The addition of relatively long and flexible alkyl side chains on polythiophene has led to the development of solution and melt processable conjugated polymers.[1] Moreover, the presence of these side chains can also modify the electrical, electrochemical, and optical properties of the resulting materials. This synthetic approach is extremely versatile and can be useful for the design of polythiophenes with tailored physical properties.[2] In this respect, it has been recently shown that the presence of strong electron-donating alkoxy substituents dramatically decreases the oxidation potential and the band gap of the polymers and leads to stable and nearly transparent conducting (oxidized) polythiophenes.[3] Other studies have revealed that it is possible to tune the oxidation potential of processable polythiophenes from +0.05 to +1.3 V vs SCE by the adequate choice of the nature and the position of the substituents.[3,4]

On the other hand, this strong dependence of the oxidation potential of the polythiophenes upon their substitution pattern could be utilized to create *quantum wells* along the polymer backbone, by analogy with inorganic semiconductors. In these systems, potential energy wells (or quantum wells) are formed by sandwiching an ultrathin low band gap layer (i.e., GaAs) between two wide gap semiconductors (i.e., AlGaAs).[5] Quantum confinement of electrons at the semiconductor interface results in quasi-two-dimensional electron systems in which the electronic motion is unbound within the interface plane but quantized perpendicularly to it. The unique electronic properties of such systems have been widely investigated for more than two decades in materials such as GaAs−AlGaAs heterostructures. One- and zero-dimensional semiconductors (quantum wire and dots) have also been extensively investigated.[6]

Similarly, the polymerization of bithiophenes bearing both electron-donating and electron-withdrawing substituents should produce a conjugated polymer with a localized and specific HOMO−LUMO gap energy. This approach was recently developed through the synthesis of asymmetrically substituted poly(bithiophene)s.[3] Preliminary studies on poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene)[7] have revealed the presence of three redox processes which were related to the successive formation of radical cations (polarons), dimerized polarons, and dications (bipolarons). A high concentration of polarons is not usually observed in polythiophenes since the delocalization along the backbone allows the formation of the more stable bipolarons.[2,8]

Therefore, to shed some light about localization effects in asymmetrically substituted poly(bithiophene)s, a more complete characterization of the physical properties of poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) has been carried out. This concept has also been extended to a poly(bithiophene) substituted by two electron-donating groups of different strengths, namely, poly(4-butoxy-4′-decyl-2,2′-bithiophene).

Experimental Section

Materials. Poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) and poly(4-butoxy-4′-decyl-2,2′-bithiophene) were synthesized following the procedures described in a previous publication.[3] These polymers are completely soluble in chloroform and tetrahydrofuran. From SEC measurements based on a calibration with polystyrene standards,[9] these polymers have a weight-average molecular weight of ca. 5000−10000.

Physical Measurements. In-situ conductivity measurements were carried out on a dual microelectrode (courtesy of Dr. G. Zotti), and the experimental setup was derived from the literature.[10] The working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with an interband spacing of 6 μm, coated by a thin polymer film of ca. 1 μm. The polymer films were held under various electrochemical potentials while a small-amplitude (ca. 10 mV) dc potential was applied between the bands. The current was recorded with a picoammeter (Keithley 485). Chemical oxidation of the polymers was performed by adding known quantities of iron trichloride solution in chloroform. UV−vis−near-IR spectra were recorded after homogeneization with a Cary 5 spectrophotometer. In-situ solid-state spectroelectrochemistry (on ITO-coated glass), cyclic voltammetry (EG&G poten-

* To whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* December 1, 1994.

0024-9297/95/2228-0284$09.00/0

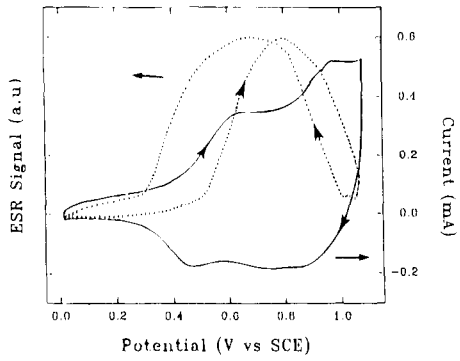

Figure 1. Cyclic voltammetry (solid line) and in-situ electron spin resonance (dotted line) measurements on poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) on a platinum electrode.

tiostat/galvanostat, Model PAR 273), and in-situ electron spin resonance (Bruker ESR spectrometer, Model ER080) measurements were carried out in solutions of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, and all potentials are relative to a saturated calomel electrode (SCE).

Results and Discussion

The cyclovoltammogram of poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) revealed three discernible quasi-reversible redox processes (Figure 1). These redox processes modify strongly the electronic structure of the polymer and give rise to the formation of paramagnetic species during the first oxidation process around +0.6 V vs SCE (Figure 1). These radicals display a strong Lorentzian ESR peak with a 6.9 G peak-to-peak width which suggests the presence of relatively localized paramagnetic species.[11-13] In a recent study, Horowitz et al.[11] found that the ESR linewidth peak-to-peak of β-substituted didecylsexithiophene is 7 G while that of β-substituted tetradecyldodecylthiophene is 4.5 G, suggesting that in the case of the present materials localization effects may occur in sequences of about six thiophene rings. This results are in agreement with theoretical calculations of Meyers et al.[14] and experimental results of Piaggi et al.[15]

During the second oxidation process (+0.9 V), diamagnetic species are created with a small change in the concentration of the previously formed radicals. Finally, during the third oxidation process (+1.0 V), diamagnetic species are formed with a drop-off of the ESR signal, indicating a simultaneous consumption of the radicals (Figure 1). Similar features can be clearly observed during the cathodic scan. This behavior is certainly not typical for polythiophenes, where only one broad redox process is usually observed with the formation of diamagnetic charge carriers.[8,16,17] However, recent studies on oligothiophenes have shown that it is possible to generate radical cations (polarons), dimerized polarons, and dications (bipolarons) in some of these low molecular weight systems.[11-13,18-20] It seems that the finite conjugation length allows the stabilization and successive formation of these different charge carriers. A similar localization effect of the charge carriers is taking place in the asymmetrically substituted poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene), which shows successive formation of different charge carriers probably resulting from sequences of high and low HOMO–LUMO gap energy.[7]

These different charge carriers can also lead to significant changes in the absorption spectrum of the materials and, consequently, in-situ spectroelectrochemical measurements have been performed on poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene). In-situ solid-state spectroelectrochemical results (Figure 2) support those obtained by cyclic voltammetry and in-situ ESR measurements (Figure 1). Indeed, during the first oxidation reaction, the intensity of the $\pi-\pi^*$ transition at 480 nm decreases while two new absorption bands appear at 750 and 1350 nm which reflect the formation of radical cations. Between +0.8 and +1.0 V, a second species appears which absorbs at 615 nm and there is a blue shift of the 1350 nm band. On the basis of the ESR measurements, this second type of charge carriers is diamagnetic and could be dimerized polarons.[13] Finally, beyond +1.0 V, a large absorption band appears around 1000 nm which could be the optical signature of bipolarons, since the ESR measurements show the gradual disappearance of the radical cations (polarons). Similar results were obtained from the chemical oxidation of the polymer in chloroform solution (Figure 3). The successive formation of the three different charge carriers is clearly observed.

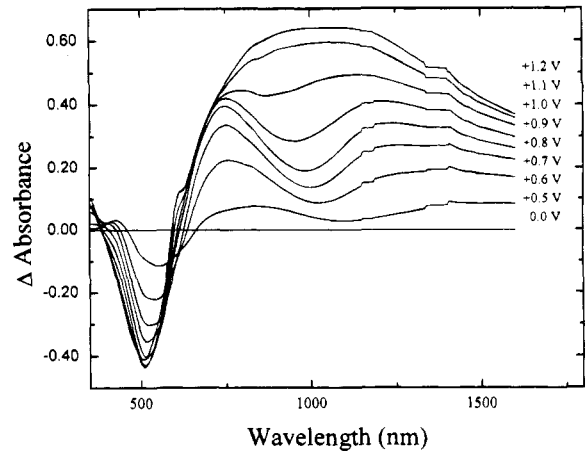

Figure 2. Differential UV–vis–near-IR absorption spectra of poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) on an ITO electrode at various electrochemical potentials.

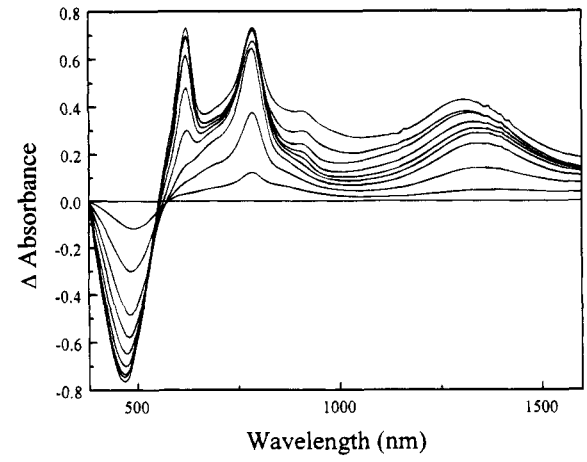

Figure 3. Differential UV–vis–near-IR absorption spectra of poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) in chloroform with increasing oxidation levels (oxidized with iron trichloride).

The oxidative generation of these different species in poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) also affects its electrical conductivity. Not surprisingly, in-situ conductivity measurements indicate that the neutral polymer is insulating (Figure 4). During the first electrochemical oxidation, the conductivity rises to a maximum of about 0.1 S/cm near +0.6 V. The conductivity level reaches a second maximum at +1.05 V with the presence of a small shoulder near +0.95 V in the

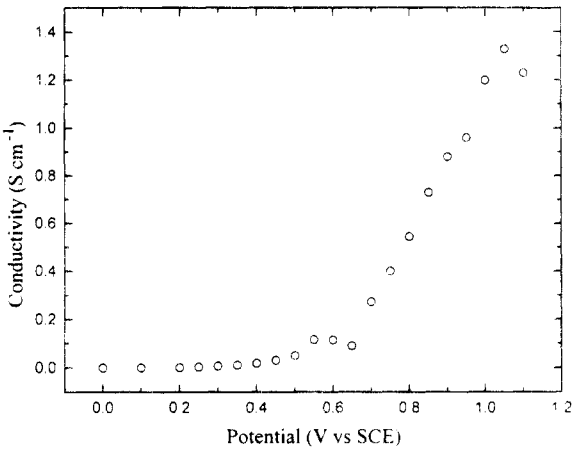

Figure 4. In-situ conductivity measurements on poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) on platinum electrodes.

conductivity curve. It is worth noting that, on the basis of the ESR (Figure 1) and optical (Figure 2) results, the first conductivity maximum (0.1 S cm^{-1}) around +0.6 V corresponds to the formation of 50% of the polarons produced during the complete redox process (magnitude of the 750 nm band and of the ESR signal at +0.6 V compared to that at +0.8 V). This result suggests that the efficiency of the charge carrier hoppings is greater when the sites are partially occupied. This is in good agreement with previous results obtained with other conjugated polymers.[21-23] To our knowledge it is the first time a mixed valence state between neutral and polaronic sites is clearly shown. Upon further oxidation of the polymer, dimerized polarons and bipolarons are formed in poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) and from the increasing conductivity (from 0.1 to 1.4 S/cm), it is clear that the dimerized polarons and bipolarons provide a more efficient pathway for the charge transport.

From all these measurements, it seems that the presence of both electron-donating and electron-withdrawing substituents along the polythiophene backbone leads to a localization of radical cations. This particular substitution pattern can create quantum wells along the main conjugated backbone. These charge localization effects may not be unique to a combination of electron-attracting and electron-releasing substituents. Two electron-donating (or electron-withdrawing) side chains of quite different strengths may also produce similar effects. To verify this hypothesis, the electrochemical, electrical, and optical properties of poly(4-butoxy-4′-decyl-2,2′-bithiophene) were characterized. Similarly to poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene), poly(4-butoxy-4′-decyl-2,2′-bithiophene) exhibits multiple quasi-reversible redox processes (Figure 5). The first oxidation peak appears at +0.35 V vs SCE and a second large peak appears around +0.75 V. However, three peaks are clearly observed in the cathodic scan at +0.55, +0.35, and +0.13 V. In-situ conductivity measurements give additional information about these redox processes. The neutral polymer is insulating and the first conductivity maximum occurs around +0.45 V. A rapid increase of the conductivity occurs during the next oxidation process and reaches a second maximum near +0.8 V.

In-situ solid-state spectroelectrochemical measurements allowed a better characterization of the different charge carriers created upon oxidation (Figure 6). During the first oxidation reaction, polarons are created which have two absorption bands at 785 and 1400 nm.

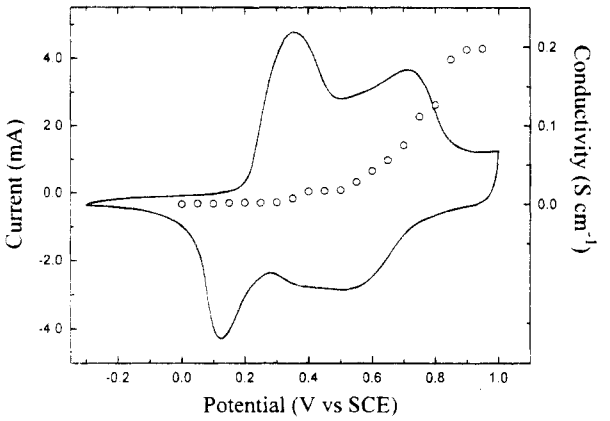

Figure 5. Cyclic voltammetry (solid line) and in-situ conductivity (open circles) measurements on poly(4-butoxy-4′-decyl-2,2′-bithiophene).

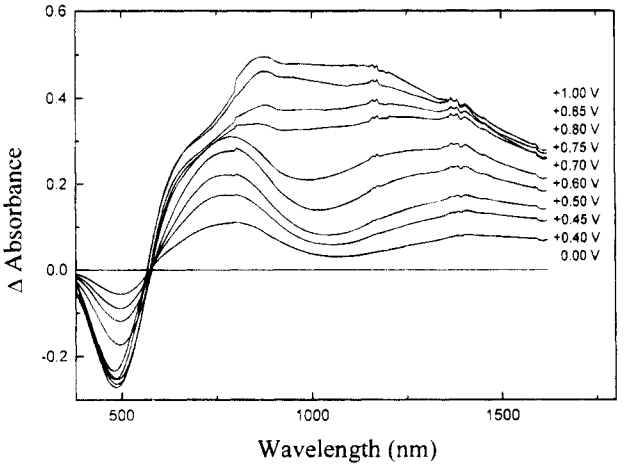

Figure 6. Differential optical UV–vis–near-IR absorption spectra of poly(4-butoxy-4′-decyl-2,2′-bithiophene) at various electrochemical potentials.

This is accompanied by the simultaneous decrease of the 500 nm band (π–π^* transition associated with the neutral form). Upon further oxidation, the 1400 nm band is slightly blue shifted while a new band appears near 640 nm. These new bands are related to the formation of dimerized polarons. Finally, a large band centered around 1000 nm associated with the presence of bipolarons is created during the third oxidation process (over +0.80–0.85 V) while the conductivity reached 0.2 S cm^{-1}. Similar successive oxidation processes (and better resolved) can be observed upon the chemical oxidation of poly(4-butoxy-4′-decyl-2,2′-bithiophene) in chloroform solution (Figure 7). All these results are consistent with the presence of successive redox processes in polythiophenes bearing substituents with different electronic properties An asymmetric substitution pattern seems to allow the formation of localized charge carriers and, for the polymers investigated in this work, lead to the successive occurrence of polarons, dimerized polarons, and bipolarons. For the first time, it has been possible to generate a high concentration of polarons in a polythiophene with the formation of dimerized polarons upon further oxidation. Up to now, only oligothiophenes with small conjugation lengths were able to support the formation and stabilization of such species.[11-13,18-20]

The unusual properties of asymmetrically substituted polythiophenes make possible the tuning of the transport properties of these polymers through band-gap engineering. The formation of both paramagnetic and

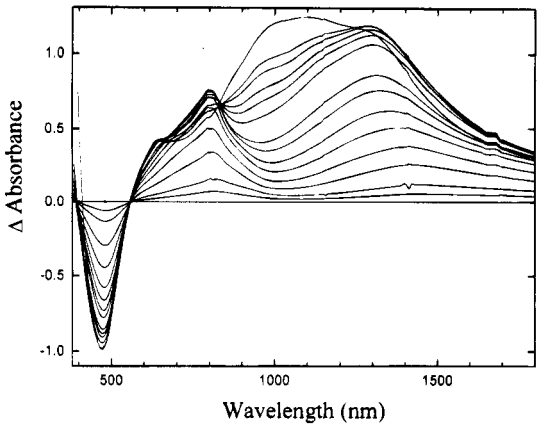

Figure 7. Differential UV–vis–near-IR absorption spectra of poly(4-butoxy-4′-decyl-2,2′-bithiophene) in chloroform with increasing oxidation levels (oxidized with iron trichloride).

diamagnetic conducting polymeric materials may be obtained by adjusting their redox state. This novel approach should apply not only to polythiophenes with different substituents but also to polymers with different repeat units. For instance, it has been recently reported that some substituted poly(1,4-bis(2-thienyl)phenylenes) exhibit a two-step redox process related to the successive formation of polarons and bipolarons.[24,25] The localization of the charge carriers is also possible in these mixed conjugated polymers and could explain these particular electrochemical features. Similarly, it has been proposed that quantum wells can be formed in phenylene–carbazole copolymers due to the existence of two distinct electronic states.[26]

On the other hand, these localization phenomena may also be very helpful for the development of polymeric light emitting diodes.[14,27] Indeed, it has been shown by Swanson et al.[28] that the conversion of polarons to singlet exciton is responsible for the electroluminescence in poly(*p*-phenylenevinylene)s. These authors also suggest that the decay of polarons to bipolarons is a significant competing process that may set an upper limit of the efficiency of polymeric light emitting diodes. The enhancement of the polaron population available for the radiative decay process through the molecular design of quantum wells along the polymer backbone is thus highly desirable. Photoluminescence and electroluminescence studies based on these concepts are currently being carried out.

Conclusion

The attachment of substituents with different electronic properties to polythiophenes leads to materials with controlled electrical and optical properties. Asymmetrically substituted poly(bithiophene)s exhibit three redox processes which are related to the successive formation of polarons, dimerized polarons, and bipolarons. The formation of stable polarons in these polythiophenes results from the presence of high and low HOMO–LUMO gap energy moieties along the polymer backbone which localize and limit the recombination of these polarons in bipolarons. These novel properties allow the formation of paramagnetic and diamagnetic conducting polythiophenes. Finally, the presence of "quantum wells" along the conjugated backbone may be of great interest for the development of efficient light emitting diodes derived from polythiophenes.

Acknowledgment. This work was made possible by the financial support of NSERC and University of Montreal (Fonds CAFIR). M.L. would like to thank his colleagues, J. Hubert and C. Reber, for their exceptional contributions. The authors acknowledge G. Zotti and G. D'Aprano for their advice and assistance. M.N. is grateful to NSERC for a postdoctoral fellowship.

References and Notes

(1) (a) Elsenbaumer, R. L.; Jen, K. J.; Oboodi, R. *Synth. Met.* **1985**, *15*, 169. (b) Sato, M. A.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873. (c) Sugimoto, R.; Tanaka, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635. (d) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212. (e) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.
(2) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(3) Faid, K.; Cloutier, R.; Leclerc, M. *Macromolecules* **1993**, *26*, 2501.
(4) Robitaille, L.; Leclerc, M. *Macromolecules* **1994**, *27*, 1847.
(5) Capaso, F. In *Physics and Applications of Quantum Wells and Superlattices*; Mendez, E., von Klitzing, K., Eds.; Plenum Press: New York, 1987; p 377.
(6) Kotthaus, J. P.; Merkt, U. In *Science and Engineering of One- and Zero-Dimensional Semiconductors*; Beaumont, S.P., Sotomayor Torres, C. M., Eds.; Plenum Press: New York, 1990; p 191.
(7) Faid, K.; Leclerc, M. *Chem. Mater.* **1994**, *6*, 107.
(8) Rughooputh, S. D. D. V.; Nowak, M.; Hotta, S.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1987**, *21*, 41.
(9) Leclerc, M.; Daoust, G. *Synth. Met.* **1991**, *41–43*, 529.
(10) Schiavon, G.; Sitran, S.; Zotti, G. *Synth. Met.* **1989**, *32*, 209.
(11) (a) Horowitz, G.; Yassar, A.; von Bardeleben, H. J. *Synth. Met.* **1994**, *62*, 245. (b) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* **1990**, *39*, 243.
(12) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.
(13) Zinger, B.; Mann, K. R.; Hill, M. G.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1113.
(14) Meyers, F.; Heeger, A. J.; Brédas, J. L. *J. Chem. Phys.* **1992**, *97*, 2750.
(15) Piaggi, A.; Tubino, R.; Borghesi, A.; Rossi, L.; Destri, S.; Luzzati, S.; Speroni, F. *Phys. Lett. A* **1994**, *185*, 431.
(16) Genoud, F.; Kruszka, J.; Nechtschein, M.; Zagorska, M.; Kulszewicz-Bayer, I.; Pron, A. *J. Chim. Phys.* **1990**, *87*, 57.
(17) Louarn, G.; Kruszka, J.; Lefrant, S.; Zagorska, M.; Kulszewicz-Bayer, I.; Pron, A. *Synth. Met.* **1993**, *61*, 233.
(18) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.
(19) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 620.
(20) Bauerle, P.; Segelbacher, U.; Gaudl, K. W.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76.
(21) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.
(22) Zotti, G.; Schiavon, G. *Chem. Mater.* **1991**, *3*, 62.
(23) D'Aprano, G.; Leclerc, M.; Zotti, G. *Macromolecules* **1992**, *25*, 2145.
(24) Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, J. L. *Macromolecules* **1992**, *25*, 849.
(25) Child, A. D.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1779.
(26) Faïd, K.; Adès, D.; Siove, A.; Chevrot, C. *Synth. Met.* **1993**, *63*, 89.
(27) Burn, P. L.; Kraft, A.; Baigent, D. R.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Jackson, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 10117.
(28) Swanson, L. S.; Shinar, J.; Brown, A. R.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L.; Kraft, A.; Holmes, A. B. *Phys. Rev. B* **1992**, *23*, 15072.

MA941034S