Highly Conductive New Aniline Copolymers Containing Butylthio Substituent

Chien-Chung Han,* Shih-Ping Hong, Ku-Feng Yang, Meng-Yi Bai, Chia-Hui Lu, and Chao-Sheng Huang

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, ROC

Received September 26, 2000; Revised Manuscript Received November 9, 2000

ABSTRACT: Highly conductive new aniline copolymers containing butylthio substituent have been first prepared from unsubstituted polyaniline, utilizing a concurrent reduction and substitution reaction performed in the solid-state matrix of polyaniline. The resultant copolymer film after one reaction treatment cycle was found to contain ca. 38 mol % of butylthio group and was as conductive (3−4 S/cm) as its parent polyaniline film (2−3 S/cm). Most surprisingly, copolymers containing butylthio group as high as 91 and 121 mol % (based on atomic ratio S/N measured by XPS) can also be easily prepared and still displayed a conductivity as high as 1 and 0.6 S/cm, respectively, despite the presence of the large amount of bulky butylthio substituent. All these new butylthioaniline copolymers are highly soluble in THF, dioxane, 2-methoxyethyl ether, and 2-methoxyethanol, which are nonsolvents for the parent polyaniline. The results suggest that the concurrent reduction and substitution route is a better way, as compared with the conventional copolymerization method, for preparing aniline copolymers with a more conjugated and regular backbone structure.

Introduction

Owing to their unique electrooptical properties and market potential, polyanilines are one of the recent focuses in the field of conducting polymer research.[1] However, as is common with other conjugated polymers, polyanilines is limited by poor thermal processability and solvent solubility. Improved solubility can be achieved by introducing various alkyl and alkoxy substituents on the polyaniline backbone.[2,3] However, such substituted polyanilines have been found to always exhibit a lower conductivity than that of the unsubstituted polyaniline. This conductivity reduction nature has been ascribed to the possible steric hindrance effect associated with the substituents. The conductivity of poly(2-alkoxyaniline)s has been reported by Leclerc et al.[3a] to be indeed decreased with the bulkiness of the alkoxy group from 0.1 (for methoxy), 3×10^{-3} (ethoxy), 2×10^{-3} (butoxy), to 1×10^{-5} S/cm (hexoxy). Similar results have also been generally observed for poly(2-alkylaniline)s, such as polymethylaniline (0.1 S/cm),[2a] polyethylaniline (10^{-5} S/cm),[2b] polypropylaniline (10^{-3}−10^{-4} S/cm),[2c] polybutylaniline (10^{-4} S/cm),[2d] and poly(hexylaniline) (10^{-7} S/cm),[2e] and for poly(*N*-alkylaniline)s,[2f] such as poly(*N*-methylaniline) (7×10^{-5} S/cm), poly(*N*-ethylaniline) (2×10^{-5} S/cm), poly(*N*-propylaniline) (9×10^{-7} S/cm), and poly(*N*-butylaniline) (8×10^{-7} S/cm). On the contrary, unsubstituted polyaniline film cast from its NMP solution typically gives a high conductivity of about 1−5 S/cm, after being doped with a protonic acid, such as HCl or *p*-toluenesulfonic acid.[4]

Combining the conductivity of polyaniline and the solubility of substituted polyanilines is important for practical applications and can be achieved through copolymerization.[5] For example, copolymers of aniline with *o*- or *m*-toluidine and *o*-ethylaniline have been reported.[2b,5a,b] These copolymers of aniline with substituted anilines show improved solubility, while maintaining fairly good conductivity as long as the amount of substituted repeat units in the copolymers stay below a certain critical level. For example, the conductivity of poly(aniline-*co*-ethylaniline) pellet (pressed from powder) was 1 S/cm when the ethylaniline repeat units were kept below ca. 30 mol %,[2b] as compared with 10 S/cm for similarly prepared pellet from unsubstituted polyaniline in the same report. For those copolymers containing more than 30 mol % ethylaniline repeat units, their conductivity decreased rapidly with the fraction of ethylaniline, to 2×10^{-5} S/cm, for poly(ethylaniline) homopolymer. Although the aniline copolymers with alkyl substituents (either on the ring or at the N atom) have been well studied and documented, the alkoxyaniline copolymers however have rarely been studied and reported.[6] Moreover, no aniline copolymers containing other type of electron-donating substituent, e.g., alkylthio group, have ever been reported.

In alkoxyaniline or alkylthioaniline copolymers, owing to the sterically less hindered structure of divalent oxygen or sulfur linkage and the stronger electron-donating nature of the alkoxy or alkylthio substituents than alkyl substituents, such copolymers should be theoretically better conducting materials than their alkylaniline copolymers counterparts. However, until now, all the alkoxyaniline polymers and copolymers that have been reported were found to be much less conductive than the unsubstituted polyaniline. Meanwhile, there have been no detailed reports on poly(alkylthioaniline)s and their copolymers. We have recently found a new synthetic route, i.e., concurrent reduction and substituent method,[7] which facilitates the synthesis of novel aniline copolymers of poly(aniline-*co*-butylthioaniline)s. These interesting new aniline copolymers with electron-donating alkylthio group have been found to be highly conductive despite the attachment of bulky substituents such as butylthio group. For example, the conductivity of a copolymer containing 38 mol % of butylthioaniline repeat unit was as high as 3−4 S/cm.

---

* To whom correspondence should be addressed. E-mail cchan@mx.nthu.edu.tw.

10.1021/ma001664w CCC: $20.00

Most interestingly, the highly conductive nature is preserved even for the highly substituted poly(aniline-*co*-butylthioaniline). For instance, the conductivity for the copolymer with a substitution degree of 120 mol % (based on atomic ratio S/N measured by XPS) was still found to be as high as 0.6 S/cm, instead of the low conductivity of $10^{-3}-10^{-5}$ S/cm as it would be expected, according to the current knowledge base in this field of study. We report herein the synthesis and characterization for these new poly(aniline-*co*-butylthioaniline)s.

Experimental Section

The free-standing polyaniline film (ca. 10 μm thick) used for this work was cast from a solution of 0.48 wt % polyaniline emeraldine base in NMP. The polyaniline thin films on electrodes were grown in a three-electrode electrochemical cell, using platinum plates as both the working and counter electrodes and a saturated calomel electrode (SCE) as reference electrode. All the electrochemical polymerization reactions were controlled by a potentiostat (EG&G 273) under a constant current density of 13.3×10^{-6} A/cm^2 for 25 min, in a 0.5 M H_2SO_4 aqueous solution that contained 0.1 M aniline. The thickness of the polyaniline electrode film thus obtained (of about 100 nm) was measured by SIMS (secondary ion mass spectroscopy) depth profiling and an α-step. Cyclic voltammograms of all resulting polyaniline films were performed on the same potentiostat in an aqueous solution of 0.5 M H_2SO_4.

The attenuated total reflectance infrared (ATRIR) spectroscopy of the resulting polyaniline films was performed, using a Perkin-Elmer 2000 FTIR spectrometer equipped with a Graseby Specac single reflection diamond ATR accessory under a nitrogen atmosphere. The active area of the diamond contact probe was 0.6 × 0.6 mm. By assuming that the refractive index of the polyaniline films on the working electrode is 1.5, the theoretical surface penetration depths of the incident IR beam, from 400 to 4000 cm^{-1}, were calculated and found to be 2.3–0.23 μm. A constant clamping pressure, applied by using a torque wrench with setting at 60 cNm/m, was employed to mount all polyaniline film specimens, to ensure good and consistent surface contact with the diamond probe head.

XPS (X-ray photoelectron spectroscopy) spectra for the resulting aniline copolymer films were collected with a Physical Electronics ESCA PHI 1600 spectrometer, using Mg Kα as the X-ray source. The excitation area was 800 × 800 μm; the step size for the survey and the chemical state spectra was 1.6 and 0.025 eV, respectively.

UV–vis spectra were performed basing on the polyaniline films on an ITO glass electrode, using a Hitachi U3501spectrophotometer.

SIMS analysis of the resulting aniline copolymer films was performed on a Cameca IMS-4f instrument, using Cs as the primary ion source. A raster area of 250 × 250 μm and an analysis area of 60 × 60 μm were employed.

Results and Discussion

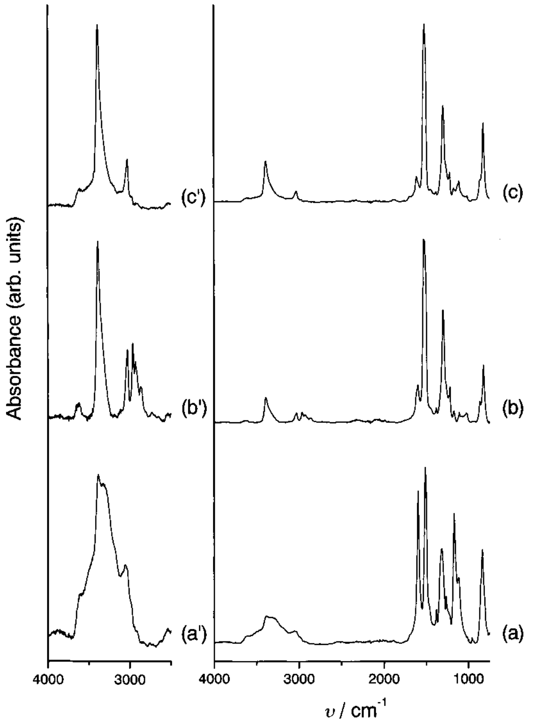
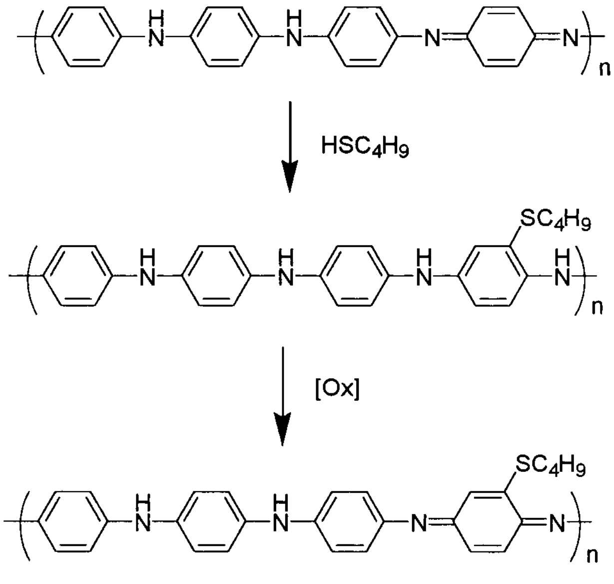


Figure 1. ATRIR spectra for the undoped polyaniline-coated electrodes: (a) before and (b) after the soaking treatment with a 0.1 M methanolic solution of butane-1-thiol for 14 h; (c) as in its fully reduced leucoemeraldine state (i.e., at −0.1 V vs SCE). The details of corresponding spectra within the region of 2500–4000 cm^{-1} (with arbitrary magnifications) are displayed in traces a′–c′.

Scheme 1



A typical poly(aniline-*co*-butylthioaniline) was prepared via the previously reported concurrent reduction and substitution route[7] as illustrated in Scheme 1, by reacting a polyaniline emeraldine base film (ca. 10 μm thick) with 0.1 M butane-1-thiol in MeOH under a N_2 atmosphere at room temperatures for an appropriate period of time, e.g., 14 h, to allow for the completion of the reaction. During the reaction treatment, the nontransparent dark blue polyaniline emeraldine film changed gradually to a transparent film with a hint of light green color, implying a possible transformation of the polyaniline backbone from the dark blue emeraldine state to a colorless leucoemeraldine state. After the treatment with butane-1-thiol, the polyaniline backbone was found to be highly reduced and substituted with butylthio groups. A similar reaction pattern has also been observed when polyaniline was treated with other thiols.[8] The reduction and substitution phenomena in the butane-1-thiol treated films were confirmed by attenuated total reflectance infrared (ATRIR) spectroscopy. The ATRIR spectrum of the resulting aniline copolymer film, as displayed in Figure 1, clearly showed reduction in the intensities of the peaks associated with diiminoquinoid rings at 1600 cm^{-1} (C═C stretching vibration of diiminoquinoid rings[9]), 1169 cm^{-1} (a vibration mode associated with the diiminoquinoid ring[9]), and 820 cm^{-1} (C–H out-of-plane vibration of 1,4-ring[9]). A similar intensity reduction of these three peaks has also been observed when polyaniline emeraldine base was

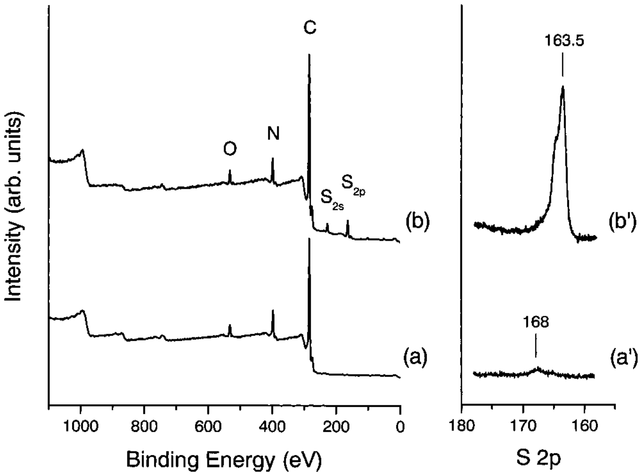


Figure 2. XPS spectra for the undoped films: (a) the original polyaniline film; (b) the polyaniline film after soaking treatment with 0.1 M methanolic solution of butane-1-thiol for 14 h. The chemical state spectra of S 2p for the corresponding polyaniline films are displayed in (a′) and (b′).

reduced by hydrazine to leucoemeraldine base. The same ATRIR spectrum of the butane-1-thiol treated film also shown three new peaks at about 2961, 2928, and 2866 cm^{-1}, which can be attributed to the asymmetric (2961, 2928 cm^{-1}) and symmetric (2866 cm^{-1}) C−H stretching of the newly introduced butylthio substituent.[10] Similar C−H stretching peaks were observed at 2957, 2929, and 2872 cm^{-1} for 2-butylthioaniline and at 2961, 2932, and 2873 cm^{-1} for butane-1-thiol.

The presence of the new butylthio substituent in the resulting polyaniline film was also confirmed by X-ray photoelectron spectroscopy (XPS). In addition to the original C 1s (with a binding energy of 284.6 eV) and N 1s (399.2 eV) lines, the XPS survey spectrum of the butane-1-thiol-treated film (Figure 2b) showed a newly appearing S 2p line at around 163.5 eV, confirming the formation of the sulfide linkage (but not disulfide or thiol).[18] The atomic ratio of sulfur to nitrogen was measured, after discounting the sulfur contribution from the trace amount of residual TsOH dopant at ca. 168 eV, to be 0.38, indicating that the resulting poly(aniline-*co*-butylaniline) film contained about 38 mol % of butylthio substituent. This result is consistent with the previous finding that the polyaniline emeraldine base will be gradually oxidized by air during the storage to yield a higher oxidation level to contain more than 25 mol % of diiminoquinoid units,[12] where the concurrent reduction and substitution reaction can take place.

The distribution of the new butylthio substituent within a polyaniline film was investigated by secondary ion mass spectroscopy (SIMS). The SIMS results for a butane-1-thiol-treated film (ca. 10 μm thick) showed an even distribution of S atom throughout the thickness of this polyaniline specimen, thus proving that the substitution reaction was not just confined to the film surface.

The cyclic voltammogram, scanned between −0.1 and 0.6 V at 30 mV/s, for the above copolymer film in 0.5 M H_2SO_4 aqueous solution, showed a quasi-reversible redox process similar to that of unsubstituted polyaniline. The oxidation potential $E°$ of the resulting aniline copolymer (0.085 V) was found to be 0.014 V lower than that of the parent polyaniline (0.099 V). This result is consistent with the expectation that the attachment of electron-donating butylthio group helps lower the oxidation potential of polyaniline backbone.[3a]

Table 1. Substitution Degree and Conductivity of Poly(aniline-*co*-butylthioaniline)

entry	polymer[a]	mol % of butylthio group[b]	conductivity (S/cm)	remark
1	Pani	0	2.7	this work
2	Pani-SBu-1	38	3−4	this work
3	Pani-SBu-2	91	1	this work
4	Pani-SBu-3	121[c]	0.6	this work
5	poly(butoxyaniline)		2×10^{-3}	ref 3
6	poly(dibutoxyaniline)		7×10^{-4}	ref 3

[a] Pani = unsubstituted polyaniline; Pani-SBu = poly(aniline-*co*-butylthioaniline). [b] Mole percent of butylthio group based on atomic ratio S/N measured by XPS. [c] Some repeat units of this copolymer may contain more than one butylthio group.

The UV−vis spectrum for the fully reduced copolymer, i.e., at an oxidation state of −0.1 V (vs SCE) in 0.5 M H_2SO_4, showed a $\pi-\pi^*$ transition band at 330 nm, which is 12 nm longer than the corresponding band of its parent polyaniline, possibly due to the enhanced electron density of the copolymer backbone as contributed by the electron-donating butylthio group. A similar red-shift effect has also been observed for methoxy-substituted polyaniline.[3a]

The freshly prepared poly(aniline-*co*-butylthioaniline) was in an oxidation state close to the leucoemeraldine form and can be reoxidized back to the emeraldine state either with air or via electrochemical means, by applying a voltage of 0.3 V (vs saturated calomel electrode) to the film, using a potentiostat (EG&G 273). Such reoxidized film was then soaked in a 1 M $HClO_4$ doping solution for at least 2 h to ensure the film was fully doped. The conductivity was measured to be 3−4 S/cm by a typical 4-in-line probe method[13] after drying (entry 2 of Table 1), which, within experimental errors, is almost the same as that for its original parent polyaniline film (2−3 S/cm). Although a much higher conductivity (ca. 200 S/cm) has been reported for the polyaniline doped with a functional dopant, such as camphorsulfonic acid,[14a] and also for the polyaniline having more extended coil structure as induced by the incorporation of a special primary dopant (camphorsulfonic acid) and a secondary dopant (*m*-cresol) using a delicate treatment process,[14b] the best conductivity reported for polyaniline film cast from its NMP solution has been consistently 1−5 S/cm.[4] Since the above substitution reaction was performed in a solid matrix of polyaniline without using any secondary dopant and primary/functional dopant, the morphological structure of the resulting copolymer is expected to be the same as that of the starting parent polyaniline film. Under this circumstance, such high conductivity associated with poly(aniline-*co*-butylthioaniline) is certainly noteworthy. Obviously, much higher conductivity for the present new copolymers can still be expected if a similar extended chain conformational transformation like the above-reported polyaniline is created.

The substitution degree of the present copolymer can be further increased and tailored by performing repeated runs of concurrent reduction and substitution reaction on the same film, starting with any specific oxidation level as controlled by the electrochemical means.[8] For example, the initial poly(aniline-*co*-butylthioaniline) film can be further electrochemically forced to 0.5 V (vs SCE) and performed a second and a third run of concurrent reduction and substitution reaction.

The degree of substitution has been found to increase up to 91 mol % (1 S/cm) and 121 mol % (0.6 S/cm) after the second and the third reaction runs, respectively. These new butylthioaniline copolymers have also been found to be highly soluble in THF, dioxane, 2-methoxyethyl ether, and 2-methoxyethanol, which are nonsolvents for the parent polyaniline. The GPC (gel permeation chromatography) study indicated that the molecular weight M_w (using polystyrene as standard) of these butylthioaniline copolymers ($>5.0 \times 10^4$) is higher than that of the parent polyaniline (3.0×10^4). The result indicated that no degradation occurred during the substitution reaction, and the enhanced solubility in THF is mainly contributed by the solubility parameter change of the resulting copolymers caused by the substitution of butylthio group. Most surprisingly, despite the presence of such a large amount of the bulky butylthio group, the highly conductive nature of these new poly(aniline-*co*-butylthioaniline)s is retained. Compared to their alkoxy analogues, e.g., poly(butoxyaniline) (2×10^{-3} S/cm) and poly(dibutoxyaniline) (7×10^{-4} S/cm), the unusually high conductivity of these new copolymers in combination with their good solubility in THF and other common organic solvents is especially worth noting.[3a] While for the previously reported poly(aniline-*co*-ethylaniline),[2b] only those copolymers containing more than about 45 mol % of ethylaniline unit showed significant solubility in THF, but in the same report such copolymers have conductivities of less than 10^{-2}–10^{-3} S/cm.

To further demonstrate the present proposed reaction pathway, a model compound was prepared by reacting *N,N′*-diphenylphenylene-1,4-diimine with butane-1-thiol via the same reduction and substitution chemistry, which yielded a butylthio-substituted *N,N′*-diphenylphenylene-1,4-diamine.[19]

It is also worth noting that when control copolymers of similar compositions were prepared by an alternative approach, using the conventional copolymerization method from aniline and butylthioaniline monomer mixtures, the resulting poly(aniline-*co*-butylthioaniline)s were, however, much less conductive. The conductivity of these control specimens with even a relatively lower substitution degree, from 10 to 32 mol %, was found to be only 10^{-2} to 10^{-5} S/cm, respectively. Such a result is consistent with the previous finding that the conventional polymerization method will create a highly irregular poly(alkoxyaniline) backbone, thus leading to poor conductivity, due to the possible electronic influence of the electron-donating alkoxy substituent.[16] Similar conductivity behavior, although its nature remains uncertain, has also been observed for the cases of sulfonated polyanilines, where sulfonated polyaniline prepared directly from polyaniline via sulfonation with fuming sulfuric acid[17a] also somehow exhibited higher conductivities (0.1 S/cm) than the sulfonated polyaniline ($\leq 10^{-3}$ S/cm) prepared from the sulfonic acid-containing aniline monomer via oxidative polymerization.[17b] However, the present results did suggest that the new copolymers prepared via this novel concurrent reduction and substitution method may have resulted in more conjugated and regular backbone structures.

Conclusions

Highly conductive new aniline copolymers containing butylthio substituent have been successfully prepared from unsubstituted polyaniline, utilizing a concurrent reduction and substitution reaction performed in the solid-state matrix of polyaniline. The resulting copolymers are highly conductive (4–0.6 S/cm), despite the presence of a large amount of bulky butylthio substituent (38–121 mol %). All these new butylthioaniline copolymers are highly soluble in common organic solvents, such as THF, dioxane, 2-methoxyethyl ether, and 2-methoxyethanol, which are nonsolvents for the parent polyaniline. Since the molecular weights of these aniline copolymers are higher than their parent unsubstituted polyaniline, the enhanced solubility in THF and other organic solvents is mainly contributed by the solubility parameter change of the resulting copolymers caused by the substitution of butylthio group. Compared to their alkoxy analogues, e.g., poly(butoxyaniline) (2×10^{-3} S/cm) and poly(dibutoxyaniline) (7×10^{-4} S/cm), the unusually high conductivity of these new butylthio-containing aniline copolymers in combination with their good solubility in THF and other common organic solvents is especially worth noting.

Acknowledgment. We acknowledge financial support from National Science Council of ROC.

References and Notes

(1) (a) *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, 1997; Vols. 1–4. (b) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vols. 1 and 2. (c) Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth. Met.* **1990,** *36*, 139.

(2) (a) Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J. Phys. Chem.* **1989**, *93*, 495. (b) Conklin, J. A.; Huang, S. C.; Huang, S. M.; Wen, T.; Kaner, R. B. *Macromolecules* **1995**, *28*, 6522. (c) Bidan, G.; Genies, E. M.; Penneau, J. F. *J. Electroanal. Chem.* **1989**, *271*, 59. (d) Bodalia, R.; Stern, R.; Batich, C.; Duran, R. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2123. (e) Genies, E. M.; Noel, P. *J. Electroanal. Chem.* **1991**, *310*, 89. (f) Chevalier, J.-W.; Bergeron, J.-Y.; Dao, L. H. *Macromolecules* **1992**, *25*, 3325. (g) Cattarin, S.; Doubova, L.; Mengoli, G.; Zotti, G. *Electrochim. Acta* **1988**, *33*, 1077. (h) Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* **1989**, *22*, 649. (i) Shenlong, W.; Fosong, W.; Xiaohui, G. *Synth. Met.* **1986**, *16*, 99.

(3) (a) D'Aprano, G.; Leclerc, M.; Zotti, G.; Schiavon, G. *Chem. Mater.* **1995,** *7*, 33. (b) Mattoso, L. H. C.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *68*, 1. (c) Dhawan, S. K.; Trivedi, D. C. *Synth. Met.* **1993,** *60*, 67. (d) MacInnis, D., Jr.; Funt, B. L. *Synth. Met.* **1988**, *25*, 235. (e) Gupta, M. C.; Umare, S. S. *Macromolecules* **1992**, *25*, 138. (f) Lacroix, J. C.; Garcia, P.; Audiere, J. P.; Clement, R.; Kahn, O. *Synth. Met.* **1991**, *44*, 117.

(4) Angelopoulos, M.; Asturias, G. E.; Ermer, S. P.; Ray, A.; Scherr, E. M.; MacDiarmid, A. G. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 151.

(5) (a) Wei, Y.; Hariharan, R.; Patel, S. *Macromolecules* **1990**, *23*, 758. (b) Dhawan, S. K.; Trivedi, D. C. *Synth. Met.* **1993**, *60*, 63. (c) Langer, J. J. *Synth. Met.* **1990**, *35*, 295. (d) Langer, J. J. *Synth. Met.* **1990**, *35*, 301. (e) Bergeron, J.-Y.; Dao, L. H. *Macromolecules* **1992**, *25*, 3332.

(6) (a) Pandey, S. S.; Annapoorni, S.; Malhotra, B. D. *Macromolecules* **1993**, *26*, 3190. (b) Prevost, V.; Petit, A.; Pla, F. *Synth. Met.* **1999**, *104*, 79.

(7) Han, C. C.; Jeng, R. C. *Chem. Commun.* **1997,** 553.

(8) Han, C. C.; Hseih, W. D.; Yeh, J. Y.; Hong, S. P. *Chem. Mater.* **1999**, *11*, 480.

(9) Wudl, F.; Angus, R. O., Jr.; Allemand, P. M.; Vachon, D. J.; Norwak, M.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987,** *109*, 3677.

(10) Socrates, G. *Infrared Characteristic Group Frequencies. Tables and Charts*, 2nd ed.; John Wiley & Sons: New York, 1994.

(11) (a) Beamson, G.; Briggs, D. *High-Resolution XPS of Organic Polymers*; John Wiley & Sons: New York, 1992. (b) *Handbook of X-ray Photoelectron Spectroscopy*; Chastain, J., Ed.; Perkin-Elmer Corp.: Eden Prairie, MN, and the references therein.
(12) Asturias, G. E.; MacDiarmid, A. G.; McCall, R. P.; Epstein, A. J. *Synth. Met.* **1989**, *29*, E157.
(13) Wieder, H. H. *Laboratory Notes on Electrical and Galvanomagnetic Measurements*; Elsevier Scientific Publishing Co.: Amsterdam, 1979.
(14) (a) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91. (b) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *65*, 103.
(15) Hjertberg, T.; Sandberg, M. *Synth. Met.* **1989,** *29*, E257.
(16) D'Aprano, G.; Leclerc, M.; Zotti, G. J. *Electroanal. Chem.* **1993**, *351*, 145.
(17) (a) Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc*, **1991**, *113*, 2665. (b) Chan, H. S. O.; Neuendorf, A. J.; Ng, S. C.; Wong, P. M. L.; Young, D. J. *Chem. Commun.* **1998**, 1327.
(18) The S $2p_{3/2}$ line was reported to be 163.66 eV for poly(phenylene sulfide) and 163.50 eV for poly(ethylene sulfide); 164.4 eV for phenyl disulfide and 164.1 eV for butyl disulfide; 163.1 eV for thiophenol, 161−163 eV for alkanethiols, and 168.23 eV for poly(sodium 4-styrenesulfonate) (ref 11).

(19) ^{13}C NMR data for the butylthio-substituted *N*,*N*′-diphenylphenylene-1,4-diamine, δ_C 13.55, 21.79, 31.39, 34.49, 116.05, 117.81, 117.97, 119.86, 120.68, 120.86, 124.96, 125.51, 129.28, 136.04, 138.52, 143.50, and 144.49; for *N*,*N*′-diphenyl-1,4-phenylenediamine δ_C 115, 118.2, 119.6, 128.93, 136.4, and 144.8. For *N*,*N*′-diphenyl-1,4-phenylenediimine δ_C 120.25, 120.38, 124.35, 125.04, 125.08, 125.29, 136.39, 137.7, 149.8, 149.83, 157.84, and 157.9, complicated by the presence of both *E* and *Z* forms (ref 15).

MA001664W