3236 *Macromolecules* **1990,** *23,* 3236-3242

(2) Potember, R. S.; Hoffman, R. C.; Kim, S. H.; Speck, K. R.; Stetyick, K. A. *J. Mol. Electron.* **1988,** *4,* 5.
(3) Dalton, L. R.; Thomson, J.; Nalwa, H. S. *Polymer* **1987,** *28,* 543. Yu, L. P.; Dalton, L. R. *Synth. Met.* **1989,** *29,* E463.
(4) Coter, F.; Belaish, Y.; Davidov, D.; Dalton, L. R.; Ehrenfreund, E. O.; McLean, M. R.; Nalwa, H. S. *Synth. Met.* **1989,** *29,* E471. Belaish, I.; Davidov, D.; Selig, H.; McLean, M. R.; Dalton, L. R., submitted for publication.
(5) Selig, H.; Luski, S. *J. Fluorine Chem.* **1988,** *39,* 421.
(6) Szita, J.; Marvel, C. S. *J. Polym. Sci.: Part A-1* **1969,** *7,* 3203. Litt, M. H.; Ruan, J. Z. *Macromolecules* **1988,** *21,* 876.
(7) Renschler, C. L.; Sylwester, A. P. *Appl. Phys. Lett.* **1987,** *50* (20), 1420.
(8) Callis, C. F.; Norris, A. C. *Carbon* **1972,** *10* (5), 525.
(9) Middleton, W. J.; Engelhardt, V. A.; Fisher, B. S. *J. Am. Chem. Soc.* **1958,** *80,* 2822.
(10) Farnier, M.; Soth, S.; Fournari, P. *Can. J. Chem.* **1976,** *54,* 1074.
(11) Danilova, T. A.; Petrov, S. N. *Nefte Khim.* **1971,** *11* (5), 756 (from *Chem. Abstr.* **1974,** *80* 133153a). For a general discussion, see: *Thiophene and Its Derivatives*; Goronwitz, S., Ed.; Wiley: New York, 1985; Part I, p 842.
(12) Lin, J. W.-P.; Dudek, L. P. *J. Polym. Sci., Polym. Chem. Ed.* **1980,** *18,* 2869.
(13) Galbraith Laboratories, 2323 Sycamore Dr., Knoxville, TN (private communication). Also see Litt and Ruan (ref 6).
(14) Lu, F.-L.; Wudl, F.; Nowak, M.; Heeger, A. J. *J. Am. Chem. Soc.* **1986,** *108,* 7863.
(15) Young, C. L.; Polis, D. W.; Bain, A. N.; Sapochak, L. S.; Dalton, L. R. *Macromolecules*, following paper in this issue.

Registry No. 1 (copolymer), 121753-88-6; **1b** (copolymer), 126724-55-8; **2** (copolymer), 126724-56-9; **7** (copolymer), 126724-57-0; **8** (copolymer), 126724-58-1; **9** (copolymer), 126724-59-2.

Electronic and Magnetic Character of Aniline-Thiophene Copolymers

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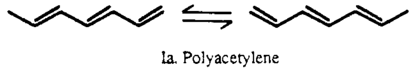
ABSTRACT: The condensation of 2,5-dibromothiophenes or 3,4-dibromothiophene with 1,4-diaminophenylenes under Ullmann conditions yielded a series of aniline-thiophene copolymers. Elevated reaction temperatures resulted in loss of the sulfur by decomposition of the thiophene ring. Lower reaction temperatures produced materials of a more rigid rod character with retention of the thiophene ring. The influence of the sulfur heteroatom was clearly visible in the optical and ESR spectra. Magnetic susceptibility measurements on the materials produced from the 2,5-dibromothiophenes (the 2,5-copolymers) revealed anomalous temperature-independent paramagnetism, or Pauli susceptibilities (χ^{Pauli}), which are usually associated with metals. Comparison of the materials produced at higher reaction temperatures with those formed at lower temperatures indicates that the sulfur atom strongly interacts with spin-carrying defects, thereby determining the electronic and magnetic character of these novel polymeric systems.

Introduction

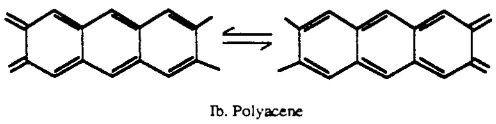
Heteroatomic polymers have been the subject of serious investigation for the past decade.[1] Many of these materials are electrically conductive upon doping and are under investigation for their potential usefulness in the production of nonlinear optical (NLO) devices.[2] The role of a heteroatom in the origin of such anomalous electronic and optical properties remains ill-defined. Polymers without heteroatomic influences, such as polyacetylene (PA) and polyacene (PAc), have degenerate bond phases and intrinsically higher symmetry (Scheme I). Systems exhibiting this degeneracy are predicted to support solitonic defects,[3] which may occupy a mid-band-gap electronic state and provide spin character that is detectable by electron spin resonance (ESR) techniques.

Heterocyclic systems such as polythiophene (PT)[4] and polypyrrole (PP),[5] as seen in Scheme Ic, have nondegenerate bond phases, and the midgap states are polaronic in nature. These systems can be synthesized and doped electrochemically, have relatively small band gaps (E_g(PT) = 2.1 eV, E_g(PP) = 3.0 eV), and are comparatively more stable and processible than other nonheteroatomic systems such as PA. The nondegenerate bond phases are quinoidal (Q) and aromatic (A), with the quinoidal being the higher energy conformation.[6] Another well-characterized heteroatomic polymer, polyaniline (PAni), also has both quinoidal and aromatic (benzoidal) character.[7]

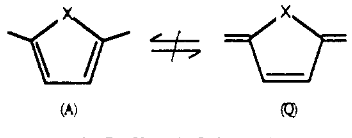
Scheme I



Ia. Polyacetylene



Ib. Polyacene



Ic. For X = NH, Polypyrrole
For X = S, Polythiophene

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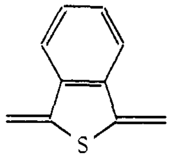
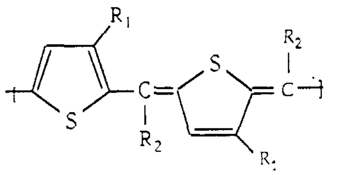
Scheme II
Polythiophene Derivatives in Quinoidal Bond Phase



a) Polyisothionapthene



b) PMTBQ, $R_1 = CH_3$, R_2 = phenyl

It is the relative proportion of quinoidal to aromatic character (Q/A) that is predicted to dramatically dictate the electro-optical signature of many polymeric systems. Theoretically, it has been shown that the aromatic phase has a lower ground-state energy while the quinoidal conformation has a smaller band gap.[6,8] Since the band gap represents the barrier to metallic conduction, the promise of decreasing band gaps with increasing quinoidal character has inspired several efforts to stabilize the higher energy bond phase. Optimizing the quinoidal character in PT has been accomplished by derivatization.[9a,10] Polyisothionaphthene (PITN) (Scheme IIa) behaves according to theoretical predictions by demonstrating that addition of the butadiene moiety to the PT backbone stabilizes the quinoidal phase and consequently reduces the band gap from 2.0 eV in the parent polymer, PT, to 0.9 eV.[9] Jenekhe has also been successful in producing materials (Scheme IIb) that optimized the quinoidal character and effectively decreased the band gap.[10] More recent findings indicate that this quinoidal character also enhances NLO activity.[11]

The importance of bond conformation on the electronic and optical properties of these materials is firmly established. The influence of the heteroatom, however, has been and remains ill-defined. Initially, in PT systems, it was assumed that the sulfur did not radically influence the defect occupying the midgap state.[4,12,13] This assumption was rationalized by the narrow line width of the electron spin resonance (ESR) signal which indicated a highly mobile electron spin species, i.e., one that was not strongly coupled to any obtrusive nuclei such as the sulfur. Further justification came from the absorption peaks at 0.65 and 1.5 eV experimentally observed in doped PT.[13] It was assumed that if the heteroatom were interacting strongly, these absorption peaks would not be located symmetrically around the band gap center or the Fermi level, $E_f \approx 1.05$ eV. The only influence of the sulfur heteroatom was speculated to be the ability of the d orbitals to stabilize interchain interactions.[4,12]

Without the inclusion of the heteroatom, the remaining polythiophene backbone resembles the structure of cis-transoid or trans-cisoid polyacetylene (Figure 1b) and was treated accordingly by the existing continuum version of the Hückel-based Su–Schrieffer–Heeger (SSH) theory.[14,15] Mintmire et al. reviewed this treatment and concluded that the aromatic conformation was actually stabilized by including the interaction of the heteroatom lone pair with the π system.[15] This would be consistent with other calculations that have predicted that zero band gaps in PTs and other heteroaromatic systems occur at other bond conformations besides that of zero bond alternation.[16] This is contradictory to that found in *trans*-PA, where the material would be a metal (have zero band gap) if the π system was equally smeared along the carbon backbone (all bond lengths would be equal), producing zero bond alternation at zero band gap. The interaction of the lone pair of the heteroatom with the HOMO and LUMO states in heterocycles such as PT and PP increases the band gap of the more stable aromatic phase while the quinoidal conformation is not affected and retains a smaller E_g.[16-18] The later paper by Mintmire et al. provides quantitative calculations with similar results; interaction of the heteroatom with the π system of the carbon backbone stabilizes the aromatic phase by effectively lowering the HOMO, i.e., decreasing the energy of the ground state.[17] Again, this interaction does not affect the HOMO of the quinoidal conformation and effectively results in a smaller band gap in the quinoidal phase as compared to that of the aromatic conformation.[18]

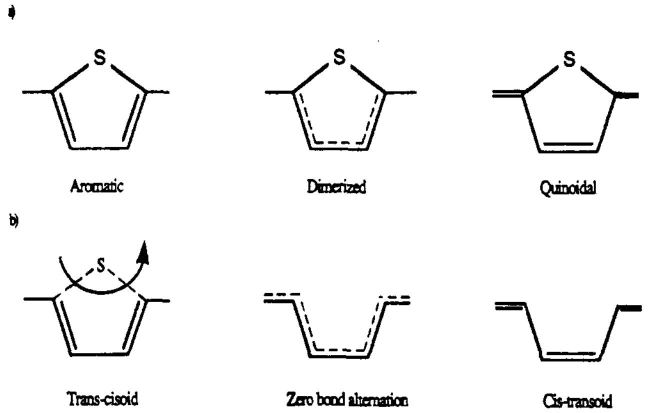


Figure 1. (a) Bond conformations of polythiophene. (b) Resemblance between polythiophene backbone and polyacetylene.

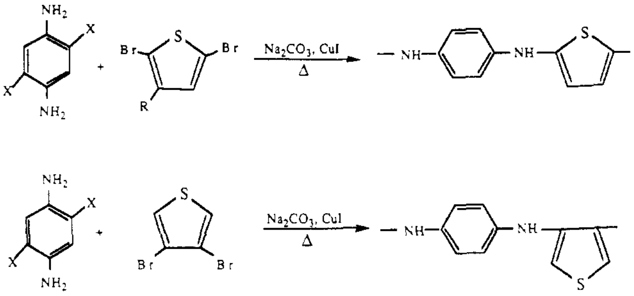
A series of aniline–thiophene copolymers have been synthesized and have been found to exhibit unresolved structure in their electron spin resonance (ESR) signal.[19] The materials provide supporting evidence that the sulfur heteroatom is indeed dominating electronic character. One cannot simplistically assume that an aniline–thiophene copolymer would exhibit a superposition of characteristics of the parent systems, PT and PAni. The effects of both the sulfur heteroatom and the torsional (dihedral) angle of the aniline component provide undefined influences that make predictions impossible. However, our preliminary studies have proved useful in that this series of copolymers allows the comparison of the electronic properties of materials that contain different concentrations of the heteroatom.

Two types of materials were synthesized by using either 2,5-dibromothiophenes or 3,4-dibromothiophene and 1,4-diaminophenylenes. Differing reaction temperatures produced systems with distinctively different properties that correlate to the degree of sulfur loss. Within the series, three different structures exhibiting rigid rod (unfused), ladder (fused), or a hybrid containing both ladder and rigid rod character were studied. Electronic and magnetic characterization is contained herein with a discussion of the results as is pertinent to other systems.

Experimental Section

Materials. Aniline–thiophene copolymers, copoly(thiophenediylaminophenylenes) (PTAPs), were prepared according to reaction Scheme III. Details of synthetic procedures, elemental analyses, and discussion of a proposed mechanism for

Scheme III
Ullmann Condensation (X = H, Cl and R = CH$_3$)



the decomposition of thiophene ring can be found elsewhere.[19] The polymers will be referred to by number as listed in Table I. All materials were handled under atmospheric conditions.

Magnetic Susceptibility. Magnetic susceptibilities were measured with an S.H.E. magnetic VTS susceptometer, Model 905. The gram susceptibilities, χ_g, were recorded at temperatures ranging between 6 and 300 K. The applied field was 10 kG.

Electron Spin Resonance. Electron spin resonance (ESR) studies were completed on an X-band ER 200D IBM-Bruker ESR spectrometer. The magnetic field was calibrated with an ER 035M Bruker Gaussmeter. Microwave frequencies were measured with an EIP Model 545A microwave frequency counter. Variable-temperature studies were accomplished in the range 100–300 K with an ER 021 VT Bruker accessory. Special care was taken to avoid signal degradation due to modulation distortion and power saturation. All materials exhibited ESR signals of easily detected strength. As can be seen in Figure 2, power saturation occurred at relatively high powers (>100 mW). The systems demonstrated a great resistance to microwave power saturation, even at liquid helium temperatures. As a result of this characteristic, electron–nuclear double-resonance (ENDOR) studies were precluded, despite strong ESR signals.

Doping and Conductivity Measurements. This series of copolymers was intrinsically insulating with conductivities below 10^{-12} S/cm. Doping was attempted according to a solution method in which the 0.50 g of dopant (NO_2BF_4, NO_2PF_6, and $NOSbF_6$) was dissolved in 50 mL of nitromethane, 0.60 g of the copolymer was added, and the resulting suspension was stirred for 2 h at room temperature. The doped copolymer was filtered over a fine fritted glass filter, washed four times with clean nitromethane, and then dried in a vacuum oven at room temperature for 2 h. The conductivity measurements were done by the standard four-point probe method on pressed pellets.[20] Conductivities remained immeasurable.

Iodine vapor phase doping was accomplished by taking carefully weighed amounts of various copolymers and placing them in an iodine chamber until their weight remained constant. Other dopants such as $SbCl_5$ and H_2SO_4 were also tried but the copolymers remained insulating.

Results and Discussion

Copolymers with distinctively different properties, depending on whether the linkage of the thiophene ring was in the 2,5- or 3,4-position with respect to the sulfur heteroatom, were investigated. Altering reaction temperatures (Δ = 250, 200, 185 °C) produced materials with varying sulfur content. The materials synthesized at higher temperatures show a severe deficiency in the expected sulfur content.[19] This deficiency is attributed to the loss of sulfur via decomposition of the thiophene ring, thus producing a more fused, graphitic type polymer matrix.

Elemental analyses confirm that the *only marked difference in the elemental constitution of the copolymers produced at different reaction temperatures is in the percentage sulfur found in the copolymer.*[19] The nitrogen content of the copolymer series remains relatively consistent, regardless of reaction temperature or starting material. The contribution of the aniline component to the electronic character is not discernible from the perspective of magnetic characterization. However, it is likely that a two-component system of aniline and thiophene would be more likely to undergo random copolymerization than a more homogeneous, one-component system, producing an intrinsically more amorphous polymer environment. This amorphous character is predicted to increase the localized character of the spin species present. It is the localized character and the influence of the sulfur heteroatom that are experimentally distinguishable, both in the susceptometry studies and in the ESR data.

Magnetic Susceptibilities. According to the relationship in eq 1, the various contributions to the total bulk magnetic susceptibility can be identified. The Pauli

$$\chi_g = \chi^{\text{Pauli}} + \chi^{\text{Curie}} + \chi^{\text{core}} \qquad (1)$$

susceptibility, χ^{Pauli}, represents the temperature-independent contribution. The Curie susceptibility, χ^{Curie}, is inversely proportional to the temperature, T, according to

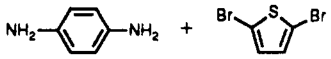
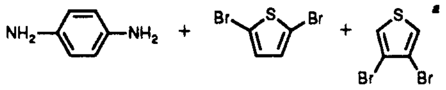
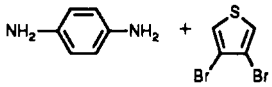
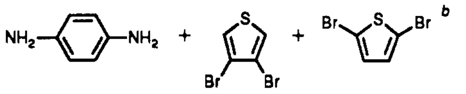
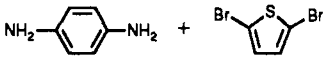
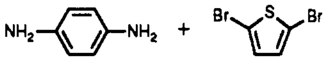
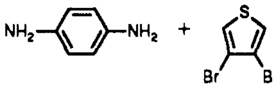
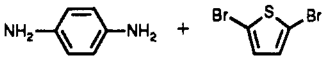
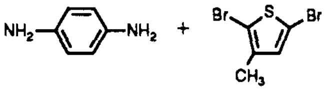
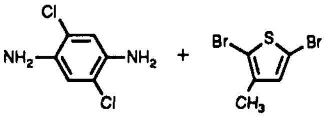
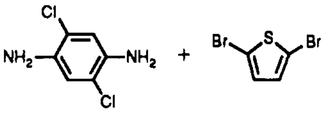
$$\chi^{\text{Curie}} = \frac{N_s g^2 \beta^2 S(S+1)}{3kT} \qquad (2)$$

where N_s is the number of spins present, g is the electronic g factor as determined by ESR studies (see Table III), β is the Bohr magneton, S is the spin quantum number ($S = {}^1/_2$), and k is Boltzmann's constant. The core susceptibility, χ^{core}, is the diamagnetic contribution from the core electronic character and can be calculated by using Pascal's constants.[21] Although the diamagnetic correction for PAni has been estimated in this way,[22] we have chosen to compare the unaltered data. Calculation of χ^{core} requires definitive and confident knowledge of the repeat unit and unlimited faith in the accuracy of the available constants. In light of the well-known structural aberrations present in this series, it is more informative to compare the bulk properties of the copolymers as measured, without excessive and perhaps erroneous interpretation. Extrapolating χ_g for $T \rightarrow \infty$, i.e., $\chi^{\text{Curie}} \rightarrow 0$, yields $\chi^{\text{Pauli}} + \chi^{\text{core}}$. For copolymers diamagnetic at room temperature (which is commonplace for organic materials), χ^{Pauli} is not discernible. In Table II, the gram susceptibilities represent a bulk susceptibility in units of emu/g. The number of spins per gram of copolymer, N_s, is calculated from eq 2 and the slope of the line derived from plotting $\chi_g - \chi_g$(300 K), the approximate χ^{Curie}, versus $1/T$, as depicted in Figure 3. As can be seen in Table II, the 3,4-copolymers (**1b**, **2**, **2b**, and **5**) all display diamagnetic character, except at very low temperatures (<50 K). The 2,5-copolymers, (**1**, **4**, **6**, **8**, and **9**), with the exception of the methyl-substituted PTAP (copolymer **7**), however, exhibit a room temperature paramagnetism somewhat unfamiliar to nonmetallic systems, as seen in Figure 4. Historically, some electroactive polymers such as polyaniline[22a] and BBL[23] do not exhibit this quality until doped into a metallic phase.

There exist two types of spins in this copolymer series. At very low temperatures (<50 K), a Curie tailing is present. In the presence of increasing thermal energy, the localized spins which exhibit Curie law behavior ($\chi \propto 1/T$) are randomized and eventually lose influence to a more temperature independent spin character. In the 3,4 series, that ambient temperature character is diamagnetic.

The 2,5 series, with the exception of copolymer **7**, as mentioned earlier, have a paramagnetic, albeit weak, susceptibility. The materials deficient in sulfur content tend

Table I
Sulfur Content of Various Aniline-Thiophene Copolymers

polymer	reactants	reacn temp, °C	% S (exptl/calcd)
1		250	8.06/17.03
1b		250	3.06/17.03
2		250	1.46/17.03
2b		250	2.97/17.03
3		200	3.91/17.03
4		200	23.35/17.03
5		185	24.54/17.03
6		185	15.99/17.03
7		185	18.53/15.85
8		185	13.21/11.82
9		185	12.66/12.47

[a] Proportionally 0.7 mol of 2,5-dibromothiophene to 0.3 mol of 3,4-dibromothiophene. [b] Proportionally 0.3 mol of 2,5-dibromothiophene to 0.7 mol of 3,4-dibromothiophene.

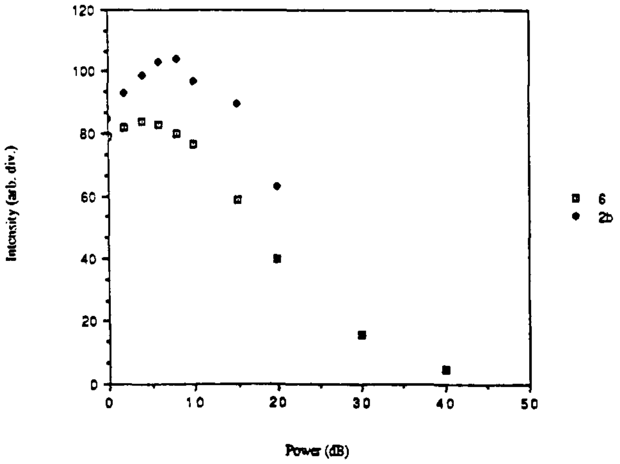


Figure 2. ESR saturation profiles for fused (Δ = 250 °C) and unfused (Δ = 185 °C) copolymers.

Table II
Gram Susceptibilities, χ_g, of Aniline-Thiophene Copolymers

polymer	χ_g(300 K), 10^{-6} emu/g	reacn temp, °C	N_s, 10^{19} g^{-1}
1	0.963195	250	2.42
1b	-0.306170	250	1.14
2	-0.332905	250	3.10
2b	-0.701921	250	2.86
4	15.9844	200	14.3
5	-0.132359	200	1.40
6	1.388558	185	10.3
6[a]	0.367416	185	7.44
7	-0.341456	185	3.25
7[a]	-0.352698	185	1.84
8	0.147078	185	17.1
9	0.412067	185	15.6
9[a]	0.194282	185	1.16

[a] Doped with iodine.

to remain linear, following more of a Curie-Weiss relationship where $\chi \propto 1/(T + \Theta)$ (Figure 4). The copolymer with the highest sulfur content, copolymer 4, exhibits almost pure Curie behavior with a tailing to zero susceptibility at higher temperatures.

In other conducting polymers such as PA[23] and PT,[24] this temperature-independent paramagnetism is associated with the Pauli susceptibility, i.e., metallic spin contribution. In systems where the delocalization is severely limited, authentic metallic behavior is highly unlikely. A better description is that of a Fermi "glass", and not that of a metal.[25] At lower temperatures, localized electronic states that describe this Fermi glass are predicted to exhibit Curie-like temperature dependence, with temperature-independent susceptibilities occurring at higher temperatures. This is consistent with the susceptibility behavior found in the series of 2,5-substituted copolymers, as depicted in Figure 4.

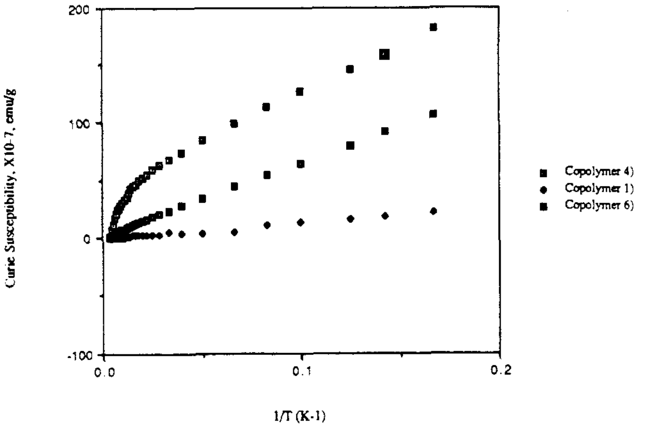


Figure 3. Curie susceptibilities of 2,5-PTAPS.

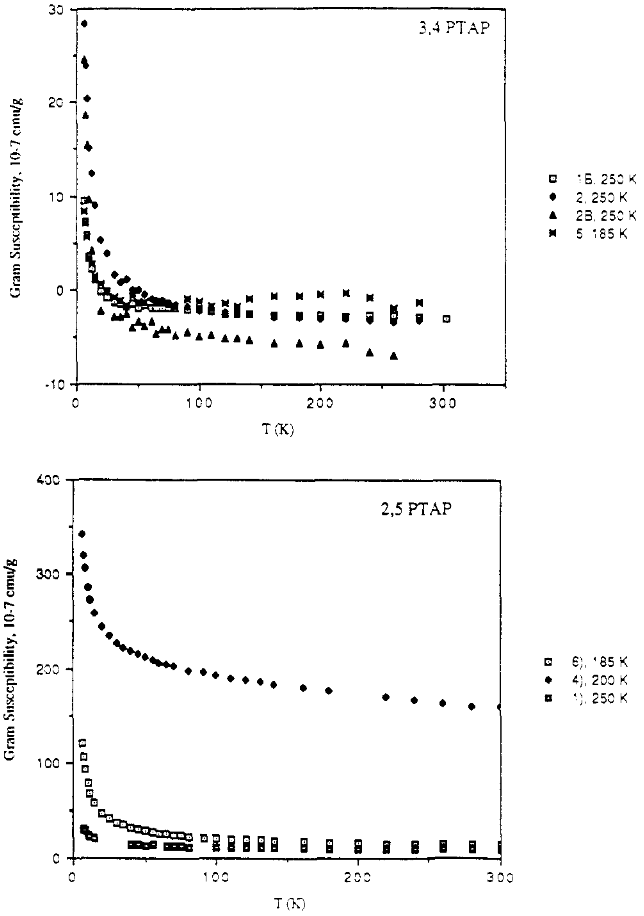


Figure 4. Comparison of magnetic character of 3,4-PTAP (top) to 2,5-PTAP (bottom).

Electron Spin Resonance. Certain copolymers exhibited structure in their ESR spectra. Materials with higher sulfur content such as copolymers **4**, **6**, **8**, and **9** all displayed line-shape anomalies (Figure 5). All the materials were produced from a 2,5-dibromothiophene starting material. This unresolved structure did not change upon cooling, at either liquid nitrogen or liquid helium temperatures. Copolymer **7** had a Lorentzian line shape and remained singular in that its line shape did not have any of the abnormalities as seen in the other 2,5-substituted copolymers. Other processes such as Heisenberg spin exchange may be providing a mechanism that effectively averages orientational dependence and produces the Lorentzian line shape. The materials produced from the 3,4-dibromothiophene also exhibited a Lorentzian line shape. These line shapes, along with the peak-to-peak line width, H_{pp} (Table III), were also independent of temperature between 100 and 300 K. This temperature independence of both the line shape and line width ($\Delta(H_{pp}) \leq 1$ G) indicates that the spins involved in the resonance process are highly localized and most likely immobilized by the amorphous nature of the material.

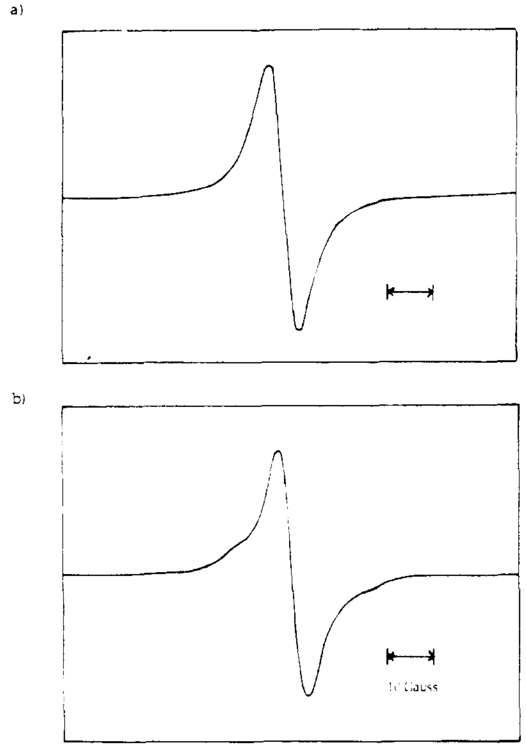


Figure 5. Comparison of the ESR line shape of two copolymers with different sulfur concentrations: (a) polymer **1**, prepared at 250 °C; (b) polymer **4**, prepared at 200 °C.

Table III
Electron Spin Resonance Results for Aniline–Thiophene Copolymers

polymer	reacn temp, °C	H_{pp}, G	$\langle g \rangle$	Δg, 10^{-3}
1	250	8.4	2.0037	1.4
1b	250	7.3	2.0032	0.9
2	250	9.2	2.0033	1.0
2b	250	7.9	2.0031	0.8
4	200	7.8	2.0042	1.9
5	185	6.8	2.0039	1.6
6	185	6.4	2.0040	1.7
7	185	6.5	2.0036	1.3
8	185	6.8	2.0040	1.7
9	185	6.8	2.0043	2.0

The parent systems both exhibit much more narrow line widths (H_{pp}(PT) = 2.0 G,[13] H_{pp}(PAni) = 3.6 G[26]), indicating a more mobile spin species. The smallest line width occurring in this series is found in the materials prepared at lower temperatures with H_{pp}(copolymer **6**) = 6.4 G. This much broader line width is expected in systems of lower symmetry or in those with a more heterogeneous lattice. Again, the intrinsic amorphous nature of the copolymer is experimentally evident.

Conductivity and Doping Studies. All pristine materials behaved as insulators, exhibiting bulk conductivities of $<10^{-12}$ S/cm. Electron spin resonance studies of the doped materials coupled with the ineffectiveness of the nitrosyl or nitrosonium type dopants indicated that these particular dopants reacted with the aniline–thiophene copolymers to alter them in an irreversible way. Iodine-doped materials had enhanced conductivities on the order of 10^{-6} S/cm and are listed in Table IV. The ESR signals of the iodine-doped materials became unsym-

Table IV
Conductivities of Several Doped Aniline–Thiophene Copolymers

polymer (doped with iodine)	conductivity,[a] Ω/cm
6	5.22×10^{-6}
7	2.37×10^{-6}
8	4.64×10^{-6}
9	2.53×10^{-6}

[a] Measured at 298 K, 1 atm.

metrical. This could be due to inhomogeneous doping. The static susceptibility of the materials was consistently decreased after doping with iodine. With the increase in conductivity, this would seem contradictory unless the charge storage was in the form of bipolarons as is theoretically predicted for PT.[8]

The temperature-independent paramagnetism common to metallic systems occurring in the pristine 2,5-substituted materials does not, in this case, correlate to an electrically conducting lattice. This irregularity is most likely due to limited interchain interactions and intrachain trapping that arises as a result of lattice disorder. Doping effectively increases the conductive nature but not substantially, indicating that the amorphous nature of the copolymers prevents the mobility of any available charge. The formation of bipolarons upon doping (as in PT)[13] of these copolymers is supported by a decrease in the bulk susceptibility that occurs simultaneously with the increase in conduction.

Conclusions

The characterization of the magnetic properties of several aniline–thiophene copolymers confirms a direct correlation between the sulfur heteroatom and the electronic character of the polymer. As can be seen in a preceding paper,[19] the optical signature of these materials as described by the UV–vis spectra supports this claim. The 3,4-copolymers undergo the most drastic change in electronic character, with the band gap, E_g, decreasing markedly, going from 3.0 eV in the materials produced at lower temperatures to 1.8 eV in the high-temperature products. The 2,5-substituted copolymers exhibit similar behavior with a band gap decrease of somewhat smaller proportions. With the loss of sulfur potentially producing a *cis*-PA type backbone, the copolymers may be forced into a greater number of quinoidal conformations.

This is more plausible for the 2,5-substituted materials, while in the 3,4-substituted copolymers prediction of the resultant bond configuration would be purely speculative. As predicted, increasing the quinoidal character should be effective in reducing E_g. This is consistent with the shift as seen in this series of copolymers. The loss of sulfur in the 2,5-substituted materials removes the added stabilization of the aromatic bond conformation, increases the quinoidal character, and produces the expected reduced E_g. The aromatic conformation is destined to be more stable in the 2,5-PTAPs, and it is the lack of stabilization that accounts for the more severe alteration of the electronic band structure in the 3,4-substituted materials, as depicted in the UV–vis spectra.

In the 2,5-substituted copolymers, the sulfur atom is actively involved in the conjugation, whereas in the 3,4-substituted copolymers the sulfur is either excluded or, at higher temperatures, lost altogether. This is supported by the ESR data. The influence of the sulfur heteroatom is seen in the greater g shift away from the free-electron value in the systems where the sulfur is involved in conjugation. Interestingly, this is not seen in the parent polymer, PT, which has $g = 2.0029$ (closer to that of the free-electron value).[4] Copolymers produced at higher temperatures (lower sulfur content) exhibited a broader line width ($H_{pp} = 7.3$–9.2 G) typical of a highly localized spin, as would be expected in a more disordered environment.

The structure in the ESR spectra is only seen in systems where the sulfur actively participates in conjugation as in the 2,5-substituted copolymers. In static susceptibility measurements, the 3,4-substituted systems are all diamagnetic. This implies that the position of the sulfur heteroatom could be exclusively responsible for the anomalous paramagnetism of the 2,5-substituted copolymers.

The trends that remain consistent within this series, i.e., decreasing band gap with decreased influence of the heteroatom, the correlation of g shift to the sulfur atom's position, and the somewhat anomalous paramagnetism of the undoped 2,5-substituted aniline–thiophene copolymers, show qualitatively that the sulfur heteroatom plays a decisive role in the determination of the electronic properties of polymeric systems. Future studies exploring the actual quinoidal to aromatic ratio coupled with controlled syntheses of various oligomers are necessary to quantify the influence of the heteroatom and are fully justified by the consistencies and trends found in this characterization of aniline–thiophene copolymers.

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References and Notes

(1) For a general review of conducting polymers including polyheterocycles, see: *Handbook of Conducting Polymers*, Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1.
(2) (a) Heeger, A. J.; Orenstein, J.; Ulrich, D. R., Eds. *Nonlinear Optical Properties of Polymers, Part II*; Materials Research Society: Pittsburgh, PA, 1988. (b) Sasabe, H.; Wada, T. *Electronic Properties of Conjugated Polymers, Springer Series 76*; Springer-Verlag: New York, 1987; p 179. (c) Heeger, A. J.; Moses, D.; Sinclair, M. *Synth. Met.* **1986**, *15*, 95.
(3) (a) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. B* **1980**, *22*, 2209; **1982**, *28*, 1138(E). (b) Heeger, A. J. *Polym. J.* **1985**, *17*, 201.
(4) Kobayashi, M.; Chen, J.; Chung, T.-C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77.
(5) (a) Kanazwa, K.; Diaz, A. F.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, G.; Kwak, J. *Synth. Met.* **1980**, *1* (3), 329. (b) *Electronic Properties of Polymers and Related Compounds*; Springer Series; Springer-Verlag: New York, 1985; p 187.
(6) Bredas, J. *J. Chem. Phys.* **1985**, *82* (8), 3808.
(7) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285.
(8) Bertho, D.; Laghdir, A.; Jouanin, C. *Phys. Rev. B* **1986**, *38*, 12531.
(9) (a) Wudl, F.; Kobayashi, M.; Colaneri, N.; Boysel, M.; Heeger, A. J. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 195. (b) Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717.
(10) (a) Jenekhe, S. *Nature* **1986**, *322*, 345. (b) Jenekhe, S. *Macromolecules* **1986**, *19*, 2663.
(11) Jenekhe, S.; Lo, S. K.; Flom, S. R. *Appl. Phys. Lett.* **1989**, *54* (25), 2524.
(12) Chung, T.-C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702.
(13) (a) Moraes, F.; Park, Y. M.; Heeger, A. J. *Synth. Met.* **1986**, *13*, 113. (b) Vardeny, Z.; Ehrenfreund, E.; Brafman, O.; Nowak, M. J.; Schaeffer, H.; Heeger, A. J.; Wudl, F. *Phys. Rev. Lett.* **1986**, *56*, 671.
(14) Takayama, H.; Lin, Y. R.; Maki, K. *Phys. Rev. B* **1980**, *21*, 2388.
(15) Mintmire, J. W.; White, C. T.; Elert, M. L. *Synth. Met.* **1986**, *16*, 235.
(16) Bredas, J. L.; Themans, B.; Fripiat, J. G.; Andre, J. M. *Phys. Rev. B* **1984**, *29* (12), 6761.

(17) Mintmire, J. W.; White, C. T.; Elert, M. L. *Synth. Met.* **1988,** *25,* 109.
(18) Lee, Y. S.; Kertesz, M. *J. Chem. Phys.* **1988,** *88* (4), 2609.
(19) Polis, D. W.; Young, C. L.; McLean, M. R.; Dalton, L. R. *Macromolecules,* accompanying paper in this issue.
(20) Van der Pauw, L. J. *Philips Res. Rep.* **1958,** *13,* 1.
(21) Boudreaux, E.; Mulay, L. N. *Theory of Paramagnetism*; Wiley: New York, 1976.
(22) (a) Epstein, A. J.; Ginder, J. M.; Zuo, F.; Bigelow, R. W.; Woo, H.-S.; Tanner, D. B.; Richter, A. F.; Huang, W.-S.; MacDiarmid, A. G. *Synth. Met.* **1987,** *18,* 303. (b) Ginder, J. M.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Solid State Commun.* **1987,** *63* (2), 97. (c) Wudl, F.; Angus, R. O.; Lu, F. L.; Allenmand, P. M.; Vachon, D. J.; Nowak, M. J.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987,** *109,* 3677.
(23) Tomkiewicz, Y.; Schulz, T.; Broom, H.; Clarke, T.; Street, G. *Phys. Rev. Lett.* **1979,** *43,* 1532.
(24) (a) Poe, M.; Roth, S.; Dransfeld, K.; Tieke, B.; Hocker, J.; Gross, H.; Grupp, A.; Sixl, H. *Solid State Commun.* **1980,** *35,* 119. (b) Moraes, F.; Chen, J.; Chung, T.-C.; Heeger, A. J. *Synth. Met.* **1985,** *11,* 271. (c) Moraes, F.; Davidov, D.; Kobayashi, M.; Chung, T.-C.; Chen, J.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1985,** *10,* 169.
(25) Roe, M. G.; Ginder, J. M.; Wigen, P. E.; Epstein, A. J.; Angelopoulos, M.; MacDiarmid, A. G. *Synth. Met.* **1989,** *29* (1), E425.
(26) Andersen, P. W. *Commun. Solid State Phys.* **1970,** *2* (6), 193.

Registry No. 1 (copolymer), 121753-88-6; **1b** (copolymer), 126724-55-8; **2** (copolymer), 126724-56-9; **7** (copolymer), 126724-57-0; **8** (copolymer), 126724-58-1; **9** (copolymer), 126724-59-2; iodine, 7553-56-2.

Synthesis, Electrochemical Characterization, and Assembly into Langmuir–Blodgett Films of Some N-Substituted Derivatives of Poly(3,6-carbazolylmethylene)

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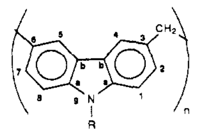
ABSTRACT: A series of condensation polymers of N-substituted carbazoles with formaldehyde were prepared by H_2SO_4-catalyzed oligomerization in dioxane. Soluble polymers having number-average degrees of polymerization of 5–30 were obtained and characterized spectroscopically. These polymers underwent irreversible one-electron oxidation in CH_2Cl_2 solution with electrodeposition and displayed intense blue and green electrochromism. Homopolymers and copolymers in which the 9-position of the carbazole ring was substituted by flexible polar groups such as $(CH_2)_4CN$, $(CH_2)_{10}COOH$, or $(CH_2)_{11}OH$ spread reproducibly from $CHCl_3$ to give monolayers at the air–water interface. Mixed monolayers containing as little as 0.25 mol of stearic acid/1 mol of repeating unit gave Y-deposition on quartz, with the formation of LB films of up to 70 monolayers in thickness.

Introduction

Monolayers at the air–water interface, which have sufficiently high collapse pressures, can be transferred as Langmuir–Blodgett (LB) films to a variety of solid substrates and then used in further applications. Interest in LB films has recently undergone a period of dramatic growth, particularly as a result of their potential applications as components of microelectronic devices, as high-resolution photoresists for microlithography, and as nonlinear optical components.[1–7] A major trend in LB film research is to move from simple saturated fatty acids, which function as insulating layers, to functional surface-active compounds, which are electrochemically or photochemically active. In addition, polymeric LB films offer the important advantage of higher mechanical stability than small-molecule films.[5–9]

In this paper we report the synthesis and characterization of stable, transferable surface-active polymers that incorporate a redox-active aromatic amine group in the backbone. Homopolymers and copolymers based on derivatives of poly(3,6-carbazolylmethylene) with the general structure



1a, R = $(CH_2)_4CN$
1b, R = $(CH_2)_{10}COOH$
1c, R = $(CH_2)_{11}OH$
1d, R = $(CH_2)_{13}CH_3$

were investigated. These polymers contain nitrile, carboxylic acid, and alcohol polar groups, which result in enhanced stability of monolayers at the air–water interface. The spreading behavior of these polymeric monolayers and of mixed monolayers with stearic acid was

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[†] Deceased.

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