polymer papers

# 'Substitutional alloys' of organic polymeric conductors

**John P. Ferraris* and Gary D. Skiles**
*Programs in Chemistry, The University of Texas at Dallas, Richardson, Texas 75083–0688, USA*

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Electrically conducting 'copolymers' of thiophene with pyrrole, *N*-methylpyrrole, and furan, whose conductivities vary as a function of (among other things) the heteroatom composition have been prepared. The use of a tri-ring monomer allows the production of these 'substitutional alloys' with a controlled heteroatom composition and formally known sequence distribution.

**(Keywords: thiophene–pyrrole copolymers; thiophene–furan copolymers; thiophene–*N*-methyl pyrrole copolymers; conductivity; electrochemistry)**

## INTRODUCTION

The preparation of self-supporting films of polyacetylene (PA) in the early seventies[1] and the discovery shortly thereafter that these could be oxidized or reduced ('doped') to afford materials with electrical conductivities variable over twelve orders of magnitude[2] mark the renaissance of the field of organic polymeric conductors. Although PA remains today one of the more highly studied conducting polymers[3], its instability toward the atmosphere and inprocessibility has motivated research on the polymers based on the heteroaromatics pyrrole, thiophene, selenophene and furan. The comparative ease of their preparation via electrochemical techniques[4], is another attraction. When doped, the conductivities of the polyheteroaromatics also increase—saturating in the 10–100 mho/cm range for the more highly doped samples[5], reminiscent of the magnitudes obtained with other disordered organic conductors[6].

The presence of the heteroatom affords, in principle, one more degree of freedom in the design and control of the electronic properties of the polymers. The importance of this variable has yet to be fully elucidated, however. Despite the relatively large difference in the band gaps of *neutral* polythiophene ($E_g = 2.0$ eV)[7] and polypyrrole ($E_g = 3.2$ eV),[5,8] the heteroatom appears to play only a minor role in the charge distribution of moderately oxidized polymers[9]. Recent calculations have shown that the band gap decreases linearly with the amount of quinoid structure the polymer can assume upon doping[10], and the energy required to attain this configuration varies somewhat with the structure of the aromatic moiety (20.1, 16.1 and 14.4 kcal mol$^{-1}$ per ring for benzene, thiophene and pyrrole, respectively). Although these differences are not great, we should be able to exploit them to control the electronic properties of the polymer over a defined range by controlling its heteroatom composition through copolymers. Production of well-defined copolymers through oxidative copolymerization of monomer mixtures is complicated, however, since the monomer oxidation potentials and reaction kinetics vary with heteroatom substitution. Such copolymers can be prepared from the three ring systsms in *Figure 1*, where the heteroatom in the central ring, X, is varied between NH [SNS, **1**][11], NMe [SMS, **2**], O [SOS, **3**][12], S [SSS, **4**][11] and Se [SSeS, **5**][13].

## EXPERIMENTAL

### *General*

All reagents were A.C.S. reagent grade and solvents were h.p.l.c. grade unless otherwise specified. Nitrosonium hexafluorophosphate and antimonate were purchased from Alfa, stored under an inert atmosphere in the deep freeze and used without further purification. Tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared and purified by literature methods[14].

Infra-red spectra were obtained on a Nicolet 5DX FTIR spectrometer. $^1$H n.m.r. were obtained on a JEOL JNM-FX200 FTNMR. U.v./visible spectra were measured on a Hewlett–Packard HP8450A spectrophotometer. Differential scanning calorimetric measurements were performed on a Perkin Elmer DSC-2. Cyclic voltammetry determinations were made with a Bio-Analytical Systems, Inc. BAS-100.

### *Monomer syntheses*

*2,5-Di-(2-thienyl)-thiophene, SSS.* The method of Wynberg and Matselaar[11] was followed without modification. SSS was obtained as a yellow solid (70% yield) and >99.5% purity (pentane recrystallization) as determined by differential scanning calorimetry (d.s.c.)[15]. Its identity was confirmed by infra-red and proton n.m.r. spectroscopy.

*2,5-Di-(2-thienyl)-pyrrole, SNS.* The method of Wynberg and Matselaar[11] was modified by the use of a

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* To whom correspondence should be addressed.

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nitrogen inert atmosphere and an extended reaction time (48 h) to afford SNS in 83% yield and >99.5% purity (from pentane). Once prepared, this material was stored and manipulated in a He-filled glove box.

*2,5-Di-(2-thienyl)-furan*[12], *SOS*. A solution of 1,4-di-(2-thienyl)-1,4-butane dione (2.0 g)[11], concentrated HCl (3.0 ml) and acetic anhydride (60 ml) was stirred at room temperature for four days. The reaction mixture was then added to water (500 ml) and neutralized with sodium carbonate. The solution was extracted with $CCl_4$, and this extract washed with saturated aqueous sodium chloride and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue chromatographed over silica gel with $CCl_4$ elution to afford SOS in 75% yield and >99.6% purity by d.s.c.[15] after recrystallization from pentane.

N-*Methyl-2,5-di-(2-thienyl)-pyrrole*, *SMS*. A 100 ml round bottom flask was charged with 1,4-di-(2-thienyl)-1,4-butane dione [2.2 g (8.8 mmol)], benzene (30 ml) and glacial acetic acid (10 ml). A 40% solution of aqueous methylamine (20 ml) was added slowly to this solution. The flask was equipped with a Dean–Stark and the reaction was stirred at reflux overnight with the constant removal of water by azeotropic distillation. The reaction mixture was concentrated *in vacuo* and the residue dissolved in diethyl ether. This solution was washed with aqueous sodium bicarbonate and saturated aqueous sodium chloride. The ethereal solution was dried over $MgSO_4$ and the solvent removed *in vacuo*. The yellow solid was chromatographed over silica gel with hexane elution to afford SMS in 91% yield as white crystals, m.p. 109°C–110°C, i.r.(KBr), 1201.8 $cm^{-1}$; $^1H$ n.m.r. (acetone-$d_6$, TMS): 7.44 $\delta$ (d of d, 2H), 7.14 $\delta$ (m, 4H), 6.30 $\delta$ (s, 2H), 3.75 $\delta$ (s, 3H).

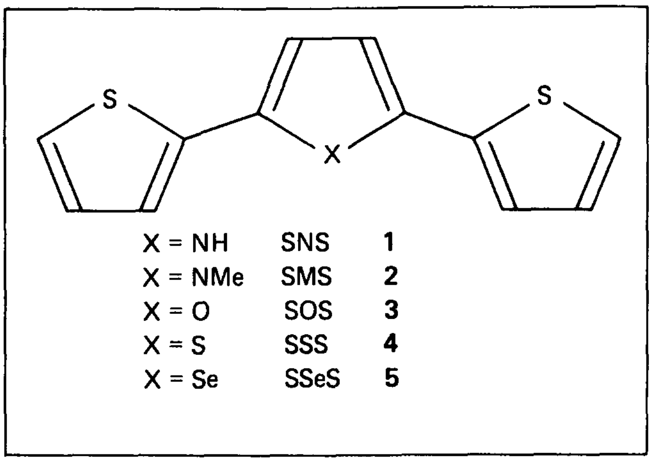

**Figure 1** Structures of and acronyms for tri-ring monomers

### *Chemical oxidation/polymerization*

All chemical oxidation/polymerizations were conducted in a He-filled glove box (Vacuum Atmospheres, Inc.). Typically, 1.0 mmole of the respective monomer was dissolved in *ca.* 15 ml of methylene chloride which had been previously dried and deoxygenated. To this solution was added 1.0 mmole of the oxidizing agent ($NOPF_6$ or $NOSbF_6$). The resultant dark mixture was stirred at room temperature for 3 h. The black precipitates were collected, washed with fresh methylene chloride and dried *in vacuo*. A 200 mg sample of oxidized SNS prepared this was was slurried in methylene chloride and treated with an additional 150 mg of $NOPF_6$. After 3 h, the product was collected, washed with fresh methylene chloride and dried *in vacuo*.

### *Conductivity measurements*

The black powders obtained from the chemical oxidations were pressed into pellets using a Perkin Elmer 13 mm evacuable die and a Carver laboratory press at guage pressures of 22 000 psi. These pellets were isolated in a nitrogen filled glove box containing the probe unit of a T-606 Resistivity Test Set (Self-Organizing Systems, Inc.). Conductivity was determined by a four-probe technique at room temperature.

## RESULTS AND DISCUSSION

*Table 1* compares the data for peak oxidation potential ($E_{pa}$) and long wavelength absorption for these monomers with the corresponding single ring systems. The expectation that the resonance and inductive effects of the flanking thiophene rings might manifest themselves in similar fashion throughout the series is approximately sustained. The electrochemistry for all these systems is irreversible, however, and the observed deviations could be due to a combination of factors, including unequal demands of the respective oxidized species for solvent stabilization, kinetics of polymerization and perhaps reaction with adventitious nucleophiles.

The variation in the energy of the long wavelength absorption ($h\nu_{min}$) for **1**–**5** reflects differences in the HOMO–LUMO separation ($\Delta$) for these systems[16]. This

**Table 1** Peak oxidation potential and long wavelength absorption for monomers

| Monomer | $\lambda_{max}$ (nm)[a] | $h\nu_{min}$ (eV) | log $\varepsilon$ ($L \cdot M^{-1} cm^{-1}$) | $E_{pa}$ (V)[b] | | |
|---|---|---|---|---|---|---|
| | | | | MC–PTE | AN–PTE | AN–GCE |
| Pyrrole | 208[16] | – | – | 1.22 | 1.27 | 1.26 |
| *N*-Methyl-pyrrole | – | – | – | 1.24 | 1.33 | 1.16 |
| Furan | 200 | – | – | 1.53 | 2.01 | 1.77 |
| Thiophene | 231[16] | – | – | 1.70 | 1.93 | 1.94 |
| **1** | 349 | 3.55 | 4.35 | 0.64 | 0.66 | 0.67 |
| **2** | 321 | 3.86 | 4.24 | 0.74 | 0.73 | 0.74 |
| **3** | 352 | 3.52 | 4.35 | 0.93 | 0.94 | 0.95 |
| **4** | 353 | 3.51 | 4.35 | 0.99 | 1.01 | 1.03 |
| **5** | 361 | 3.43 | 4.32 | 1.01 | – | – |

[a] Spectra for **1**–**5** taken in 100% EtOH

[b] Determined from cyclic voltammetry; Pt (PTE) or glassy carbon (GCE) electrodes, 0.1 M TBAHFP in dry, deoxygenated methylene chloride (MC) or acetonitrile (AN), vs. Ag/AgCl with ferrocene as an internal standard. Values are corrected to SCE

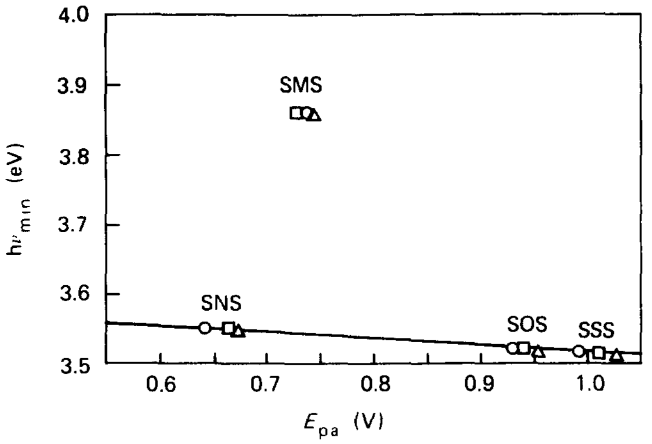

**Figure 2** HOMO–LUMO separation ($h\nu_{min}$, eV) vs. peak anodic potential ($E_{pa}$, V) for SXS monomers. ○, MC–PTE; □, AN–PTE; △, AN–GCE; where MC is methylene chloride, AN is acetonitrile, PTE and GCE mean platinum and glassy carbon electrodes, respectively

parameter is similar for SNS, SOS and SSS, where a planar conformation can be achieved for both ground and excited states. The situation is different for SMS whose rings would have difficulty attaining coplanarity due to steric interaction of the $N$-methyl group with the $\beta$-hydrogens (or the sulphur lone pair) of the adjacent rings[17]. This loss of resonance stabilization should raise the energies of both the HOMO and LUMO. The observed increase in Δ suggests that this destabilization is greater for the LUMO. The peak oxidation potentials for **1**, **3** and **4** track Δ for these systems in contrast to **2** (see *Figure 2*).

If one makes the simple assumption that *trends in* Δ will be similarly manifested in the band gaps of the polymer, these data suggest that the gaps ($E_g$) of polymers derived from **1**, **3** and **4** might be comparable despite the rather large differences between $E_g$ for polythiophene[7] and polypyrrole[5,8]. Even if this is the case, the placement of the Fermi levels in our polymers may be different since the HOMO energies of their respective monomers (in so far as they may be deduced from $E_{pa}$ values)[16] span a 400 mV range. The effects of these differences should become most pronounced for lightly doped systems.

When solutions of the tri-ring monomers in methylene chloride are treated under an inert atmosphere with chemical oxidants such as nitrosonium salts, black precipitates form in moderate to high yields. The highly coloured supernatant presumably contains lower molecular weight oligomers but these were not studied any further. Under these conditions all isolated products from **1**–**4** were highly doped (21–49 mole per cent, based on elemental analyses), i.e., in a regime where the conductivity might be expected to saturate. For comparable dopant levels, however, there is over an order of magnitude difference in the conductivities of these polymers (see *Table 2*). This difference is greater than two orders of magnitude when one compares $PF_6$-doped polythiophene prepared by oxidation/polymerization of thiophene with the analogous polymer obtained from SSS. Differences like this have been observed before[18,19] and have been ascribed to a smaller degree of non-α,α'-crosslinking in the polymer prepared from SSS as compared with that from thiophene. We expect a similar suppression of this undesirable mode of coupling in our three-ring systems.

Somewhat surprisingly, the conductivities of the polymers derived from SMS are comparable to those from SOS and SNS even though the rings in the SMS-based materials are expected to be non-coplanar. If coplanarity is not a necessary condition for conductivity in these copolymers, one can envision a large number of $N$-substituted derivatives which might exhibit a wide range of mechanical and solubility properties and still remain conducting.

The data suggest that the heteroatom composition may play an important (though not exclusive) role in determining the transport properties of these materials. The exact nature of its contribution must await the results of transport and optical studies as a function of dopant nature and concentration. These are being performed on films of these systems prepared by electrochemical polymerization techniques[20]. However, we note that the thiophene ring is the least easily oxidized of the heteroaromatics studied here. Perhaps in the oxidized polymers, the cationic species are more 'localized' on those rings bearing the non-S heteroatom. These sites could then serve as hole traps, which would limit their mobility and hence the conductivity. Copolymerization of pyrrole with SSS has recently been achieved[21] due in large part to their similar oxidation potentials, although neither the amount of pyrrole incorporation nor the sequence distribution was deduced. Our systems offer a wider range of potentials over which combinations of monomers may be electro-copolymerized. While this work was in progress, a report describing the electrochemical polymerization of SNS and the electrical properties of these polymers appeared[22]. The reported potentials at which these films were grown are at variance with the peak anodic potentials that we measure. The conductivities lie in the range of 0.02 to 0.1 S cm$^{-1}$ for films highly doped with *para*-toluene sulphonate, however, and are comparable in magnitude to our chemically doped systems.

## CONCLUSIONS

In summary, we have prepared electrically conducting copolymers of heteroaromatics which may be viewed as 'substitutional alloys' of poly(thiophene) with poly(pyrrole), poly($N$-methyl)pyrrole or poly(furan),

**Table 2** Conductivity of oxidized polymers

| Compound | Conductivity (S cm$^{-1}$) | Rings/anion | Footnote |
|---|---|---|---|
| poly(S) ·$PF_6$ | $1.7\times10^{-5}$ | 1.8 | *a* |
| poly(S)·$PF_6$ | $1.8\times10^{-3}$ | – | *b,c* |
| poly(SS)·$BF_4$ | $6.9\times10^{-2}$ | 1.2 | *a* |
| poly(SSS)·$SbF_6$ | 1.9 | – | *b,c* |
| ·$PF_6$ | $5.5\times10^{-1}$ | 2 | *b,d* |
| poly(SOS)·$SbF_6$ | $2.5\times10^{-3}$ | 3.4 | *b,c* |
| ·$PF_6$ | $5.6\times10^{-2}$ | – | *b,d* |
| poly(SNS)·$SbF_6$ | $2.7\times10^{-3}$ | – | *b,c* |
| ·$PF_6$ | $3.6\times10^{-3}$ | 4.6 | *b,d,e* |
| ·$PF_6$ | $9.0\times10^{-2}$ | 2.3 | *b* |
| poly(SMS)·$SbF_6$ | $2.4\times10^{-3}$ | – | *b,c* |
| ·$PF_6$ | $2.7\times10^{-2}$ | 2.1 | *b,d* |

[a] Ref. 18
[b] Four probe d.c. measurements on compacted pellets; $T=300$ K
[c] Present work; compacted pellets; oxidant: $NOSbF_6$ in $CH_2Cl_2$
[d] Present work; compacted pellets; oxidant: $NOPF_6$ in $CH_3Cl_2$
[e] This material was reoxidized with excess $NOPF_6$ to give the next entry

whose conductivity varies as a function of (among other things) the heteroatom composition. The use of a tri-ring monomer allows the production of copolymers with a controlled heteroatom composition (2S: 1X, X=S, O, NH, NR) and a formally known sequence distribution since the degree of non-$\alpha,\alpha'$-bonding is expected to be suppressed[18]. We anticipate that other properties such as solubility, processibility and mechanical strength may be varied by judicious choice of substituent and/or heteroatom and are exploring these possibilities.

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