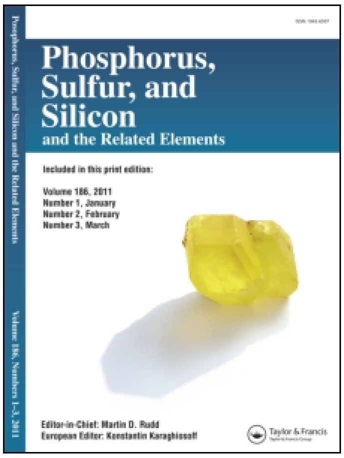


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Study of a Sulfur Heterocycle Fused *p*-Phenylene Vinylene Conducting Polymer

Martin Pomerantz[a]; Jiping Wang[a]; Seeyearl Seong[a]; Kyle P. Starkey[a]; Long Nguyen[a]; Dennis S. Marynick[a]
[a] Center for Advanced Polymer Research, Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas, USA

To cite this Article Pomerantz, Martin , Wang, Jiping , Seong, Seeyearl , Starkey, Kyle P. , Nguyen, Long and Marynick, Dennis S.(1994) 'Synthesis and Study of a Sulfur Heterocycle Fused *p*-Phenylene Vinylene Conducting Polymer', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 507 — 508

To link to this Article: DOI: 10.1080/10426509408034296

URL: http://dx.doi.org/10.1080/10426509408034296

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 507–508
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND STUDY OF A SULFUR HETEROCYCLE FUSED *p*-PHENYLENE VINYLENE CONDUCTING POLYMER

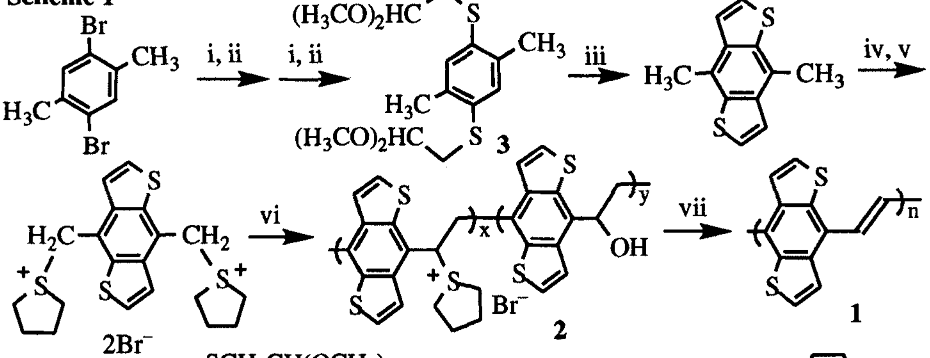
MARTIN POMERANTZ, JIPING WANG, SEEYEARL SEONG, KYLE P. STARKEY, LONG NGUYEN, AND DENNIS S. MARYNICK
Center for Advanced Polymer Research, Department of Chemistry and Biochemistry, Box 19065, The University of Texas at Arlington, Arlington, Texas 76019, USA

Abstract Poly(benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-diyl vinylene) (**1**) has been prepared by the pyrolysis of the precursor polymer **2** and studied. Quantum mechanical calculations on the aromatic and quinoid monomers, oligomers and polymers indicate that **1** is a planar aromatic polymer.

As part of our long-standing program in electrically conducting polymers[1-4] we are designing, preparing and studying materials which might show enhanced conductivity. They are modeled after the flat, broad conjugated conducting (and superconducting) charge transfer complexes which contain a number of sulfur atoms.[5]

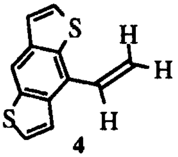
Our initial system is poly(benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-diyl vinylene) (**1**) whose synthesis via the soluble precursor polymer **2** is shown in Scheme 1. In the preparation of **3** two elimination products were observed and in polymer **2** the ratio of x:y was 61:39. The thermal elimination of **2** to produce **1**, which was followed by UV-vis spectroscopy, was best carried out at 300 °C for 2-3 hr. in a vacuum oven with a residual reducing atmosphere of 10% H_2 / 90% Ar.[6] The polymer showed λ_{max} = 503 nm, it was thermally stable (onset of decomposition = 370 °C), and it could be doped with $FeCl_3$ to give a material with a fairly high conductivity of 60 S cm^{-1}. Upon doping the polymer changed from burgundy to light bluish-green, the absorption at 503 nm decreased and two new absorptions at 860 and 1860 nm grew in.

Scheme 1

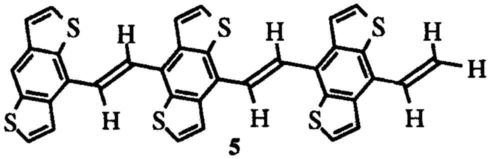


i, BuLi/−78 °C; ii, $\begin{matrix} SCH_2CH(OCH_3)_2 \\ | \\ SCH_2CH(OCH_3)_2 \end{matrix}$; iii, polyphosphoric acid; iv, NBS; v,  ;
vi, NaOH; vii, vacuum oven/300 °C/residual 10% H_2 / 90% Ar

The electronic structures of monomer **4**, trimer **5** and polymer **1**, both aromatic and quinoid with suitable end groups, were calculated using quantum mechanical calculations based on the PRDDO,[7] ab-initio (STO-3G)[8] and Extended Hückel[9] methodologies. The most significant difference between the two types of structures (aromatic and quinoid) is that in the aromatic forms the dihedral angle between the vinyl group and the flat aromatic ring is about 40° while the quinoid structure is planar. However, the barrier to rotation about the vinyl-aryl C–C bond in the aromatic structure is calculated to be only about 1.5 kcal/mol. In addition, the aromatic form of the polymer is calculated to be about 24 kcal/mol per repeat unit more stable than the quinoid form by extrapolation of oligomers up to a hexamer.[10] These calculations, together with a comparison of the calculated UV-vis absorption maximum with that observed for polymer **1** suggest the solid state structure of the polymer is aromatic and planar.



4



5

Acknowledgment. We thank the U. S. Air Force Office of Scientific Research, the Robert A. Welch Foundation (Grant Nos. Y-0684 and Y-0743) and and the National Science Foundation for financial support.

REFERENCES

1. M. Pomerantz, J. Wang, S. Seong, K. P. Starkey, L. Nguyen and D. S. Marynick, Mat. Res. Soc. Symp. Proc., 328, 227 (1994)
2. M. Pomerantz, B. Chaloner-Gill, L. O. Harding, J. J. Tseng and W. J. Pomerantz, Synth. Met., 55, 960 (1993).
3. M. Pomerantz, B. Chaloner-Gill, L. O. Harding, J. J. Tseng and W. J. Pomerantz, J. Chem. Soc., Chem. Commun., , 1672 (1992).
4. M. Pomerantz, J. J. Tseng, H. Zhu, S. J. Sproull, J. R. Reynolds, R. Uitz, H. J. Arnott and M. I. Haider, Synth. Met., 41, 825 (1991).
5. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, Organic Superconductors (including Fullerenes): Synthesis, Structure, Properties, and Theory, (Prentice Hall, Englewood Cliffs, NJ, 1992), .
6. F. Papadimitrakopoulos, T. M. Miller, E. A. Chandross and M. E. Galvin, Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.), 35 (Number 1), 215 (1994).
7. T. A. Halgren and W. N. Lipscomb, J. Chem. Phys., 58, 1569 (1973). D. S. Marynick and W. N. Lipscomb, Proc. Nat. Acad. Sci. U. S. A., 79, 1341 (1982). D. S. Marynick, F. U. Axe, C. M. Kirkpatrick and L. Throckmorton, Chem. Phys. Lett., 99, 406 (1982). D. S. Marynick and R. D. Reid, Chem. Phys. Lett., 124, 17 (1986).
8. M. J. Frisch, et al., Gaussian 92, Revision C (Gaussian Inc., Pittsburgh, 1992).
9. R. Hoffmann, J. Chem. Phys., 39, 1397 (1963). M. H. Whangbo and R. Hoffmann, J. Am. Chem. Soc., 100, 6093 (1978). M. H. Whangbo, R. Hoffmann and R. B. Woodward, Proc. Roy. Soc. (London), A366, 23 (1979).
10. K. Nayak and D. S. Marynick, Macromolecules, 23, 2237 (1990). S. Y. Hong and D. S. Marynick, Macromolecules, 25, 4652 (1992).