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Synthesis and Photochemistry of Sulfonium Ion Polymers. Arylated and Alkylated Poly(*p*-phenylene sulfide) Derivatives

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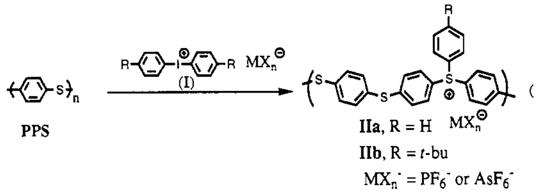
Triarylsulfonium salts have been used extensively as photoactive cationic initiators[1] and for the photogeneration of protic acids (chemical amplification) in the lithographic resist field.[2] For these and other applications, we were interested in determining whether we could synthesize new polymeric sulfonium ion materials that would maintain their photophysical properties.[3] Toward this end, we found that poly(phenylene sulfide) (PPS) can be directly arylated at the sulfur centers by allowing the preformed polymer to react with excess diaryliodonium salts[4] (eq 1).

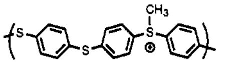


(1)

The reaction is best accomplished in a homogeneous manner by slowly adding diaryliodonium salts, $(C_6H_5)_2I^+X^-$ [where X = PF_6^- (**Ia**) and AsF_6^- (**Ib**)], to a chloronaphthalene solution of PPS at ≈220 °C. The elevated temperature is necessary only to solubilize the PPS. Compound **I** decomposes nearly instantaneously at these temperatures, and high concentrations of PPS must be present in solution in order to trap the putative phenyl cation intermediate before side reactions occur. In contrast with PPS (soluble only at temperatures above *ca.* 220 °C), arylated PPS, **II**, with substitution levels above *ca.* 30% is freely soluble in solvents such as acetone and DMSO at room temperature. Using excess arylating agent, **I**, the maximum degree of arylation obtainable on PPS was found to be approximately 42% (i.e., substitution at nearly every other sulfur center). Under identical reaction conditions, quantitative arylation of the model compound, diphenyl sulfide, is obtained.

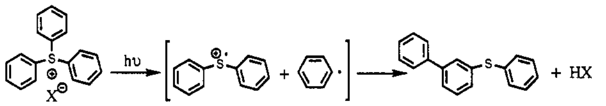
Characterization and structural assignments of these new charged polymers were based on solubility, molecular-weight analysis, ^{1}H, ^{2}H, and ^{13}C NMR spectroscopy, UV/vis spectroscopy, SIMS-EDS, and elemental analysis. The resonances for the aromatic protons in the ^{1}H NMR spectrum of cationic **IIa** ($MX_n^- = PF_6^-$) show an expected downfield shift of 0.6 ppm from 7.2 to 7.8 ppm. The ^{13}C NMR resonances of the sulfur-bound carbons in **II** are shifted upfield from *ca.* 146 to 125 ppm. This same upfield shift is observed in the triarylsulfonium model salts ($[(C_6H_5)_3S]^+PF_6^-$) as well.[5] Isotopic labeling studies clearly demonstrate that arylation of PPS occurs under the reaction conditions. The deuterium NMR spectrum of the material (**IIa**-d_5) obtained by allowing PPS to react with the perdeutero salt, diphenyliodonium-d_{10} hexafluorophosphate (**Ia**-d_{10}), shows a single broad resonance at 7.84 ppm, a result which is also consistent with arylation of the sulfur centers of PPS. In relation to $[S(C_6H_5)_3]^+PF_6^-$ (λ_{max} = 274 nm), the UV/vis spectrum of **IIa** is red shifted to λ_{max} = 320 nm. This is in good agreement with the value (λ_{max} = 316 nm) reported for the model compound $[(C_6H_5)_2S(C_6H_4)S(C_6H_4)S(C_6H_5)_2]^{2+}2PF_6^-$.[6] Elemental analysis values for a typical sample of highly substituted **II** converge on a substitution value of 41.7%.[7] A substitution level of 41.7% was also calculated using the P/S ratio obtained from SEM-EDS.

Although many electrophiles such as CH_3I and $C_6H_5CH_2Br$ failed to react with PPS, we found that PPS could be methylated (**III**) by allowing PPS to react with excess methyl triflate in a sealed bomb at elevated temperatures.[8]


III

The maximum substitution level was again determined to be slightly above 40%, leading us to conclude that the reactivities of neighboring sulfurs are determined by electronic rather than steric considerations (i.e., introducing a positive charge through substitution on one sulfur reduces the electron densities on the two neighboring 1,4-para sulfurs and, hence, attenuates their nucleophilicity). Modeling this as a random substitution process using statistical simulations with the imposed constraint of not allowing substitutions to occur on adjacent sulfurs predicts a maximum substitution level of *ca.* 43% which is in good agreement with our experimentally determined values.

Based on the photochemistry of triarylsulfonium salts (eq 2),[1,9] the photolysis of **II** is predicted to result in the


(2)

homolytic cleavage[10] of one of the three inequivalent phenyl–sulfur bonds to produce, as intermediates, a diphenylsulfinyl radical cation embedded in the polymer backbone and a phenyl radical, as either the free phenyl radical (path "a", Scheme 1) or a phenyl radical chain end (path "b", Scheme 1). In the absence of added aryl radical traps (i.e., in the solid state), either of these two aryl radicals would be expected to rapidly undergo irreversible aromatic substitution reactions along the polymer backbone.[11] Phenyl radicals from pathway a fragmentation should react to form phenyl-substituted PPS derivatives, while the radicals produced via pathway b should yield branched and/or cross-linked materials. Consistent with these predictions, when thin, dry films of **IIa** ($M_w \approx$ 12 000) free of all H-atom sources are photolyzed in the solid state (medium-pressure Hg vapor lamp), varying amounts of two products, an insoluble, cross-linked component and a chloroform-soluble component, **IV** ($M_w \approx$ 37 900),[12] are obtained. The ^{1}H NMR aromatic resonances of cationic **IIa** appearing at 7.8 ppm are shifted back upfield to 7.18 ppm in polymer **IV**. Likewise, polymer **IV**-d_5 obtained from the photolysis of **IIa**-d_5, possessing a perdeuterophenyl substituent, shows a shift of the ^{2}H NMR resonance from 7.84 to 7.40 ppm, clearly indicating that the deuterated phenyl substituents are still present but are now found in a neutral, rather than a charged environment. Furthermore, polymer **IV** (resulting from the photolysis

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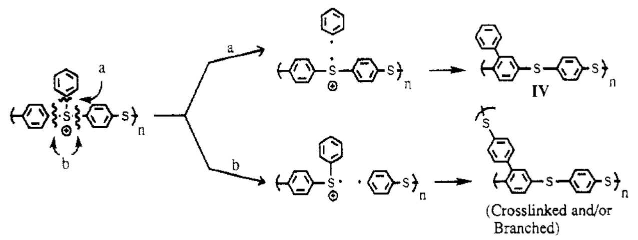
Scheme 1



of the PF_6^- salt of **IIa**) shows no ^{31}P NMR resonances and was found to be nonmobile in gel electrophoresis experiments. The properties of polymer **IV** are consistent with its assignment as a neutral, branched, phenylated PPS derivative resulting from substitution of the phenyl radicals along the aromatic backbone (i.e., pathway a, Scheme 1). The increase in molecular weight (due to branching) and the formation of insoluble (cross-linked) materials indicate that chain scission (pathway b, Scheme 1) is also occurring to some extent. Direct evidence for the intermediacy of the sulfinyl radical cation in the photochemical reaction can be obtained using EPR. The EPR spectrum of photolyzed **IIa** (solid-state photolysis) shows a resonance signal at a g-value of 2.0064 which is in agreement with the value obtained for the sulfur-centered, radical cation formed upon oxidizing PPS with AsF_5.[13]

Trapping the phenyl radicals by the addition of H-atom donors before they can undergo aromatic substitution reactions should yield benzene from pathway a and low molecular weight oligomers from pathway b. When **IIa** is photolyzed in an acetone solution (a good H-atom source for aryl radicals), no insoluble, cross-linked material is obtained, and the molecular weight of **IV** drops from its solid state value of 37 900 to 1300, indicating that a chain-scission process has occurred. Furthermore, the presence of a peak corresponding to C_6D_5H ($m/z = 83$) in the GC/MS spectrum of the volatiles produced from the photolysis of **IIa**-d_5 in the solid state signals that path a cleavage is occurring as well. In summary, our evidence indicates that both fragmentation pathways are operative and that, as predicted, chain cleavage to low molecular weight materials can be turned either on or off by the presence (or absence) of H-atom donors that trap aryl radicals formed by main-chain scission before they can recombine or undergo phenyl substitution reactions. Photolyzed in the presence of radical traps, polymer **IV** has the potential of acting as a duo-role (positive and/or negative) photoresist by exploiting a photochemically induced solubility change in **II** [i.e., from a polar, ionic material (soluble in acetone, DMSO, etc.) to a nonpolar, neutral material (soluble in chloroform, toluene, etc.)].

The parent polymer, PPS, is a high-performance material which has already shown promise as a versatile, low dielectric material in the electronics industry.[14] The photophysical properties of arylated or alkylated PPS suggest the possibility of expanding the repertoire of aryl sulfide polymers from their traditionally passive functions to new, active roles as photoresists or other electronic components.[15] Current efforts are directed at exploring the potential of these materials in lithographic and other applications.

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References and Notes

(1) (a) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307. (b) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2677.

(2) Miller, R. D.; Renaldo, A. F.; Ito, H. *J. Org. Chem.* **1988**, *53*, 5571.

(3) At least one polyimide containing sulfonium linkages has been reported. See: Crivello, J. V.; Lee, J. L.; Donlon, D. A. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 3293.

(4) Wildi, B. S.; Taylor, S. W.; Potratz, H. A. *J. Am. Chem. Soc.* **1951**, *73*, 1965.

(5) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2677.

(6) Watt, W. R.; Hoffman, H. T.; Pobiner, H.; Schkolnick, L. J.; Yang, L. S. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1789.

(7) Anal. Calcd for $C_{8.50}H_{6.09}SP_{0.417}F_{2.50}$: C, 50.87; H, 3.03; P, 6.44. Found: C, 50.36; H, 2.97; P, 5.98.

(8) A particularly elegant synthesis of polymer **III** was recently reported; see: Yamamoto, K.; Shouji, E.; Nishide, H.; Tsuchida, E. *J. Am. Chem. Soc.* **1993**, *115*, 5819.

(9) (a) Davidson, R. S.; Goodin, J. W. *Eur. Polym. J.* **1982**, *18*, 589. (b) Knapczyk, J. W.; McEwen, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 145. (c) Knapczyk, J. W.; McEwen, W. E. *J. Org. Chem.* **1970**, *35*, 2539. (d) Knapczyk, J. W.; Lubinkowski, J. J.; McEwen, W. E. *Tetrahedron Lett.* **1971**, 3739. (e) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977. (f) Pappas, S. P.; Pappas, B. C.; Gatechair, L. R.; Jilek, J. H.; Schnabel, W. *Polym. Photochem.* **1984**, *5*, 1. (g) McKean, D. R.; Schaedeli, U.; Kasai, P. H.; MacDonald, S. A. *Proc. Am. Chem. Soc., Polym. Mater. Sci. Eng.* **1989**, *61*, 81.

(10) A series of detailed mechanistic studies relating the cleavage pathway to spin states has recently been published. See: (a) Walsh, K. M.; Dektar, J. L.; Garcia-Garibaya, M. A.; Hacker, N. P.; Turro, N. J. *J. Org. Chem.* **1992**, *57*, 4179. (b) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1991**, *56*, 1838. (c) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639.

(11) The mechanism discussed herein is simplified. Aromatic substitution reactions are two-step processes involving radical attack on the aromatic ring followed by H-atom extraction. This latter step requires interaction with some other radical or oxidizing agent (i.e., another phenyl radical or O_2 for films photolyzed in air). For a general review, see: Perkins, M. J. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 231.

(12) Molecular weights were determined using gel permeation chromatography in $CHCl_3$ on a Waters Model 150C, equipped with four Ultrastyragel columns (5×10^2, 10^3, 10^4, 10^5 Å), and are reported relative to polystyrene standards.

(13) Kispert, L. D.; Files, L. A.; Frommer, J. E.; Shacklette, L. W.; Chance, R. R. *J. Chem. Phys.* **1983**, *78*, 4858.

(14) Endean, M. H. *Third International Conference on Plastics in Telecommunications*; Plastics Institute: London, 1983; Chapters 3 and 4.

(15) (a) Novak, B. M.; Hagen, E.; Viswanathan, A.; Magde, L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 482. (b) Rabolt, J. F.; Clarke, T. C.; Kanazawa, K. K.; Reynolds, J. R.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1980**, 347. (c) Chance, R. R.; Shacklette, L. W.; Miller, G. G.; Ivory, D. M.; Sowa, J. M.; Elsenbaumer, R. L.; Baughman, R. H. *J. Chem. Soc., Chem. Commun.* **1980**, 348.