Organometallic Polymers Based on S–S and Se–Se Linked *n*-Butylferrocenes

David L. Compton, Paul F. Brandt,[†] Thomas B. Rauchfuss,*
Darren F. Rosenbaum, and Charles F. Zukoski

*School of Chemical Sciences, the Materials Research Laboratory, and the Beckman Institute,
University of Illinois, Urbana, Illinois 61801*

Polyferrocenylene persulfides, $[(BuC_5H_3)(C_5H_4)FeS_2]_n$, have been prepared by desulfurization of butyltrithiaferrocenophane $(BuC_5H_3)(C_5H_4)FeS_3$. The molecular precursor was prepared by dilithiation of butylferrocene followed by treatment with elemental sulfur and isolated as a 7:1 mixture of the 1,3,1′ and 1,2,1′ isomers. The trisulfide was converted to polymer by treatment with the desulfurization agent PBu_3. The rate of this desulfurization and the nature of the polymer depends critically on the reaction solvent. Desulfurization in DMF and THF afforded insoluble but swellable rubbers. Desulfurization of $BufcS_3$ in mixed CH_2Cl_2–THF solutions gave soluble polymers with M_n ranging from 12 000 to 359 000, with lower molecular weight products being favored at high $[CH_2Cl_2]$. The effect of high $[CH_2Cl_2]$ was modeled by the reaction of $[fcS_2]_n$ with a CH_2Cl_2 solution of PBu_3 to give fcS_2CH_2. Molecular weights for $[BufcS_2]_n$ were confirmed by light scattering measurements. Soluble $[BufcS_2]_n$ undergoes reversible electrochemical oxidation in two steps, centered at 780 V (vs Ag/AgCl) and separated by ~300 mV. The first oxidation potential is similar to that for the trisulfide monomer and is thought to correspond to oxidation of alternating Fe centers, followed by conversion of the remaining Fe^{II} sites. The polymers photodegrade upon exposure to UV light in air. Deselenization of $BufcSe_3$ gave red soluble $[BufcSe_2]_n$ with only moderate molecular weights and with high polydispersities. The microstructure of this polymer was established by ^{77}Se NMR studies which support the presence of head-to-head, head-to-tail, and tail-to-tail dyads.

Introduction

Organometallic compounds represent a rich source of structurally and electronically diverse precursors to materials.[1] In the area of organometallic polymers, ferrocenes have played a central role.[2] The ferrocene entity is thermally robust, electroactive, and readily substituted.[3] The study of ferrocene and related metallocene-based polymers has however long been hampered by poor solubilities and low degrees of polymerization. This theme has been reinvigorated with the discovery of new approaches to the polymerization of metallocenes which rely on heteroatom linkages via novel polymerization processes including desulfurization-induced ring-opening polymerization,[4,5] radical-induced additions of ferrocenedithiols,[6] and ring-opening

polymerization of strained ferrocenophanes.[7,8] An additional advantage to this new generation of polymetallocenes is that the metal is situated in the polymer chain, not pendant to it. In this way the redox state of the metal more strongly affects the polymer properties and intermetallic electronic coupling is enhanced.

In our first report in this area we described that desulfurization of butylferrocene trisulfide affords poly-

† Current address: Department of Chemistry and Physics, Western Carolina University, Cullowhee, NC, 28723.
⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1995.
(1) *Polymer Science and Engineering: The Shifting Research Frontiers*; National Academy Press: Washington, 1994.
(2) Zeldin, M.; Wynne, K.; Allcock H. A. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; American Chemical Society: Washington, D.C., 1988. Mark, J. E.; Allcock, H. A.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992.
(3) Herberhold, M. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim: 1995.
(4) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992,** *114,* 1926. Galloway, C. P.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1319.
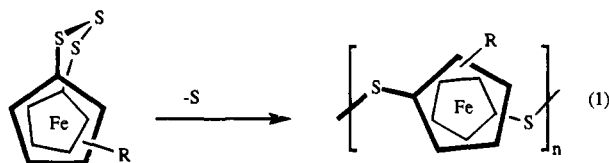(5) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994,** *13,* 4367.
(6) Nuyken, O.; Pöhlmann, Y.; Herberhold, M. *Macromol. Rep.* **1992,** *A29* (suppl 3), 211. Herberhold, M.; Brendel, H.-D.; Nuyken, O.; Pöhlmann, T. *J. Organomet. Chem.* **1991,** *413,* 65.

(7) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992,** *114,* 6246. Foucher, D. A.; Manners, I. *Makromol. Chem. Rapid Commun.* **1993,** *14,* 63. Foucher, D. A.; Ziembinski, R.; Tang, B.-Z.; MacDonald, P. M.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1993,** *26,* 2878. Tang, B.-Z.; Petersen, R.; Foucher, D. A.; Lough, A.; Coombs, N.; Sodhi, R.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1993,** 523. Finckh, W.; Tang, B.-Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993,** *12,* 823. Foucher, D. A.; Nelson, J. M.; Honeyman, C. H.; Tang, B.-Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1709. Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993,** *115,* 7035. Angelakos, C.; Zamble, D. B.; Foucher, D. A.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1994,** *33,* 1709. Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994,** *116,* 797. Nelson, J. M.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 989. Nelson, J. M.; Lough, A. J.; Manners, I. *Organometallics* **1994,** *13,* 3703. Foucher, D. A.; Edwards, M.; Burrow, R. A.; Lough, A. J.; Manners, I. *Organometallics* **1994,** *13,* 4959. Lough, A. J.; Manners, I.; Rulkens, R. *Acta Crystallogr. C* **1994,** 1667. Zeichel, D. L.; Rulkens, R.; Ni, Y. Z.; Manners, I. *J. Am. Chem. Soc.* **1994,** *116,* 12121. Zeichel, D. L.; Foucher, D. A.; Pudelski, J. K.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1995,** 1893. Rashburn, J.; Petersen, R.; Jahr, T.; Rulkens, R.; Manners, I. *Chem. Mater.* **1995,** *7,* 871. Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Barlow, S.; O'Hare, D. *Organometallics* **1995,** *14,* 2470. Fossum, E.; Matyjaszewski, K.; Rulkens, R.; Manners, I. *Macromolecules* **1995,** *28,* 401. Pudelski, J. K.; Manners, I. *J. Am. Chem. Soc.* **1995,** *117,* 7265.
(8) Dement'ev, V. V.; Cervantes-Lee, F.; Parkanyi, L.; Sharma, H.; Pannell, K. H. *Organometallics* **1993,** *12,* 1983. Nguyen, M. T.; Diaz, A. F.; Dement'ev, V.; Pannell, K. H. *Chem. Mater.* **1993,** *5,* 1389.

mers of the formula $[Fe(BuC_5H_3S)(C_5H_4S)]_n$, henceforth referred to as butyl ferrocenylene persulfide or $[BufcS_2]_n$.[4] This polymer consists of metallocene units interconnected by persulfide (S—S) linkages (eq 1). The orga-

nometallic chemistry of the monomer and some oligomeric derivatives have recently been described by us for the *tert*-butyl-substituted ferrocenes, which are stereochemically simpler than the *n*-butyl derivatives.[8] We have completed studies on the polymerization conditions and the properties of the *n*-Bu polymers which are of higher molecular weights than analogous compounds with *tert*-butylcyclopentadienyl ligands. Parallel studies have led to rare examples of perselenide polymers.

There has been recent interest in persulfide polymers based on S—S linkage for use in lithium batteries wherein the discharge involves the reduction of persulfide bonds by Li.[9] The cathodes in a recently reported device featured the oxidized derivatives of dimercaptothiadazole (eq 2).[10]
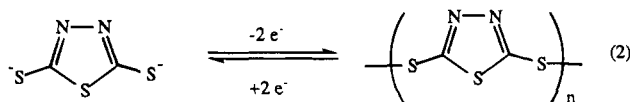
Results

Butylferrocene Trisulfide. The species $BufcS_3$ was obtained in 65% yield by sequential dilithiation and sulfurization of $(BuC_5H_4)Fe(C_5H_5)$.[11] ^1H NMR studies of this red oily $BufcS_3$ indicated a ~1:7 mixture of 1,2,1′ and 1,3,1′ isomers, the ratio reflecting the regiochemistry of the lithiation (Figure 1). The ^1H NMR spectra are complicated by the fact that each of these regioisomers exists as a pair of slowly interconverting conformers which differ based on the relative orientation of the trisulfide strap (Scheme 1). We were able to enrich samples of $BufcS_3$ in the more abundant and more polar 1,3,1′-isomer by chromatography on silica gel. In its ^1H NMR spectrum, the 1,3,1′ isomer gives rise to 12 multiplets in the region 3.5—4.4 ppm. The observation of 12 and not the expected 14 resonances (there are seven diastereotopic cyclopentadienyl protons in each conformer) can be explained by the fact that two multiplets (4.19 and 3.53 ppm) integrate for two protons each. The integrated spectra also establish that the conformers exist in a ~1:1 ratio. This indicates that there is little interaction between the Bu group and the trisulfide strap. Samples of $BufcS_3$ which appear pure by ^1H NMR were sometimes found to contain an

(9) Liu, M.; Visco, S. J.; De Jonghe, L. C. *J. Electrochem. Soc.* **1991**, *138*, 1891. Liu, M.; Visco, S. J.; De Jonghe, L. C. *J. Electrochem. Soc.* **1991**, *138*, 1896. Visco, S. J.; Mailhe, C. C.; De Jonghe, L. C.; Armand, M. B. *J. Electrochem. Soc.* **1989**, *136*, 661. Yang, X. Q.; Xue, K. H.; Lee, H. S.; Guo, Y. H.; McBreen, J.; Skotheim, T. A.; Okamoto, Y.; Lu, F. *J. Electrochem. Soc.* **1993**, *140*, 943.

(10) Oyama, N.; Tatsuma, T.; Sato, T.; Sotomura, T. *Nature* **1995**, *373*, 598.

(11) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241. Davison, A.; Smart, J. C. *J. Organomet. Chem.* **1979**, *174*, 321.
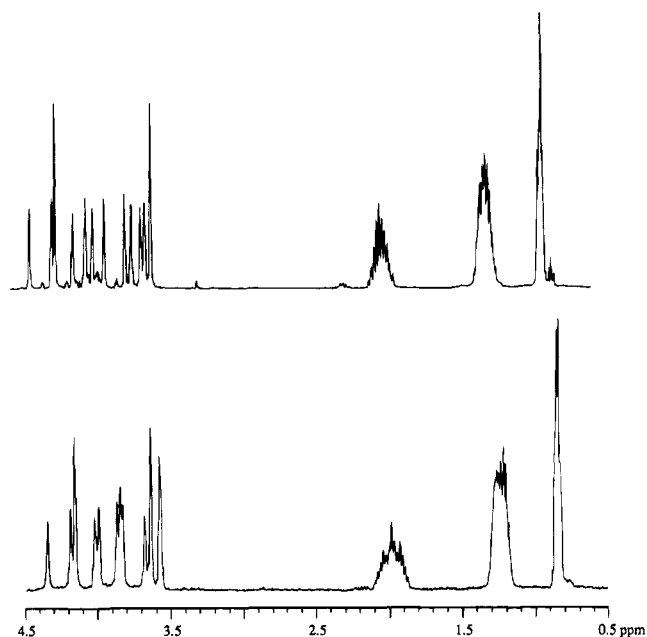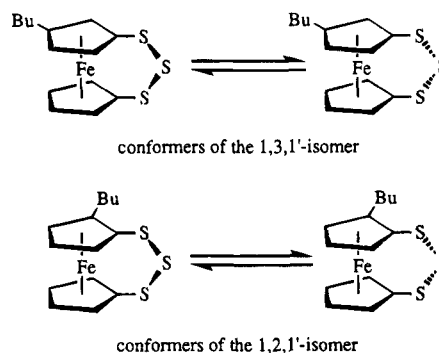
Figure 1. 300 MHz ^1H NMR spectra of C_6D_6 solutions of $(BuC_5H_3)Fe(C_5H_4)E_3$, where E = S (top), Se (bottom) showing the relative regiochemical purity of the triselenide. Recall that for each regioisomer, there are two conformers.

Scheme 1

conformers of the 1,3,1′-isomer

conformers of the 1,2,1′-isomer

impurity of elemental sulfur. The desulfurization-induced polymerization (see below) is very sensitive to this impurity, which we removed by chromatography on a crosslinked polystyrene.

Butylferrocene Triselenide. Dilithiation of butylferrocene followed by treatment with gray selenium afforded the corresponding triselenide $BufcSe_3$, isolated as a deep red liquid. This compound consists of almost pure 1,3,1′-isomer as indicated by its ^1H NMR spectrum (Figure 1). In contrast, $BufcS_3$ is isolated as a 7:1 mixture of the 1,3,1′ and 1,2,1′ isomers.

The parent $fcSe_3$ serves as a useful reference compound[12] in the ^{77}Se NMR analysis of $BufcSe_3$. This spectrum features two signals of ~2:1 intensity ratio at 303 and 922 ppm, which are assigned as C_5H_4Se and Se—Se—Se, respectively. The ^{77}Se NMR spectrum of $BufcSe_3$ showed the expected six resonances (Figure 2). Signals at 928 and 938 ppm are assigned to the central Se atoms for the two conformers while the four peaks

(12) Osborne, A. G.; Hollands, R. E.; Howard, J. A. K.; Bryan, R. F. *J. Organomet. Chem.* **1981**, *205*, 395. Wrackmeyer, B.; Biersack, M.; Brendel, H.-D.; Herberhold, M. *Inorg. Chim. Acta* **1992**, *47b*, 1397. Akabori, S.; Kumagai, T.; Sato, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2026. Blake, A. J.; Gould, R. O.; Osborne, A. G. *J. Organomet. Chem.* **1986**, *308*, 297.
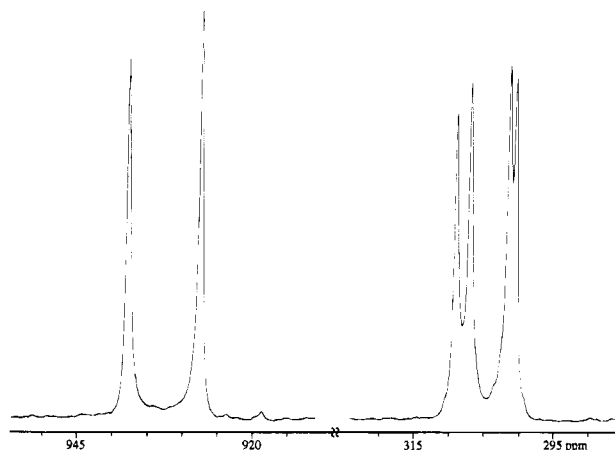
2344 *Chem. Mater., Vol. 7, No. 12, 1995*

Compton et al.

Figure 2. 57.29 MHz ^{77}Se NMR spectrum of a C_6D_6 solution of BufcSe$_3$.

Table 1. Polymerization Conditions and Associated Data for [BufcS$_2$]$_n$, [BufcSe$_2$]$_n$, and [BufcS$_{2-x}$Se$_x$]$_n$

polymer	solvent	$M_w{}^a$	$M_n{}^a$	M_w/M_n	rxn time
[BufcS$_2$]$_n$	THF^b				5 min
[BufcS$_2$]$_n$	50% CH$_2$Cl$_2$ in THF	143 500^c	99 500	1.4	24 h
[BufcS$_2$]$_n$	1.5% CH$_2$Cl$_2$ in THF	143 500^c	350 500	1.1	24 h
[BufcS$_2$]$_n$	CH$_2$Cl$_2$	40 000^d	12 000	3.3	24 h
[BufcSe$_2$]$_n$	THF	15 300	4 700	3.3	24 h
[BufcS$_{2-x}$Se$_x$]$_n$	THF	8 200	3 300	2.5	24 h

^{a} Determined by SEC analysis in CH$_2$Cl$_2$ vs polystyrene standards. ^{b} Desulfurizations of BufcS$_3$ in THF (0–0.5% CH$_2$Cl$_2$) produce insoluble rubbers. ^{c} M_w = 232 000 determined by light scattering on toluene solutions. ^{d} M_w = 32 000 determined by light scattering.

in the 300–310 ppm region are assigned to the Se positions attached to the cyclopentadienyl rings. These four signals occur in pairs, the pairs being separated by 6.5 ppm. On the basis of the spectrum for fcSe$_3$, the farthest upfield pair of signals in the BufcSe$_3$ spectrum are assigned to the C$_5$H$_4$Se sites, while the signals centered at 310 ppm arise from BuC$_5$H$_3$Se sites. We prepared BufcSe$_2$S wherein the central Se is replaced by sulfur. In this case the splitting pattern in the high field signals remained almost unchanged although their chemical shifts occurred 78 ppm further downfield. No signals were located in the 900 ppm region.

Desulfurization of Butylferrocene Trisulfide. Solutions of BufcS$_3$ were converted to polymers by treatment with the desulfurization agent Bu$_3$P (see eq 1). We used a slight deficiency (0.95 equiv) of the phosphine since previous work[5] had shown that excess led to depressed molecular weights. The polymerizations are signaled by a deepening of the solution color to dark orange. ^{31}P NMR studies on related reactions have shown that this transformation is accompanied by the formation of SPBu$_3$.[5]

Treatment of THF and DMF solutions of BufcS$_3$ with PBu$_3$ resulted in the precipitation of dark orange rubbery solids, identified by microanalysis as [BufcS$_2$]$_n$. This material proved to be insoluble in all organic solvents. Upon thorough drying, the material hardened; the resulting brittle product swelled upon exposure to THF.

Desulfurization of Ferrocene Trisulfide in CH$_2$-Cl$_2$ Solutions. In contrast to the polymerizations using THF and DMF as solvents, desulfurization of CH$_2$Cl$_2$ solutions of BufcS$_3$ gave *soluble* products. Size exclusion chromatography (SEC) indicated that the purified samples had relatively low molecular weights (M_n ~12 000, see Table 1). Microanalysis and ^{1}H NMR spectra for these samples were consistent with the formulation as [BufcS$_2$]$_n$. The empirical formulas for the polymers prepared in CH$_2$Cl$_2$ proved to be the same as those from DMF or THF.

We examined the desulfurization of solutions of BufcS$_3$ in various mixtures of THF and CH$_2$Cl$_2$ with surprising results (Figure 3). Polymerizations conducted in THF containing 5–95% CH$_2$Cl$_2$ gave *soluble* polymers with M_n ~ 10^5 (Table 1). At [CH$_2$Cl$_2$] > 95% the molecular weights decreased. On the other hand, when [CH$_2$Cl$_2$] < 5% the molecular weights increased

almost 3-fold together with a narrowing of the polydispersity. At [CH$_2$Cl$_2$] = 0.5% we observed precipitation of the polymer (77% yield) just as seen for pure THF, the soluble fraction having M_n ~ 77 000.

Control experiments probed the influence of CH$_2$Cl$_2$ on the polymerization. THF solutions of the highest molecular weight polymer (M_n = 316 000) did not give a precipitate upon the seeding with some of the insoluble polymer obtained from pure THF. We also found that the insoluble polymer from pure THF did not dissolve in CH$_2$Cl$_2$, thus demonstrating that the chlorinated solvent must be present in the reaction medium.

The effect of high concentrations of CH$_2$Cl$_2$ on the polymerization process were modeled by studies on the insoluble polymer [fcS$_2$]$_n$. Suspensions of [fcS$_2$]$_n$ in CH$_2$-Cl$_2$ were found to dissolve upon addition of 2 equiv of Bu$_3$P. Chromatographic work up of the resulting orange solution gave the known[13] ferrocenophane fcS$_2$CH$_2$ in 21% yield (eq 3).
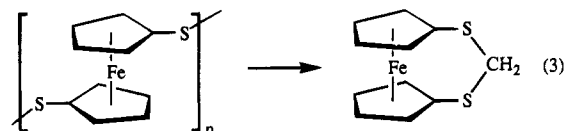
Physical Properties of the Polymers. The polymers were examined by dilute solution viscometry, although lacking monodisperse standards it was not possible to determine molecular weights by this method. The data follow the Huggins relationship[14] (Figure 4, eq 4):

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c^2 \qquad (4)$$

where $\eta_{sp} = (\eta_{sample} - \eta_{solvent})/\eta_{solvent}$. It is interesting that the intrinsic viscosity, $[\eta]$, for the polymer was 3-fold greater in THF (0.44 dL/g) than in dichloromethane (0.16 dL/g).

The polymers are air stable both in the solid state and in solution as confirmed by ^{1}H NMR and SEC measurements. THF solutions of [BufcS$_2$]$_n$ (M_n ~ 99 500) were stable to UV radiation in the absence of air. In air, however, UV irradiation caused substantial

(13) Broussier, R.; Abdulla, A.; Gautheron, J. *J. Organomet. Chem.* **1987**, *332*, 165. Abel, E. W.; Booth, M.; Brown, C. A.; Orrell, K. G.; Woodford, R. L. *J. Organomet. Chem.* **1981**, *214*, 93.

(14) Young, R. J.; Lovell, P. A. *Introduction to Polymers*; Chapman and Hall: London, 1981.
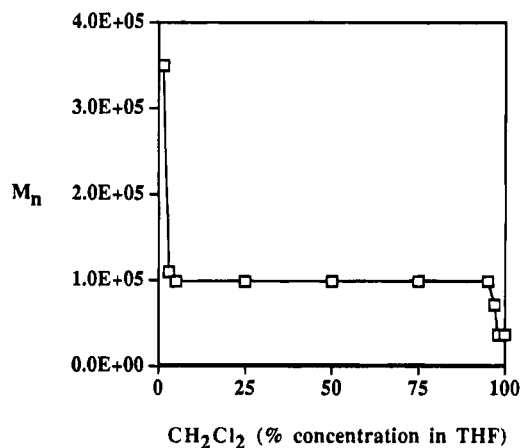
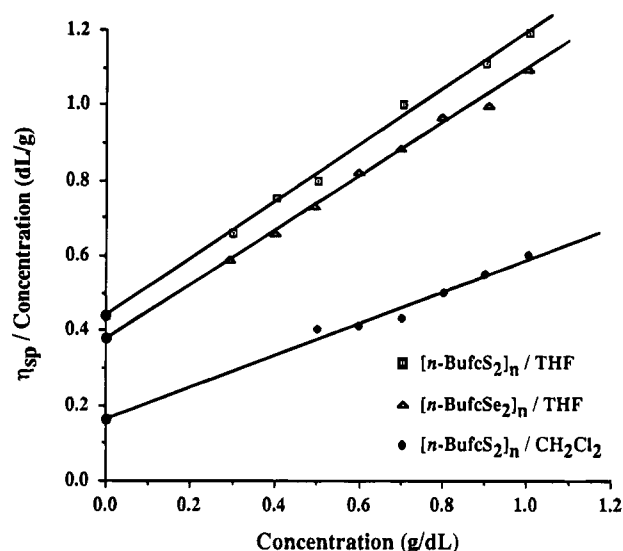**Figure 3.** Plot showing the dependence of polymer MW on % CH_2Cl_2 in THF.

Figure 4. Plot of specific viscosity, $[\eta]$, vs concentration (g/dL) at 30 °C in THF and CH_2Cl_2 solutions.

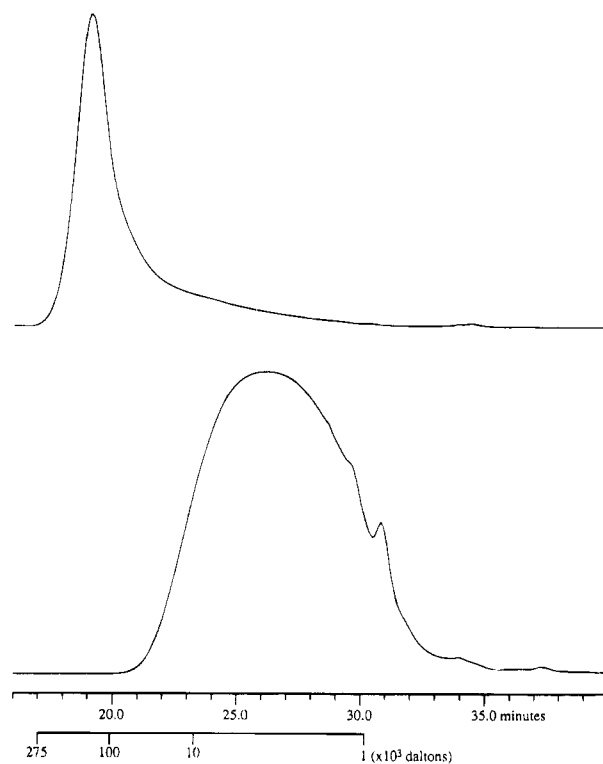**Figure 5.** GPC traces showing the effects of UV irradiation on THF solutions of $[BufcS_2]_n$. Top: a solution of $[BufcS_2]_n$ in THF. Bottom: same solution after 24 h irradiation in air.

degradation of the polymer to low molecular weight fragments (M_n = 2400, Figure 5). Solutions of the polymers in amber colored flasks were stable for extended periods under normal laboratory conditions.

Perselenide Polymers. Conversion of BufcSe₃ to polymers was effected in THF solution using PBu₃ to give a soluble, dark red solid which was purified by fractional precipitation. The resulting polymer was completely soluble in contrast to the situation for the persulfide prepared in THF. The perselenide polymer was of relatively low molecular weight and of high polydispersity (Table 1). The optical spectrum of $[BufcS_2]_n$ shows a shoulder and a peak at 330 and 442 nm, respectively, while the spectrum of $[BucSe_2]_n$ shows two lower energy absorptions at 372 and 454 nm (Figure 6). Copolymers of the type $[BufcS_2]_m[BufcSe_2]_n$ were briefly examined,[15] but the results were inconclusive and the products were of low molecular weight (Table 1). Using the perselenide polymers we showed that their intrinsic viscosities correlated with the relative molecular weights as determined by SEC measurements ($[BufcS_2]_n$: 0.44 dL/g, $[BufcSe_2]_n$: 0.37 dL/g, and $[BufcS_{2-x}Se_x]_n$: 0.33 dL/g).

---

(15) Compton, D. L. Ph.D. Thesis, University of Illinois at Urbana–Champaign, 1996.

⁷⁷Se NMR Studies on $[BufcSe_2]_n$. Above we discussed the ⁷⁷Se spectra of BufcSe₃ including the 6.7 ppm separation for the signals of BuC_5H_3Se vs C_5H_4Se. The ⁷⁷Se NMR spectrum of $[BufcSe_2]_n$ also consists of two multiplets separated by 6.7 ppm which we attribute to BuC_5H_3Se vs C_5H_4Se, as seen in the triselenide (Figure 2). The fine structure within the two multiplets is considered to reflect more subtle differences in the polymer microstructure. Our analysis is as follows:

(i) Three dyad structures must be considered at the outset: head-to-head, head-to-tail, and tail-to-tail. The head group is defined as BuC_5H_3Se (note that a simplifying feature of the selenides vs the sulfides is the absence of 1,2-BuC_5H_3E subunits).

(ii) Since we are dealing with *chiral* repeat units, the relative chirality of the subunits must be considered.

(iii) Diastereoisomers cannot be distinguished for the tail-to-tail dyads, apparently because in that case the butyl groups are most distant.

This analysis allows us to explain the multiplicity of the ⁷⁷Se NMR spectrum as seen in Figure 7. In the high-field region one signal is observed for the head-to-tail dyad and two signals are observed for the two diastereoisomeric head-to-head dyads. In the low-field region we expect to see one signal for the tail-to-tail dyad and one signal for the tail-to-head dyad. Further support for this model comes from a qualitative analysis of the spectral intensities. The head-to-tail dyad should give signals of equal intensity in both the low- and high-field positions. For the head-to-head dyad, one expects a low-field signal (for the tail-to-tail linkage) whose intensity is equal to the sum of the two other high-field signals.

Analysis by Light Scattering. The weight-averaged molecular weight, M_w, of $[BufcS_2]_n$ ($M_{w\text{-}SEC}$ = 1.4 × 10⁵) was evaluated in toluene by static light scatter-
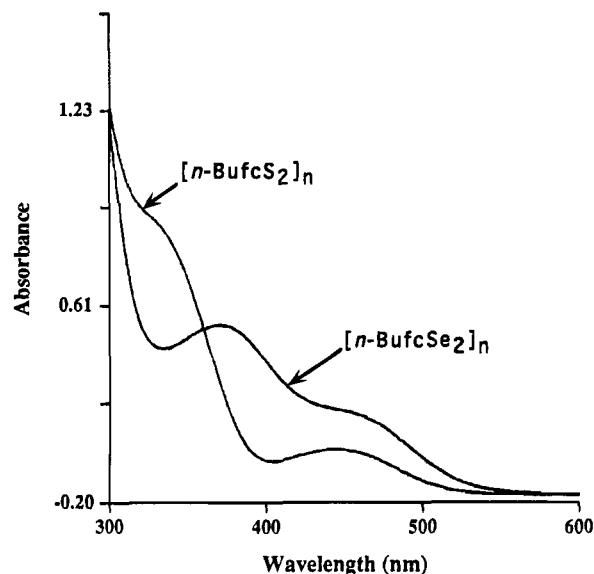
Figure 6. Optical spectra of THF solutions of [BufcS$_2$]$_n$ and [BufcSe$_2$]$_n$.
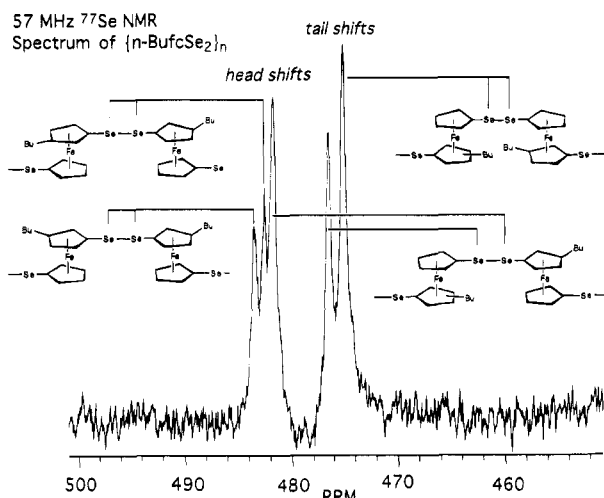

Figure 7. 57.29 MHz ^{77}Se NMR spectrum of a C$_6$D$_6$ solution of [BufcSe$_2$]$_n$.

ing. Differential refractometry provided a value of 0.1672 ± 0.0039 mL/g for dn/dc for this solute/solvent system. This parameter together with the angular dependence of the scattering power allowed determination of M$_w$ = (2.32 ± 0.1) × 10^5 g/mol as can be seen by the intersection (=M_w^{-1}) of the data extrapolated to Θ = 0 and concentration (c_2) = 0 in the plot of $Kc_2/\Delta R_\Theta$ vs sin^2 Θ/2 + concentration (Figure 8).

The light-scattering data also allow us to evaluate the radius of gyration which was found to be 20 nm. The second virial coefficient (A_2), revealed by dependence of the light scattering on concentration extrapolated to zero concentration was found to be 3.65 × 10^{-4} mol mL g^{-1}. This parameter provides a measure of the nonideality of the solution of [BufcS$_2$]$_n$ in toluene. The extent of the nonideality can be better appreciated by consideration of the concentration dependence of the osmotic pressure (Π, eq 5).[16] For our sample the magnitudes of

$$\Pi/RTc_2 = M^{-1} + A_2c_2 \qquad (5)$$

M_n^{-1} and A_2c_2 are 10^{-5} and ~10^{-7}, respectively.

We characterized M_w for samples of [BufcS$_2$]$_n$ prepared in neat CH$_2$Cl$_2$ ($M_{w\text{-SEC}}$ = 4 × 10^4); the results
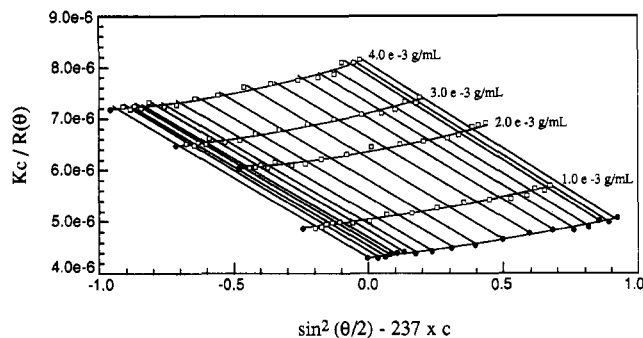

Figure 8. Zimm plot showing the angular and concentration dependence of light scattering at 632.8 nm and 298 K.

Table 2. Electrochemical Data for the BufcE$_3$ and [BufcE$_2$]$_n$ (E = S, Se)

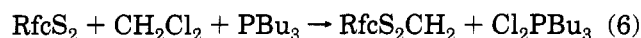| sample	$E_{1/2}{}^{1a}$	$E_{1/2}{}^{2a}$	ΔE^a
BufcS$_3{}^b$	771		
BufcSe$_3{}^b$	645		
[BufcS$_2$]$_n$	643	946	303
[BufcSe$_2$]$_n$	614	901	287

[a] See Experimental Section for details; all potentials are reported in millivolts. [b] The trichalcogen compounds undergo only one oxidation, so the other entries are not applicable.

confirm the SEC-derived values (Table 1). As expected, there was little angular dependence in the scattering intensity for this smaller polymer.

Electrochemistry. Samples of [BufcS$_2$]$_n$ prepared in CH$_2$Cl$_2$-containing solvents were studied by cyclic voltammetry (Table 2). Pt, Au, and glassy carbon working electrodes gave similar cyclic voltammograms, although the glassy carbon gave better peak resolution perhaps because the sulfur compounds adsorb onto the Au and Pt surfaces. The results are comparable to those seen for the lower molecular weight [(t-Bu)$_{1or2}$fcS$_2$]$_n$ polymers.[8] The cyclic voltammogram for [BufcS$_2$]$_n$ feature a pair of equally intense oxidations at $E_{1/2}$ = ~640 and ~950 mV. The first event is similar to that in the parent BufcS$_3$ ($E_{1/2}$ = 771 mV). For [BufcSe$_2$]$_n$ we again observed two redox events with $E_{1/2}$ = ~615 and ~900 mV (ΔE = 285 mV). The first event is similar to that in the parent BufcSe$_3$ ($E_{1/2}$ = 645 mV).

Conclusions

The desulfurization of ferrocene trisulfides affords organometallic polymers. Unsubstituted ferrocene trisulfides give insoluble solids,[4] *tert*-butyl-substituted ferrocene trisulfides give low molecular weight polymers,[5] and, as shown in the present paper, n-butylferrocene trisulfides gives high molecular weight soluble polymers. Polymerizations in THF and DMF produced insoluble but swellable persulfido rubbers which we assume to be of high molecular weight. Polymerizations in neat dichloromethane gave lower molecular weight products reflecting the reactivity of the polymer toward PBu$_3$ and CH$_2$Cl$_2$. The hypothesis that this process involves S-alkylation was tested through the reaction of [Fe(C$_5$H$_4$S)$_2$]$_n$ with CH$_2$Cl$_2$ solutions of PBu$_3$ to give Fe(C$_5$H$_4$S)$_2$CH$_2$. This is a new reaction of S—S bonds, and we propose that it follows the stoichiometry in eq 6. A remarkable finding was the nonlinear dependence

$$\text{RfcS}_2 + \text{CH}_2\text{Cl}_2 + \text{PBu}_3 \rightarrow \text{RfcS}_2\text{CH}_2 + \text{Cl}_2\text{PBu}_3 \quad (6)$$

Organometallic Polymers

Chem. Mater., Vol. 7, No. 12, 1995 2347

of polymer MW on the concentration of CH_2Cl_2 in THF (Figure 4). At moderate to low [CH_2Cl_2] in THF the polymers have M_n ranging from 10^5 to 3×10^5. The nonlinear dependence of MW on [CH_2Cl_2] indicates that the CH_2Cl_2 has at least two effects, one leading to low molecular weights, which we have modeled, and the other, operative at low [CH_2Cl_2], permitting the formation of high MW *soluble* polymers.[15]

The ferrocene persulfide polymers distinguish themselves by the multiple pathways by which they can be degraded. As discussed in a prior report,[4] the polymers are cleaved by the action of reducing agents such as $LiBHEt_3$ resulting ultimately in the formation of $BufcS_2$-Li_2. The nucleophile PBu_3 also converts the polymers into lower molecular weight fragments.[5] This report discloses the photosensitized oxidation of the polymer. This process could be of interest as a means of photodemasking films of [$BufcS_2$]$_n$. There is surprisingly little literature on the photooxidation of organic disulfides, although it is known that thioethers are cleaved by singlet oxygen.[17]

We have extended this study to Se analogues beginning with the synthesis of $BufcSe_3$ which was isolated almost exclusively at the 1,3,1' isomer. Since the selenium obviously cannot influence the regiochemistry of the lithiation step, we assume that the regioselectivity arises because 1,2,1'-$BufcSe_3$ is either unstable[18] or 1,2,1'-$BufcLi_2$ is less reactive toward Se. The triselenide was readily deselenized to give a low molecular weight perselenide polymers. A few polymers are known with Se–Se bonds, e.g., gray selenium itself and [Se_2S_5]$_n$,[19] but ours is a rare example of a *soluble* Se-rich polymer.[20] We cannot state unequivocally the reasons for the lower molecular weights for the perselenide polymers although we suggest that the longer interchalcogen bonds in the perselenides facilitate cyclization relative to chain extension. Our main interest however in the perselenide polymers arises from the insights their spectroscopy provides vis-à-vis the persulfides. The high chemical shift dispersion offered by ^{77}Se NMR spectroscopy reveals microstructural details that can be analyzed in a self consistent manner based on C–Se–Se–C linkages.

Experimental Section

General Methods. Schlenk techniques were employed throughout the preparation of the organometallic trichalcogen compounds and in all steps employing phosphines. Solvents were dried, degassed, and freshly distilled. Tetramethylethylenediamine (TMEDA) was distilled from Na, and Bu_3P was purified by vacuum distillation at 0.1 Torr and 110 °C. Fe-(BuC$_5$H$_4$)(C$_5$H$_5$) was purchased from Aldrich.

SEC traces were recorded using a Waters 501 pump and 486 detector using HP PL-gel Mixed-D (10^4 Å), Waters μ-Styragel (10^3 Å), and Jordi-gel (10^2 Å) columns in tandem

eluting at 1.0 mL/min with a detector wavelength of 300 nm. M_w and M_n were calculated using Millenium 2010 Chromatography Manager 1.10 software. The columns were calibrated with 10 polystyrene standards (TSK) whose M_w range from 500 to 355 000 (M_w/M_n ranging from 1.01 to 1.14).

Cyclic voltammograms were recorded on 0.5 mM solutions of sample with 0.1 M Bu_4NPF_6 in CH_2Cl_2 vs Ag/AgCl. IR spectra, recorded on KBr disks for solids and as neat samples for liquids, were measured using on a Galaxy Series FT-IR 3000. The peak listings for the Raman and IR spectra are for medium-intensity absorptions unless they are indicated as st for strong.

^{1}H and ^{77}Se NMR spectra were recorded on Varian U-400 and GE 300 NB spectrometers, respectively. The following abbreviations are employed in describing the spectra: s for singlet, d for doublet, t for triplet, m for multiplet, and b for broad. UV–vis spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer. Elemental analyses were performed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory.

BufcS$_3$. A solution of 5.15 g of Fe(BuC$_5$H$_4$)(C$_5$H$_5$) (21.3 mmol) in 150 mL of hexanes was treated with 26.6 mL of a 1.6 M solution of BuLi (42.6 mmol) followed by 6.45 mL of TMEDA (42.6 mmol). After 24 h of stirring, 6.8 g of S$_8$ (213 mmol) was added to the dark red solution in five portions, and the red slurry was refluxed for 24 h. The dark red-brown slurry was filtered in air through a bed of Celite. The Celite was extracted with three 100 mL portions of Et$_2$O. The orange filtrate was washed with five 80 mL portions of 10% aqueous NaOH. The aqueous layer was separated and washed with two 80 mL portions of Et$_2$O. The combined organic layers were dried over Na$_2$SO$_4$, and the solvent was removed to give a red oil. The first, yellow band was unreacted ferrocene and the second, orange band was the trisulfide. Excess S$_8$ was removed from the BufcS$_3$ by chromatography of a concentrated THF solution through a 30 × 3 cm column of Bio-Beads SX-8, eluting with THF. Only the first three-quarters of the broad orange band was collected. Evaporation of this fraction afforded a red oil. Yield: 4.7 g (65%). Anal. Calcd for C$_{14}$H$_{16}$-FeS$_3$: C, 50.00; H, 4.80; S, 28.60; Fe, 16.61. Found: C, 49.88; H, 4.83; S, 28.75; Fe, 16.57. ^{1}H NMR (C$_6$D$_6$) δ 4.36 (m, 1H), 4.21 (m, 1H), 4.19 (m, 2H), 4.06 (m, 1H), 3.97 (m, 1H), 3.92 (m, 1H), 3.85 (m, 1H), 3.71 (m, 1H), 3.66 (m, 1H), 3.60 (m, 1H), 3.57 (m, 1H), 3.53 (m, 2H), 1.96 (m, 4H), 1.23 (m, 8H), 0.86 (m, 6H). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 93.8 (1C), 91.3 (1C), 90.8 (1C), 90.3 (1C), 90.1 (1C), 90.0 (1C), 79.8 (1C), 79.9 (1C), 78.6 (2C), 75.6 (1C), 72.8 (1C), 72.2 (1C), 71.9 (1C), 69.8 (1C), 69.6 (1C), 69.8 (1C), 68.2 (1C), 68.0 (1C), 67.7 (1C), 33.4 (1C), 29.2 (1C), 28.8 (1C), 22.9 (1C), 14.4 (1C). IR (neat): 3056, 2955 (st), 2928 (st), 2467, 2856, 1466, 1441, 1346, 1378, 1263, 1160, 1033, 1023, 902, 820 (st), 735 (st), 509, 503, 492 (st), 474 cm^{-1}. Raman (neat) 610, 450 (st), 370 (st) cm^{-1}. UV–vis (CH$_2$Cl$_2$) 378 nm. EI MS (70 eV) 336 (M$^+$).

BufcSe$_3$. A solution of 5.0 g of Fe(BuC$_5$H$_4$)(C$_5$H$_5$) (20.6 mmol) in 300 mL of hexanes was treated with 28.5 mL of a 1.6 M solution of BuLi (41.3 mmol) followed by 6.3 mL of TMEDA (41.3 mmol). After 24 h of stirring, 16.3 g of gray Se (206 mmol) was added and the dark red slurry was refluxed for 24 h. The dark brown-red slurry was filtered through a bed of Celite. The Celite was extracted with four 75 mL portions of hexane. The combined orange filtrate was washed with three 100 mL portions of 10% aqueous NaOH. The aqueous layer was separated and washed with two 50 mL portions of Et$_2$O. The combined organic layers were dried over Na$_2$SO$_4$, and the solvent was removed to give a red oil. Unreacted ferrocene was removed by flash column chromatography as the fastest moving yellow band. The third band, which was red, was the triselenide. Three other red bands which did not elute with hexanes were observed. BufcSe$_3$ was further purified by elution of a concentrated THF solution through a Bio-Beads SX-8, as in the trisulfide case affording a dark red oil. Yield 4.6 g (47%). Anal. Calcd for C$_{14}$H$_{16}$-FeSe$_3$: C, 35.26; H, 3.38; Se, 49.66; Fe, 11.71. Found: C, 35.58; H, 3.52; Se, 49.23; Fe, 11.41. ^{1}H NMR (C$_6$D$_6$) δ 4.37 (s, 1H), 4.19 (s, 1H), 4.16 (s, 2H), 4.02 (s, 1H), 3.99 (s, 1H), 3.87 (s, 1H), 3.85 (s, 1H), 3.83 (s, 1H), 3.68 (s, 1H), 3.64 (s, 2H), 3.57

(16) Hiemenz, P. C. *Polymer Chemistry. The Basic Concepts*; Marcel Dekker: New York, 1984.

(17) Pasto, D. J.; Cottard, F.; Jumelle, L. *J. Am. Chem. Soc.* **1994,** *116*, 8978.

(18) For example chloroferrocene and aminoferrocene decompose to give ferrocene via cleavage of the C–Cl(N) bond, see: Knox, G. R.; Pauson, P. L.; Willison, D.; Solcaniova, E.; Toma, S. *Organometallics* **1990,** *9*, 301 and references therein.

(19) Steudel, R.; Pridöhl, M.; Hartl, H.; Brüdgam, I. *Z. Anorg. Allg. Chem.* **1993,** *619*, 1589.

(20) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley: New York, 1986; Vol. 1, 2.

(21) Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1992,** 1764.

(s, 2H), 1.98 (m, 4H), 1.24 (m, 8H), 0.84 (m, 6H). ^{77}Se (C_6D_6) δ 938 (s, 1Se), 928 (s, 1Se), 309 (s, 1Se), 307 (s, 1Se), 302 (s, 1Se), 301 (s, 1Se). ^{13}C{^{1}H} NMR (C_6D_6) δ 92.4, 90.8, 89.1, 88.6, 88.5, 78.8, 78.4, 77.7, 77.6, 74.5, 73.0, 71.8, 71.0, 70.7, 70.4, 69.4, 69.3, 33.4, 25.2, 28.7, 22.8, 14.2. IR (neat) 3093, 2953 (st), 2926 (st), 2868, 2854, 2464, 1383, 1145, 1032, 1021, 1012, 887, 817 (st), 491 (st) cm^{-1}. UV–vis (CH_2Cl_2) 316, 436 nm. EI MS (70 eV): 478 (M$^+$).

Fe(C$_5$H$_4$)$_2$S$_2$CH$_2$. A slurry of 2.57 g of [fcS$_2$]$_n$ (9.2 mmol) in 100 mL of CH_2Cl_2 was treated with 4.48 mL of Bu$_3$P (18.0 mmol), added dropwise. After 2 h the yellow solid had dissolved to give an orange solution. After 12 h the solvent was evaporated to give a yellow solid and a red oil. This mixture was rinsed with 10 mL of cold hexanes and the yellow solid was dissolved in a minimal amount of hot CH_2Cl_2 (2 mL). Cooling this red solution to -20 °C gave 0.51 g of orange crystals (21%). Anal. Calcd for $C_{11}H_{10}FeS_2$: C, 50.39; H, 3.86; S, 24.46. Found: C, 50.30; H, 3.81; S, 24.29. ^{1}H NMR (200 MHz, CS$_2$) δ 4.10 (t, 4H), 3.92 (s, 2H), 3.85 (t, 4H).

BufcSe$_2$S. A solution of 0.414 g of [BufcSe$_2$]$_n$ (1.04 mmol) in 10 mL of THF was treated with 2.08 mL of LiBHEt$_3$ (2.08 mmol). The dark red solution foamed and its color lightened to orange-red. The solution was stirred for 6 h and then cooled to -78 °C with a dry ice/acetone bath. An excess of S$_8$ (0.067 g, 2.51 mmol) was added to the solution, and the slurry was allowed to warm to room temperature causing all of the sulfur to dissolve. After 14 h of stirring, the solvent was removed from the dark orange solution. The resulting viscous red oil was extracted with 10 mL of hexane, and the extract was purified by column chromatography on silica gel eluting with hexane. The only band to elute was orange, and removal of the solvent gave a red oil that was dried in vacuo. Yield 0.072 g (16% based on [BufcSe$_2$]$_n$). Anal. Calcd for $C_{14}H_{16}FeSe_2S$: C, 39.10; H, 3.75; Fe, 12.98; Se: 36.72; S, 24.46. Found: C, 38.84; H, 3.72; Fe, 13.12; Se: 36.54; S, 24.37. ^{1}H NMR (C_6D_6) δ 4.33 (m, 1H), 4.18 (m, 1H), 4.14 (m, 2H), 4.05 (m, 1H), 4.02 (m, 1H), 3.91 (m, 1H), 3.87 (m, 1H), 3.82 (m, 1H), 3.68 (m, 1H), 3.63 (m, 3H), 3.60 (m, 1H), 1.98 (m, 4H), 1.24 (m, 8H), 0.83 (m, 6H). ^{77}Se (C_6D_6) δ 387 (s, 1Se), 385 (s, 1Se), 379 (s, 1Se), 378 (s, 1Se). EI MS (70 eV) 432 (M$^+$).

[BufcS$_2$]$_n$ Rubbers. A solution of 0.95 g of BufcS$_3$ (2.8 mmol) in 5 mL of THF or DMF was treated with 0.65 mL of Bu$_3$P (2.6 mmol). A dark orange precipitate formed immediately. The insoluble rubbery precipitate was collected by filtration and washed with three 20 mL portions of MeOH and dried in vacuo. Yield 0.80 g (95%, based on Bu$_3$P). Anal. Calcd for $C_{14}H_{16}FeS_2$: C, 55.27; H, 5.30; Fe, 18.36; S, 21.08. Found: C, 54.86; H, 5.07; Fe, 17.13; S, 20.12.

Desulfurization of BufcS$_3$ in CH$_2$Cl$_2$ Solutions. A solution of 0.93 g of BufcS$_3$ (2.8 mmol) in 5 mL of CH_2Cl_2 was treated with 0.65 mL of Bu$_3$P (2.6 mmol), resulting in an orange solution. After 24 h, 25 mL of MeOH was added to the now dark orange solution precipitating an orange solid. The precipitate was collected by filtration and washed with three 20 mL portions of MeOH. The crude solid was dissolved in 5 mL of THF and reprecipitated with 15 mL of MeOH. After washing with three 20 mL portions of MeOH, the orange solid was dried in vacuo. Slow evaporation of THF solutions of this material gave orange films. Yield: 0.68 g (85%, based on Bu$_3$P). Anal. Calcd for $C_{14}H_{16}FeS_2$: C, 55.27; H, 5.30; Fe, 18.36; S, 21.08. Found: C, 55.34; H, 5.45; Fe, 18.13; S, 20.89. ^{1}H NMR (C_6D_6) δ 4.18 (b m, 4H), 3.92 (b m, 3H), 2.05 (b m, 2H), 1.38 (m, 2H), 1.18 (m, 2H), 0.87 (m, 3H). UV–vis (CH_2Cl_2) 330, 442 nm.

Higher molecular weight materials were prepared when the desulfurization was conducted in mixed THF–CH$_2$Cl$_2$ solutions. A solution of 0.95 g of BufcS$_3$ (2.8 mmol) in 5 mL of a 50% (by volume) mixture of CH_2Cl_2 and THF was treated with 0.65 mL of Bu$_3$P (2.6 mmol). Over the course of several hours the solution darkened. After 24 h, the dark orange solution was diluted with 25 mL of MeOH to precipitate an orange solid which was collected by filtration and washed with three 20 mL portions of MeOH. The crude solid was dissolved in 5 mL of THF and reprecipitated with 15 mL of MeOH, again washing with three 20 mL portions of MeOH. After vacuum drying the yield of orange solid was 0.70 g (88% based on

Bu$_3$P). IR (neat film) 2975 (st), 2929 (st), 2869, 1464, 1384, 1260, 1165, 1087 (m), 1026 (st), 888, 822 (st), 504 cm^{-1}. TGA (5.0 °C/min, 40 → 500 °C, He): loss of 37 wt at ~90 °C. Raman (neat film) 470 cm^{-1}.

Closely related experiments polymerizations were conducted using varying amounts of CH_2Cl_2 in THF with the following results:

0.5% CH_2Cl_2, insol product (77% yield)

1.5% CH_2Cl_2, $M_w = 350\,000$, $M_n = 316\,000$, $M_w/M_n = 1.1$

3% CH_2Cl_2, $M_w = 140\,000$, $M_n = 110\,000$, $M_w/M_n = 1.4$

5% CH_2Cl_2, $M_w = 144\,000$, $M_n = 99\,500$, $M_w/M_n = 1.4$

25% CH_2Cl_2, $M_w = 144\,000$, $M_n = 99\,500$, $M_w/M_n = 1.4$

50% CH_2Cl_2, $M_w = 144\,000$, $M_n = 99\,500$, $M_w/Mn = 1.4$

75% CH_2Cl_2, $M_w = 144\,000$, $M_n = 99\,500$, $M_w/M_n = 1.4$

95% CH_2Cl_2, $M_w = 144\,000$, $M_n = 99\,500$, $M_w/M_n = 1.4$

97% CH_2Cl_2, $M_w = 77\,000$, $M_n = 26\,000$, $M_w/M_n = 3.0$

98% CH_2Cl_2, $M_w = 40\,000$, $M_n = 12\,000$, $M_w/M_n = 3.3$

100% CH_2Cl_2, $M_w = 40\,000$, $M_n = 12\,000$, $M_w/M_n = 3.3$

[BufcSe$_2$]$_n$ from BufcSe$_3$. A solution of 0.20 g of BufcSe$_3$ (0.42 mmol) in 10 mL of THF was treated with 0.10 mL of Bu$_3$P (0.40 mmol) resulting in a red solution. After 24 h, 30 mL of MeOH was added to the now dark orange solution precipitating a red solid. The precipitate was collected by filtration and washed with three 20 mL portions of MeOH. The crude solid was dissolved in 10 mL of THF and reprecipitated with 20 mL of MeOH. After washing with three 20 mL portions of MeOH, the red solid was dried in vacuo. Yield 0.110 g (69%, based on Bu$_3$P). Anal. Calcd for $C_{14}H_{16}FeSe_2$: C, 42.24; H, 4.05; Fe, 14.03; Se, 39.67. Found: C, 42.53; H, 4.34; Fe, 13.89; Se, 39.14. ^{1}H NMR (C_6D_6) δ 4.20 (t, 4H), 3.88 (b s, 3H), 2.05 (b m, 2H), 1.28 (m, 2H), 1.18 (m, 2H), 0.83 (m, 3H). UV–vis (CH_2Cl_2) 372, 454 nm. IR (neat film) 3079 (st), 2955 (st), 2920 (st), 1464 (st), 1377, 1146, 1030, 1020, 1012, 890, 877, 822 (st), 495 (st) cm^{-1}. Raman (neat film) 613 (weak), 312 (weak), 263 (st) cm^{-1}. TGA (5.0 °C/min, 40–500 °C, He atmosphere) revealed two distinct events corresponding to losses of 24 (~295 °C) and 45 wt % (340 °C).

Light Scattering. Light-scattering experiments were performed on a Wyatt Technology (Santa Barbara, CA) Dawn DSP-F laser photometer through a K5 flow cell. Four solutions of [BufcS$_2$]$_n$ in toluene were examined: $4n \times 10^{-3}$ g/mL, where $n = 1, 0.75, 0.5, 0.25$. The [BufcS$_2$]$_n$ solutions were prefiltered through an Alltech 0.45 μm syringe filter before entering the flow cell (0.5 mL/min). M_w calculations employed the Dawn 2.04 software package based on the following function:[13]

$$Kc/\Delta R_\Theta = \{M_w^{-1} + 2A_2c_2 + 3A_3c_2^2 + ...\} \times$$
$$\{1 + (16\pi^2 n_0^2 \sin^2(\Theta/2)/3\lambda^2)\}\langle s^2\rangle_z$$

where

$$K = 2\pi^2 n_0^2 (dn/dc_2)^2/N_A\lambda^4,\ \text{known as the optical constant}$$

where

$$n_0 = \text{refractive index of toluene at 632.8 nm}$$

$dn/dc_2 = $ the refractive index increment
(in this case, 0.1672 ± 0.0039 mL/g)

$$N_A = 6.023 \times 10^{23}$$

$\lambda = $ wavelength of scattering light
(He–Ne laser, $\lambda = 632.8$ nm)

$$c_2 = \text{concentration in g/mL}$$

$$\Delta R_\Theta = R_{\Theta\text{soln}} - R_{\Theta\text{solvent}} \quad \text{where } R_\Theta = i_\Theta r^2 / I_0 (1 + \cos^2\Theta)$$

$$M_w = \text{weight average molecular weight}$$

Θ is the scattering angle (17 angles were monitored from

$$26.56° \leq \Theta \leq 144.46°)$$

A_2, A_3 are virial coefficients, only the A_2 term was

considered

$$\langle s_2 \rangle_z = \text{mean-squared radius of gyration}$$

The refractive index increment dn/dc was determined using $2n \times 10^{-3}$ g/mL stock solution of $[BufcS_2]_n$ in toluene, where n = 1, 0.66, 0.50, 0.33, and 0.25. The solutions were passed through a gravity flow cell of a Wyatt/Optilab Interferometric refractometer through a P2 cell ($\lambda = 633$ nm). The Na-distilled toluene had been filtered through a 0.02 μm filter before use.

A $M_w = (2.32 \pm 0.1) \times 10^5$ g/mol was determined from the Zimm plot where the term $Kc/\Delta R_\Theta$ was plotted vs $\sin^2(\Theta/2) - 237c$, the -237 scaling factor being arbitrarily selected. The $\Theta = 0$ data and the $c = 0$ data intercept at M_w^{-1}.

The radius of gyration was also calculated using the relation in eq 5 using the M_n value determined from SEC. The segment length was calculated starting with the atomic coordinates of ferrocene[21] and replacing two H atoms with sulfur with C–S distances set at 1.75 Å, as seen in the structure of $(t\text{-BuC}_5\text{H}_3)_2\text{FeS}_3$.[5]

At $\Theta = 0$ the following equation applies:

$$Kc/\Delta R_\Theta = M_w^{-1} + 2A_2c_2$$

Plots of $Kc/\Delta R_\Theta$ vs c_2 were linear, from which we determined the second virial coefficient A_2, which proved to be 3.65×10^{-4} mol mL g^{-1}.

CM950350Y