

Poly(ferrocenylpersulfide)s

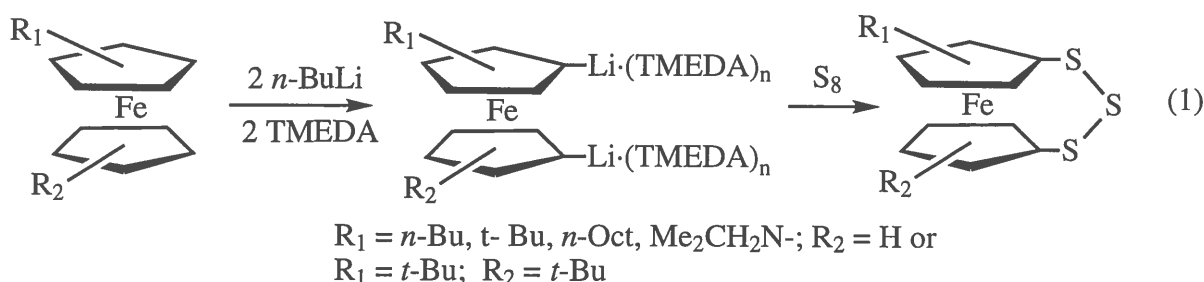
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Final Seminar

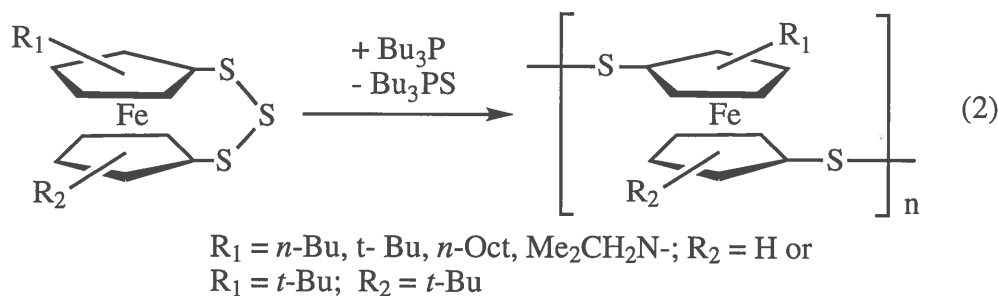
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Organometallic polymers are of interest because they combine the desirable electronic properties of transition metals with the processing advantages of organic polymers [1]. There are potential applications of organometallic polymers as electron-conductive materials, non-linear optical materials, and batteries [2].

A new family of organometallic polymers based on ferrocene persulfide units has been discovered by this group [3]. The precursors for these polymers are obtained by treatment of dilithioferrocenes with elemental sulfur (eq 1) [4].



The addition of one equivalent of tertiary phosphine to solutions of these trisulfide precursors effects the polymerization (eq 2). The desulfurization of the parent, unsubstituted ferrocene trisulfide produces a yellow insoluble material [3]. We were interested in obtaining more information about *soluble* ferrocenylpersulfide polymers through the use of various alkyl-substituted ferrocene sulfides.

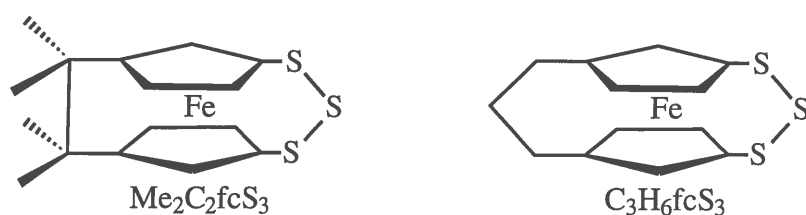


The tert-butyl substituted trithiaferrocenophane, $(t\text{-BuC}_5\text{H}_3)_2\text{FeS}_3$ was obtained as the 1,3,1',4' isomer, as established by ^1H NMR measurements and X-ray crystallography [5]. This and the corresponding mono(*t*-Bu) derivative were converted to the polymers $[(\text{RC}_5\text{H}_3)_2\text{FeS}_2]_n$ upon desulfurization with Bu_3P , which was shown by ^{31}P NMR spectroscopy to be converted to Bu_3PS . The rate of this desulfurization increases with the polarity of the reaction solvent as predicted by model studies [6]. GPC measurements indicated that the (*t*-Bu)- and (*t*-Bu)₂- substituted polymers are polydisperse with $M_n = 3,700$ ($M_w = 26,000$) and $M_n = 2,400$ ($M_w = 19,000$), respectively. These soluble polymers display a number of interesting chemical properties. Cyclic voltammetric measurements show that they undergo reversible electrochemical oxidation in two steps, separated by ~ 290 mV. Reduction of $[(t\text{-BuC}_5\text{H}_3)_2\text{FeS}_2]_n$ with LiBHET_3 gave $(t\text{-BuC}_5\text{H}_3)_2\text{FeS}_2\text{Li}_2$, which can be reoxidized (I_2) to the polymer, sulfurized (S_8) to give the trisulfide, and selenized (Se_8) to give $(t\text{-BuC}_5\text{H}_3)_2\text{FeS}_2\text{Se}$. Treatment of the S_2Se species with PBu_3 gave SePBu_3 and the persulfido polymer.

Studies were also conducted on the n-butyl derivative, $(\text{BuC}_5\text{H}_3)(\text{C}_5\text{H}_4)\text{FeS}_3$ [3,7], which was obtained as a ~ 7:1 mixture of 1,3,1' and 1,2,1'-isomers. The rate of desulfurization of this trisulfide and the molecular weight of the polymer depends critically on the reaction solvent. Desulfurization in THF afforded a very high molecular weight polymer ($M_n > 400,000$ dalton). Desulfurization in mixed CH_2Cl_2 -THF solutions gave polymers with M_n ranging from 45,000 to 4,000, with lower molecular weight products being favored at high $[\text{CH}_2\text{Cl}_2]$. Molecular weights for $[(\text{BuC}_5\text{H}_3)(\text{C}_5\text{H}_4)\text{FeS}_2]_n$ were confirmed by light scattering measurements.

Deselenization of $(\text{BuC}_5\text{H}_3)(\text{C}_5\text{H}_4)\text{FeSe}_3$ gave red soluble $[(\text{BuC}_5\text{H}_3)(\text{C}_5\text{H}_4)\text{FeSe}_2]_n$ with only moderate molecular weights and with high polydispersities. Since the triselenide was obtained exclusively as the 1,3,1' isomer, the stereochemistry of the polymer is simplified relative to the trisulfides. 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.

The synthesis and desulfurization of the doubly strapped ferrocenes $\text{C}_3\text{H}_6(\text{C}_5\text{H}_3)_2\text{FeS}_3$ and $\text{Me}_2\text{C}_2(\text{C}_5\text{H}_3)_2\text{FeS}_3$ (see below) were examined to probe the importance of C_5R_5 ring rotation in the desulfurization-induced polymerizations. These were prepared by lithiation/sulfidation of the corresponding $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Fe}$ and $(\text{CH}_2)_3(\text{C}_5\text{H}_4)_2\text{Fe}$, respectively. The former was characterized crystallographically. Dynamic NMR studies of the trimethylene-strapped species revealed two dynamic processes resulting from conformational equilibria involving the S_3 and the $(\text{CH}_2)_3$ straps. SEC and FAB mass spectroscopic measurements show that desulfurization of these trisulfides does not produce high molecular weight polymers.



References

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