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Polymerization of Fluorothiocarbonyl Compounds

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Synopsis

Recently it was shown that the C=S group in fluorothiocarbonyl compounds readily undergoes addition polymerization. This review describes polymers obtainable from such compounds as $CF_2{=}S$, $CF_3CF{=}S$, $ClCF_2CF{=}S$, $HCFClCF{=}S$, and hexafluorothioacetone. The polymerization of $CF_2{=}S$ is readily brought about in anionic systems at low temperatures, giving a high-molecular-weight poly(thiocarbonyl fluoride) with a number-average molecular weight in the range of 300,000 to 400,000. It is believed that the major portion of this polymer is composed of chains of $CF_3{-}S{-}({-}CF_2S{-})_n{-}CF{=}S$. Poly(thiocarbonyl fluoride) is a highly resilient elastomer in the amorphous form but suffers the disadvantage of slow crystallization at temperatures below 35°C and concomitant loss of rubbery properties. Above 175°C it depolymerizes. Fluorothioacyl fluorides also undergo anionic polymerization, but the products are logy elastomers. Copolymers of fluorothioacyl fluorides with $CF_2{=}S$ have better thermal stability but poorer resilience than poly(thiocarbonyl fluoride). Hexafluorothioacetone has been polymerized at −110°C to give a white elastomer that slowly depolymerizes at room temperature to regenerate monomer. Thiocarbonyl fluoride is also susceptible to free-radical polymerization, and in free-radical systems it copolymerizes with conventional vinyl monomers, giving a wide variety of new elastomeric products.

In the last several years a number of investigations have been made concerning the preparation and chemistry of fluorine compounds containing the C=S group (*1–3*). The simplest of these compounds, thiocarbonyl fluoride ($CF_2{=}S$), has been prepared by a number of means. One method (*4*) starts with thiophosgene, which is converted to its cyclic dimer by ultraviolet irradiation followed by fluorination with antimony trifluoride, giving 2,2,4,4-tetrafluoro-1,3-dithietane. Pyrolysis of the dithietane at 500°C smoothly converts it to $CF_2{=}S$. A second method (*5*) also starts with thiophosgene; this compound is chlorinated, giving trichloromethyl sulfenyl chloride, a compound that is then converted to CF_2ClSCl. The removal of chlorine from the chlorodifluoromethyl sulfenyl chloride with tin leads to $CF_2{=}S$. A third method (*6*) involves the reaction of the mercury salt of trifluoromethyl mercaptan with iodosilane:

$$(CF_3S)_2Hg + SiH_3I \rightarrow SiH_3SCF_3 \rightarrow SiH_3F + CF_2{=}S$$

Fluorothioacyl fluorides have been synthesized by the addition of hydrogen sulfide to appropriate fluoroolefins under the influence of high-energy x-rays (*7*). The mercaptans formed in this way react with sodium fluoride to form acid fluorides:

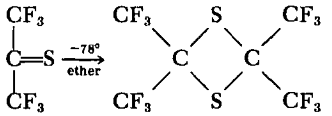
$$ClCF{=}CF_2 + H_2S \xrightarrow{\text{x-rays}} ClCFHCF_2SH \xrightarrow{NaF} ClCFHCF{=}S$$

$$CF_2{=}CF_2 + H_2S \rightarrow HCF_2CF_2SH \xrightarrow{NaF} HCF_2CF{=}S$$

Another method that has quite wide applicability is the reaction of perfluoromercurials with sulfur vapor at 450°C (*1*):

$$(CF_3CF_2)_2Hg + S \rightarrow CF_3CF{=}S$$

The reaction of perfluoromercurials with sulfur has also been applied to the synthesis of hexafluorothioacetone (*1*). For example, the reaction of hexafluoropropene with mercuric fluoride in anhydrous HF leads to bis(hexafluoroisopropyl)mercury (*8*). This mercurial, upon reaction with sulfur vapor at 450°C, gives hexafluorothioacetone in good conversion. This fluoroketone is a blue compound that boils at 8°C. It is a very reactive compound and, unless kept very cold, dimerizes and gives 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane. This dimerization tendency is so strong that it takes place rapidly at −78°C in the presence of compounds having atoms with unshared electrons, such as ether:



All of the fluorothiocarbonyl compounds are very reactive materials. Probably the most reactive is hexafluorothioacetone, and its reactions have been used for illustrating the types of transformation that thiocarbonyl compounds undergo. Hexafluorothioacetone readily undergoes Diels-Alder addition (9). The ketone also adds to olefins containing allylic hydrogen and so forms allyl sulfides (*10*). It reacts abnormally with sodium bisulfite, giving Bunte salts (*11*), and it also adds abnormally to mercaptans and forms disulfides (*11*). Hexafluorothioacetone also undergoes polymerization, which is the reaction of most interest here, but for this purpose the simpler thiocarbonyl compounds provide much better examples.

ANIONIC POLYMERIZATION

One of the most unusual features of thiocarbonyl compounds is the ease with which the simpler members of this class polymerize. For example, $CF_2{=}S$ is very susceptible to anionic polymerization at low temperatures (2). The addition of a trace of a very mild base, such as dimethyl formamide, to a solution of $CF_2{=}S$ in dry ether solution at −78°C promotes a very rapid polymerization that results in a very-high-molecular-weight polymer. The number-average molecular weight of such a polymer is of the order of 300,000 to 400,000 and the weight-average molecular weight is in excess of 1,000,000. It is a tough elastomer that is surprisingly resistant to acids and aqueous alkali. For example, the polymer can be boiled in nitric acid for periods of an hour or so without apparent damage. It also can be boiled in 40% aqueous alkali for 24 hr or longer without suffering diminution of molecular weight, although some weight is lost. On the other hand, it is very rapidly attacked by amines. Exposure to excess triethylamine leads to an almost complete destruction of the polymer in a matter of minutes. Though elastomeric as isolated and when formed into films by melt pressing, the polymer does slowly crystallize at temperatures below 35°C to a nonrubbery, plastic form. Moreover, it is not stable above 175°C.

Chemical and spectral studies of poly(thiocarbonyl fluoride) have indicated that it is mainly long chains of $CF_3S{-}({-}CF_2{-}S{-})_n{-}CF{=}S$. Reaction with methanol-^{14}C established that there is approximately one methanol reactive group per polymer chain. Degradation of the polymer by reaction with antimony pentafluoride gave low-molecular-weight oils composed of $CF_3S—(—CF_2—S—)_x—CF_3$, in which x varied from about 3 to about 25. These oils show strong infrared absorption at 13.1 μ and fluorine NMR resonance at 37.6-ppm higher field than that of CCl_3F, used as an external standard. That these values are representative of $CF_3S—$ was indicated by comparison with values obtained from $CF_3SCF{=}S$ used as a model. This compound also has fluorine NMR resonance at 71.5-ppm lower field than the standard, which has been assigned to the fluorine in $SCF{=}S$. These same values can be discerned in low-molecular-weight poly(thiocarbonyl fluoride) obtained by anionic polymerization at the relatively high temperature of −25°C. A résumé of the infrared and chemical data is given in Table 1.

TABLE 1

Identification of End Groups by Infrared

End group	IR absorption at:	Reactivity with methanol
$CF_3S—$	13.1 μ	IR band unaffected by reaction with methanol
$-SCF{=}O$	5.4 μ	IR band removed in reaction with methanol
$-SCF{=}S$	8.2 μ	IR band removed in reaction with methanol

Polymer prepared by initiation with dimethyl formamide does not contain initiator fragments. This was established by the use of dimethyl formamide tagged with ^{14}C. This fact, a knowledge of end groups, and an indication that the polymerization involves a chain-transfer factor of at least 10 have led to the proposal (2) that the polymerization occurs as follows:

Initiation:

$$\text{DMF} + \begin{matrix}\text{monomer}\\ \text{solvent}\\ \text{impurity}\end{matrix} \rightarrow B^{\ominus}$$

$$B^{\ominus} + CF_2—S \rightarrow BCF_2S^{\ominus}$$

$$F^{\ominus} + CF_2{=}S \rightarrow CF_3S^{\ominus}$$

Propagation:

$$BCF_2S^{\ominus} + nCF_2{=}S \rightarrow BCF_2S—(—CF_2S—)_{n-1}—CF_2S^{\ominus}$$

$$CF_3S^{\ominus} + nCF_2{=}S \rightarrow CF_3S—(—CF_2S—)_{n-1}—CF{=}S^{\ominus}$$

Termination:

$$BCF_2S\text{—}(\text{—}SCF_2S\text{—})_{n-1}\text{—}CF_2S^{\ominus} \rightarrow BCF_2S\text{—}(\text{—}CF_2S\text{—})_{n-1}\text{—}CF{=}S + F^{\ominus}$$

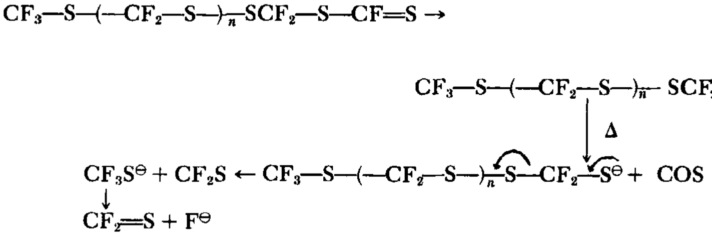
$$CF_3S\text{—}(\text{—}CF_2S\text{—})_{n-1}\text{—}CF_2S^{\ominus} \rightarrow CF_3S\text{—}(\text{—}CF_2S\text{—})_{n-1}\text{—}CF{=}S + F^{\ominus}$$

Polymers have been obtained in the anionic polymerization of fluorothioacyl fluorides. Such compounds as $CF_3CF{=}S$, $ClCF_2CF{=}S$, and $HCFClCF{=}S$ have been polymerized under conditions similar to those used for $CF_2{=}S$. The products in each case are logy elastomers. The fluorothioacyl fluorides also copolymerize with $CF_2{=}S$. The $CF_2{=}S\text{—}HCFClCF{=}S$ copolymer has better chemical and thermal stability than poly(thiocarbonyl fluoride), but it is not as resilient as the homopolymer.

Hexafluorothioacetone provides a good example of the ceiling-temperature effect. At −78°C all anionic initiators rapidly promote the conversion of hexafluorothioacetone to its dimer, 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane. At −110°C or less, however, the ketone polymerizes to a white elastomer. Unfortunately, this polymer slowly depolymerizes at room temperature with regeneration of monomer.

POLYMER STABILITY

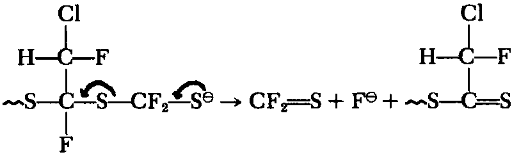
It has been mentioned that poly(thiocarbonyl fluoride) decomposes above 175°C. The product from this decomposition is $CF_2{=}S$ monomer, which can be recovered almost quantitatively. The exact mechanism of this decomposition is not known, but it has been suggested (2) that the first step is hydrolysis of the unstable end to form a chain that could eliminate carbon oxysulfide, as follows:



$$CF_3\text{—}S\text{—}(\text{—}CF_2\text{—}S\text{—})_n\text{—}SCF_2\text{—}S\text{—}CF{=}S \rightarrow CF_3\text{—}S\text{—}(\text{—}CF_2\text{—}S\text{—})_n\text{—}SCF_2\text{—}S\text{—}C(\text{=}O^{\ominus})S$$

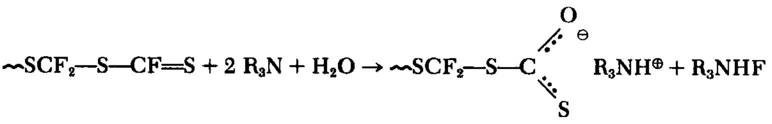
$$\xrightarrow{\Delta} CF_3\text{—}S\text{—}(\text{—}CF_2\text{—}S\text{—})_n\text{—}S\text{—}CF_2\text{—}S^{\ominus} + COS \rightarrow CF_3S^{\ominus} + CF_2S;\quad CF_2S \rightarrow CF_2{=}S + F^{\ominus}$$

This mechanism could also explain the superior thermal stability of the $CF_2{=}S\text{-}HCFClCF{=}S$ copolymer. Here decomposition is visualized as proceeding to the point at which a comonomer is encountered, in which case a dithiol ester of somewhat superior thermal stability could be formed:



$$\sim S-\underset{\displaystyle F}{\overset{\displaystyle H-\overset{\displaystyle Cl}{C}-F}{C}}-S-CF_2-S^{\ominus} \rightarrow CF_2{=}S + F^{\ominus} + \sim S-\overset{\displaystyle H-\overset{\displaystyle Cl}{C}-F}{C}{=}S$$

Decomposition by triethylamine is also visualized as a consequence of the unstable end of the polymer. In this case the first step could be a reaction of the amine and of traces of water that might be present in the polymer:



$$\sim SCF_2-S-CF{=}S + 2\,R_3N + H_2O \rightarrow \sim SCF_2-S-C\overset{\displaystyle O}{\underset{\displaystyle S}{\lessgtr}}{}^{\ominus}\ R_3NH^{\oplus} + R_3NHF$$

FREE-RADICAL POLYMERIZATION

One of the surprising aspects of fluorothiocarbonyl compound polymerization is the susceptibility of the compounds to free-radical initiation (*12*). In this case the most critical feature is the use of very low temperatures for the polymerization. A major problem was the development of a means of generating free radicals chemically in sufficient quantities at low temperatures. A very salutary solution was the use of the trialkylborane–oxygen redox couple. The polymerization of $CF_2{=}S$ either in bulk or in solution at −78°C in the presence of a trialkylborane and oxygen led to high-molecular-weight poly(thiocarbonyl fluoride). A study of the initiator has shown that radicals are generated in a two-step reaction (*12*). In the first step the trialkylborane is oxidized to boron peroxide, which then reacts with additional trialkylborane to generate radicals:

$$R_3B + O_2 \rightarrow R_2BOOR$$

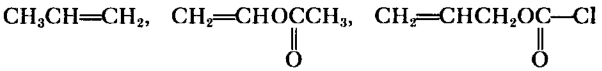
$$R_2BOOR + 2R'_3B \rightarrow R_2BOBR'_2 + R'_2BOR + 2R'\cdot$$

It is important to use less than 1 mole of oxygen per mole of trialkylborane because of the requirements of the second reaction shown above. Furthermore, because the initiation reaction occurs in two steps, it is possible to carry out the first step prior to polymerization. A convenient procedure is to prepare standardized solutions of a peroxyborane solution and a trialkylborane solution and to use appropriate amounts of each as needed.

COPOLYMERIZATION WITH VINYL COMPOUNDS

An important feature of the free-radical polymerization system is its ability to bring about the copolymerization of $CF_2{=}S$ with unsaturated compounds. At −78°C and in the presence of a borane initiator $CF_2{=}S$ copolymerizes with a wide variety of $C{=}C$ compounds, including olefins, polymerizable vinyl monomers, and allyl compounds. A brief list of typical polymerizable monomers follows:

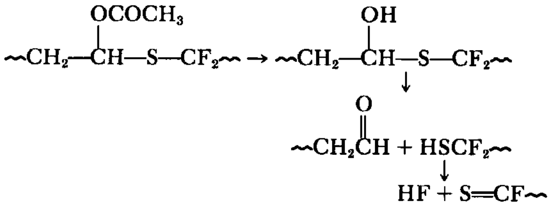
$CH_2{=}CH_2$, $CH_2{=}CHCl$, $CH_2{=}CHCH_2Cl$,



$$CH_3CH{=}CH_2,\quad CH_2{=}CHO\underset{\underset{O}{\|}}{C}CH_3,\quad CH_2{=}CHCH_2O\underset{\underset{O}{\|}}{C}{-}Cl$$

There are three copolymer types that deserve particular mention. The first is the $CF_2{=}S$-propylene copolymer. In this case there appears to be a preference for 2:1 $CF_2{=}S$-propylene composition. If an excess of propylene is used in the polymerization, a 2:1 copolymer will be obtained. In contrast to the $CF_2{=}S$ homopolymer, which melts at 35°C, the $CF_2{=}S$-propylene copolymer has a crystalline melting point of −57°C.

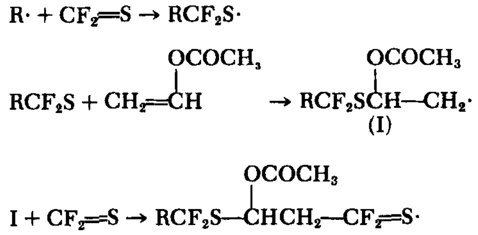
The second copolymer type is that obtained with vinyl acetate. These products upon hydrolysis are converted to materials of much lower molecular weight. This seems to indicate that sulfur and acetate are on the same carbon atom. Such a polymer would be expected to decompose upon hydrolysis:



To form the proposed structure it would appear necessary that

$CF_2{=}S$ react abnormally at some stage in the polymerization. Mechanisms that might account for this behavior are shown below.

Mechanism 1:

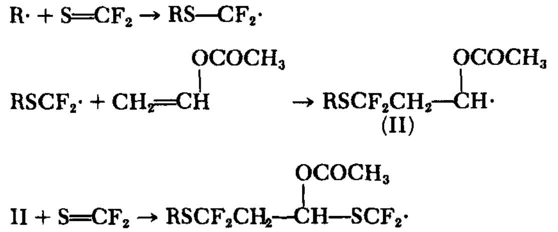


$$R\cdot + CF_2{=}S \rightarrow RCF_2S\cdot$$

$$RCF_2S + CH_2{=}\overset{OCOCH_3}{\overset{|}{C}}H \rightarrow \underset{(I)}{RCF_2S\overset{OCOCH_3}{\overset{|}{C}}H{-}CH_2\cdot}$$

$$I + CF_2{=}S \rightarrow RCF_2S{-}\overset{OCOCH_3}{\overset{|}{C}}HCH_2{-}CF_2{=}S\cdot$$

Mechanism 2:



$$R\cdot + S{=}CF_2 \rightarrow RS{-}CF_2\cdot$$

$$RSCF_2\cdot + CH_2{=}\overset{OCOCH_3}{\overset{|}{C}}H \rightarrow \underset{(II)}{RSCF_2CH_2{-}\overset{OCOCH_3}{\overset{|}{C}}H\cdot}$$

$$II + S{=}CF_2 \rightarrow RSCF_2CH_2{-}\overset{OCOCH_3}{\overset{|}{C}}H{-}SCF_2\cdot$$

That the decrease in molecular weight upon hydrolysis is not the fault of the acetate group was demonstrated by the copolymerization of $CF_2{=}S$ with 3-butenyl acetate. The product was a high-molecular-weight polymer that could be hydrolyzed to give a tough high-molecular-weight hydroxyl-containing copolymer.

The third special copolymer type is that formed from the copolymerization of $CF_2{=}S$ and allyl chloroformate. Copolymers containing as little as 3 mole-% of allyl chloroformate have melting points below 0°C. Because they contain an active group, they can be cross-linked by means of a reaction with zinc oxide. Thus, this is a thiocarbonyl fluoride polymer that can be vulcanized by means of a simple chemical reaction involving a group on the polymer chain.

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