MFN 1007

ES-3178

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
WILMINGTON 98, DELAWARE

CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION

R.R.I. OF INDIA
NO 3189
DATE 1-3-66
KOTTAYAM

Lib
n
D.D C&RT [illegible]

DHS
4/3.

December 29, 1965

Ch
5.3.

Dr. K. T. Jacob, Director
The Rubber Research Institute of India
Rubber Board P.O., Kottayam
Kerala
India

Dear Dr. Jacob:

Some time ago, I promised to send you drafts of our papers on "Thiocarbonyl Fluoride Polymers" after these papers had been completed. Such has now been accomplished, and I am enclosing drafts that describe anionic and free-radical polymerization of thiocarbonyl fluoride.

Sincerely yours,

William H. Sharkey

W. H. Sharkey

mac
5*

Lib
+
D. DeVRT
1m
11-17-60

FLUOROTHIOCARBONYL COMPOUNDS. V.[1]

POLYMERIZATION OF THIOCARBONYL COMPOUNDS[†]

by

W. J. Middleton, H. W. Jacobson, R. E. Putnam,
H. C. Walter, D. G. Pye, and W. H. Sharkey,
Central Research Department* and Elastomer Chemicals Department
of E. I. du Pont de Nemours and Company

Synopsis

Thiocarbonyl fluoride, fluoroalkylthio acid fluorides, and fluorothioketones are converted to high molecular weight polymers by anionic initiation at low temperatures. Amorphous polythiocarbonyl fluoride, $(CF_2S)_n$, is a tough elastomer that is extraordinarily resilient. Because polythiocarbonyl fluoride has a melting point of 35°, it slowly crystallizes at room temperature to an opaque, stiff plastic. The glass transition point of the polymer is very low, being -118°. Polytrifluorothioacetyl fluoride and polyhexafluorothioacetone are also elastomeric, but neither have the high resilience that is characteristic of polythiocarbonyl fluoride. Polyhexafluorothioacetone slowly depolymerizes at room temperature.

* * *

A new and unusual series of polymers has been obtained through study of thiocarbonyl fluoride, CF_2S, and its close

---

* Contribution No. 1088.

[†] Presented in part at the 145th Meeting of the American Chemical Society, September, 1963, New York, N.Y.

relatives, which have been described in earlier papers.[2,3] In our early studies of these compounds, it was discovered that thiocarbonyl fluoride can be polymerized by storage in stainless steel cylinders. Products so obtained are waxes having molecular weights in the 2000-5000 range. More careful examination of the polymerizability of thiocarbonyl fluoride and other fluorothio acid fluorides established that these compounds undergo polymerization in anionic and in free-radical systems. This paper describes polymers obtained by anionic initiation. Free-radical polymerization will be the subject of a later paper.

Polythiocarbonyl Fluoride. - Anionic polymerization of thiocarbonyl fluoride takes place rapidly at low temperatures under anhydrous conditions in aprotic solvents, of which anhydrous ether appears best. The polymer is a high molecular weight, linear chain of structure I.

$$nCF_2{=}S \longrightarrow \left(CF_2 - S \right)_n$$

I

Such a structure is supported by nuclear magnetic resonance, which shows only one resonance at 43.5 ppm. higher field than that of CCl_3F used as an external standard. The proposed structure is also supported by its infrared absorption spectrum, which shows a broad absorption band near 9 μ for C-F and a strong band at 12.25 μ for C-S.

The molecular weight of polythiocarbonyl fluoride is greatly influenced by polymerization temperature and polymerization medium. Low temperatures favor high molecular weight. At -78°, polymers with inherent viscosities of 4 to 6 are readily obtained if the polymerization is carried out in anhydrous ether using dimethylformamide as an initiator. Higher temperatures favor lower molecular weight. For example, at -50° products can be obtained that have inherent viscosities around 2.0.

The molecular weight of the polymer is also influenced by the initiator employed. Tetraisopropyl titanate is somewhat like dimethylformamide in that it also leads to high molecular weights. Polymers with inherent viscosities of 2 to 4.5 are obtained with this initiator at low temperatures in either ether or petroleum ether. Intermediate molecular weights are formed with tetraisopropyl titanate in ether by use of isopropyl alcohol as a chain-transfer agent. At a relatively high temperature, such as -25°, in chloroform and in the presence of a relatively large amount of tetraisopropyl titanate, thiocarbonyl fluoride is converted to low molecular weight oils. Other compounds effective as initiators include aluminum isopropoxide, di(hydrogenated-tallow)dimethylammonium methoxide[12] and chloride, N-nitrosodimethylamine, diisopropylamine, and triethylamine.

The high molecular weight polymer is a tough elastomer that is highly resilient and surprisingly resistant to chemical attack. Pressed films, when stretched and then released, retract with the lively snap of a highly resilient rubber. Measurements by the Yerzley method indicate a resilience of 95%, which is an exceptionally high value.

The crystalline-amorphous transition for polythiocarbonyl fluoride is 35°. As a result, rubbery films obtained by hot-pressing slowly crystallize on storage at room temperature to opaque, nonelastic films. Upon sufficient extension at room temperature, the rubbery films cold-draw with simultaneous crystallization of the polymer and orientation of the chains. Oriented crystalline films have tensile strengths of about 11,000 psi. and an ultimate elongation of roughly 90%. These films are easily remelted to reform the highly resilient elastomer.

Though its melting point is high for use as an elastomer, the polymer has an exceptionally low glass transition temperature. This point, as measured by the torsion pendulum method, is -118°.

Polythiocarbonyl fluoride survives brief treatments in boiling fuming nitric acid without apparent damage. However, it is slowly degraded in such a medium. For example, boiling in fuming nitric acid for 21 hours caused the inherent viscosity of one sample to drop from 3.45 to 0.54. The polymer is also surprisingly resistant to boiling aqueous sodium hydroxide. It shows no change when boiled for short periods, although it slowly loses weight upon long-term treatment. After 21 hours in boiling 10% NaOH, the polymer loses about 9% of its weight with essentially no change in inherent viscosity. However, polythiocarbonyl fluoride is rapidly attacked by bases that wet the surface of the polymer. For example, triethylamine or pyridine cause it to decompose rapidly and completely at room temperature. The products are thiocarbonyl fluoride monomer and a small amount of a black solid. Sensitivity to organic bases is believed to involve reactive end groups. Oils (II) capped with CF_3-, which have been formed by reaction of antimony pentafluoride with polythiocarbonyl fluoride, are totally unaffected by amines, even at elevated temperatures.

$$\left(CF_2-S\right)_n \xrightarrow{SbF_5} CF_3S\left(CF_2-S\right)_{<25}CF_3$$

II

The maximum service temperature of polythiocarbonyl fluoride is about 175°. At higher temperatures, the polymer unzips to regenerate thiocarbonyl fluoride monomer. This behavior also has been traced to the reactive end groups of the polymer. The oils capped with CF_3- (II) are stable to 300° when heated in nitrogen, although they do oxidize when heated in air.

An insight into the mechanism of the formation of polythiocarbonyl fluoride can be deduced from an examination of end groups coupled with spectral and molecular weight data. Reaction of methanol-C^{14} with high molecular weight polymer prepared by dimethylformamide initiation indicated that, on the average, there is one group per chain capable of reacting with methanol. Infrared studies indicate this reactive group is -CF=S, although some chains also contain -CF=O. Low molecular weight polymer prepared by dimethylformamide initiation in methylene chloride at -25° has infrared bands at 5.4, 8.2, 10.1, and 13.1 μ. The 5.4 μ band is assigned to -SCF=O; COF_2 absorbs at 5.25 μ and R_fCFO absorbs at 5.3 μ. This band is not present in the spectrum of polymer that has been reacted with methanol. The amount of -SCF=O end group is small, however, because it cannot be detected by fluorine NMR. The 8.2 μ band is assigned to -CF absorption in -SCF=S. The basis for this assignment is that the band is present whether or not there is -SCF=O absorption, and polymer in which -SCF=O absorption is missing reacts with methanol to liberate HF and to form a product that does not absorb at 8.2 μ but does show CH stretching absorption at 3.3 μ, CH_2 deformation absorption at about 6.9 μ, and a strong band at

7.9 μ that is believed to be -C-O- stretching absorption. These results are in fair agreement with changes in infrared absorption of the model compound $CF_3SCF=S$ that are brought about by reaction with methanol to form $CF_3SCSOCH_3$. Exact assignments are difficult because of several discrete CF absorptions that do not appear as resolved peaks in the spectra of the polymers. Additional support for the -SCF=S end group has been obtained by identification of a small amount of fluorine resonance at 71.5 ppm. lower field than that of CCl_3F (external standard) in the NMR assignable to F in -SCF=S. This resonance is eliminated by the methanol reaction.

The 10.1 μ infrared band has not been assigned. That it is associated with a reactive group is demonstrated by its removal upon reaction of the polymer with methanol.

The 13.1 μ band is assigned to the $-SCF_3$ end group. This grouping has a characteristic absorption at about 13 μ as is shown by the infrared spectra of such model compounds as $CF_3SCF=S$ and $CF_3SCSOCH_3$. Also, fluorine NMR of low molecular weight oils have a definite resonance at 37.6 ppm. higher field than that of CCl_3F (external standard) in agreement with data obtained for SCF_3 in $CF_3SCF=S$. Intensity of the 13.1 μ band varies with molecular weight but is unaffected by the methanol reaction. Increased intensity of the 13.1 μ band is achieved by reaction of the polymer with antimony pentafluoride or sulfur tetrafluoride. These results support the assignment because both treatments convert -SCF=O and -SCF=S to $-SCF_3$.

End group studies on low molecular weight polymers made by initiation with tetraisopropyl titanate show that initiator fragments are in the polymer. The polymers examined were made in chloroform at -25°. In the infrared spectra of these products, a double peak appears at 7.24 μ, which is characteristic of <u>gem</u>-dimethyl groups. The spectra further show the expected CH absorption at about 3.3 μ and CH_2 deformation absorption at about 6.8 μ. These absorptions are not noticeably affected by treatment with methanol. On the other hand, reaction with thionyl chloride reduces <u>gem</u>-dimethyl absorption to the point where it cannot be detected and at the same time leads to the formation of the 5.4 μ band assignable to $-SCF=O$, which is not present in the spectrum of the untreated polymer. Since the only reasonable source of the <u>gem</u>-dimethyl group is the isopropoxy unit in tetraisopropyl titanate, it seems probable that initiation in this case involves generation of isopropoxy anions from the titanate. Such isopropoxy ends are destroyed by reaction with thionyl chloride, which converts them to acid fluoride groups.

Polythiocarbonyl fluoride prepared by dimethylformamide initiation does not appear to contain initiator fragments. This conclusion is based on polymerizations in which the initiator was C^{14}-tagged dimethylformamide having sufficient activity to be detectable even if the kinetic chain length were in excess of 10 million. Polymers from such polymerizations were inactive, which may mean the initiator is very loosely held and readily replaced during work-up or, as we believe more likely, the dimethylformamide is not the primary initiator.

We propose that the first step in initiation with dimethylformamide is reaction of the amide with other material to form a base.

$$\mathrm{DMF} + \mathrm{HB} \longrightarrow \mathrm{DMFH}^{\oplus} + \mathrm{B}^{\ominus}$$

This other material could be an impurity, such as traces of HF. Then, initiation would be

$$\mathrm{B}^{\ominus} + \mathrm{CF_2{=}S} \longrightarrow \mathrm{BCF_2{-}S}^{\ominus}$$

In the case of tetraisopropyl titanate initiation, $\mathrm{B}^{\ominus}$ is $(\mathrm{CH_3})_2\mathrm{CHO}^{\ominus}$. Propagation is visualized as a straightforward anionic chain reaction.

$$BCF_2\text{-}S^{\ominus} + nCF_2{=}S \longrightarrow B(CF_2S)_nCF_2S^{\ominus}$$

If, in the course of dimethylformamide-initiated polymerizations, such end groups as $-SCF_2OH$ are formed, acid fluoride groups would be generated by spontaneous loss of HF.

The occurrence of $-CF{=}S$ end groups in the polymer is compatible with a chain-transfer mechanism for chain termination. This could involve ejection of a fluoride ion to form III.

$$—SCF_2SCF_2S^{\ominus} \longrightarrow —SCF_2SCF{=}S + F^{\ominus}$$

III

Addition of a proton supplied by traces of water or HF to give IV is also conceivable.

$$—SCF_2SCF_2S^{\ominus} + H^{\oplus} \longrightarrow —SCF_2SCF_2SH$$

IV

Attempts to identify $—SCF_2SH$ in the polymer have failed, and we believe this method of termination is unlikely. In any event, IV would spontaneously lose HF to regenerate III.

The fluoride ion supplied by the termination reaction is responsible for initiation of additional chains. This and subsequent reactions are visualized as follows:

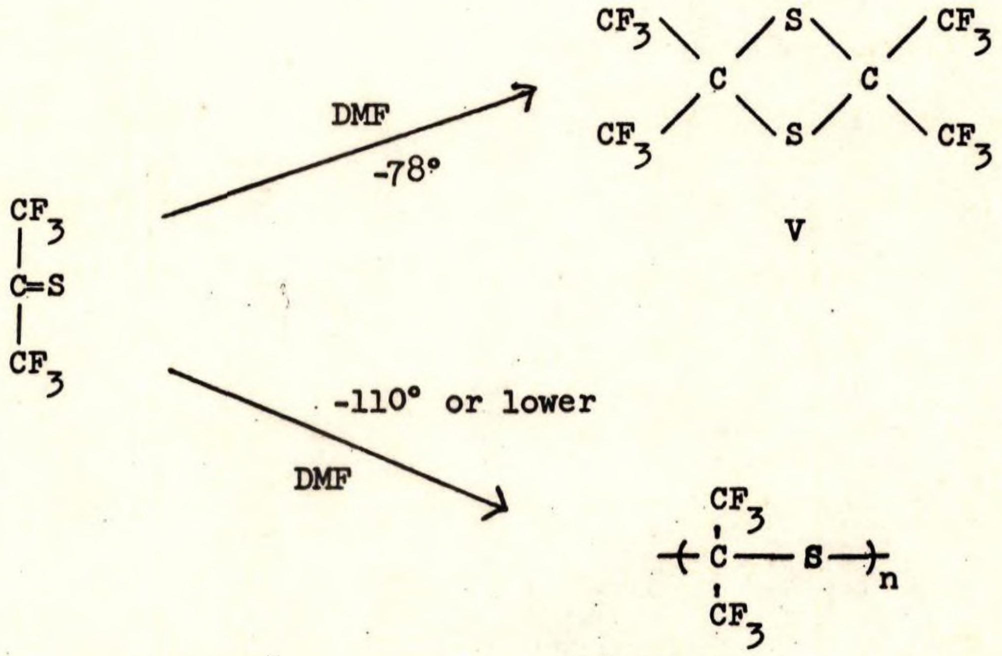
$$F^{\ominus} + CF_2{=}S \longrightarrow CF_3S^{\ominus}$$

$$CF_3S^{\ominus} + nCF_2{=}S \longrightarrow CF_3S\text{-}(CF_2S)_{n-1}\text{-}CF_2\text{-}S^{\ominus}$$

$$CF_3S\text{-}(CF_2S)_{n-1}\text{-}CF_2\text{-}S^{\ominus} \longrightarrow CF_3S\text{-}(CF_2S)_{n-1}\text{-}CF{=}S + F^{\ominus}$$

Polymers from Fluoroalkylthioacyl Halides and Fluorothioketones. - Compounds obtained by substitution of fluoroalkyl for the fluorine in $CF_2{=}S$ also respond to anionic initiation. Trifluorothioacetyl fluoride and difluorothioacetyl fluoride each polymerize under the optimum conditions for thiocarbonyl fluoride. The polymerizability of the C=S group extends to thioacyl chlorides. Chlorodifluorothioacetyl chloride reacts similarly to the thioacyl fluorides. In these cases polymerization is slower than with thiocarbonyl fluoride, and the products are either logy elastomers or brittle solids.

The polymerization of fluorothioketones is complicated by the ease with which these compounds dimerize to give 1,3-dithietanes. This dimerization is catalyzed by anionic catalysts. For example, the speed with which hexafluorothioacetone dimerizes to tetrakis(trifluoromethyl)-1,3-dithietane (V) is greatly increased by addition of a trace of dimethylformamide.



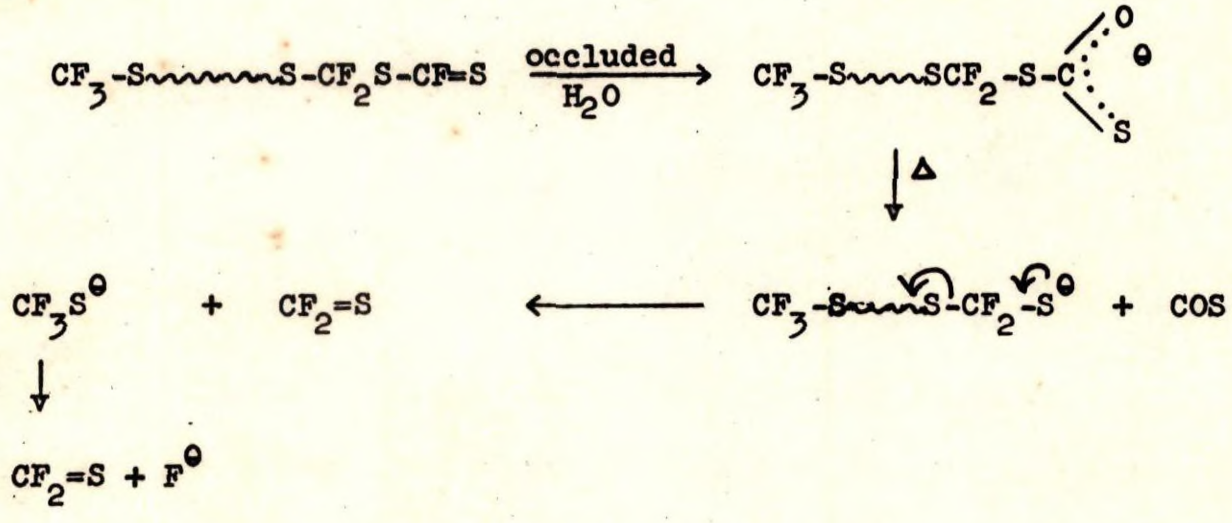
At lower temperatures, the dimerization can be suppressed sufficiently for moderate amounts of polymer to be formed. A better procedure is polymerization at very low temperatures with the etherate of boron trifluoride.

Polyhexafluorothioacetone is a white elastomeric substance insoluble in most common organic solvents. The polymer can easily be pressed into films, but these gradually degrade upon storage at room temperature. The degradation reaction is a spontaneous depolymerization to monomer, which then dimerizes to form V.

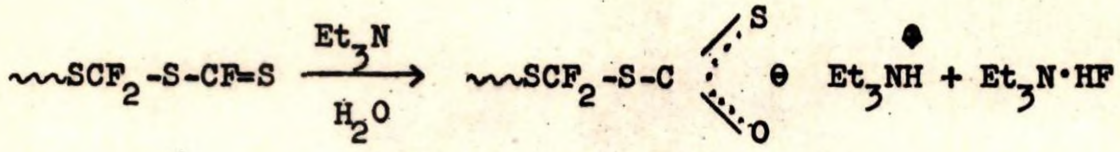
<u>Copolymers</u>. - Thiocarbonyl fluoride copolymerizes in anionic systems with a number of fluorothioacyl fluorides and with hexafluorocyclobutanone. These comonomers are not as reactive as thiocarbonyl fluoride and invariably become the minor component of the copolymer even if used in quite large proportion in the polymerizing mixture. The products are markedly different from the homopolymer of thiocarbonyl fluoride, though copolymers containing low proportions of comonomer are elastic and quite resilient. They also have lower crystallization temperatures.

Copolymerization of thiocarbonyl fluoride with chlorofluorothioacetyl fluoride, $ClCFHCF{=}S$, by dimethylformamide initiation has given high molecular weight products containing 1-3% of the latter monomer. These polymers do not cold-draw at room temperature and those containing close to 3% of the comonomer have crystallization temperatures below 0°. Copolymers containing 10-50% of chlorofluorothioacetyl fluoride are obtained by initiation with tetraisopropyl titanate in ether or petroleum ether. These polymers are of relatively low molecular weight and are much less rubbery than thiocarbonyl fluoride.

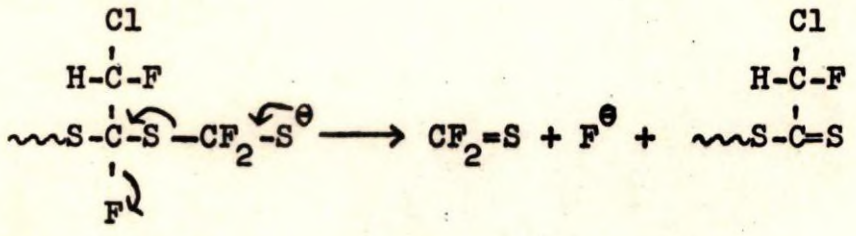
The thiocarbonyl fluoride/chlorofluorothioacetyl fluoride copolymers have better thermal and chemical stability than thiocarbonyl fluoride homopolymers. For example, they retain 50-80% of their weight when heated one hour at 225° in air, conditions under which the homopolymer retains no more than 15-30% of its weight. Also, copolymers are degraded much more slowly by triethylamine than is the homopolymer. These results indicate that the $-CF(CClFH)-S-$ group resists depolymerization better than $-CF_2-S-$. These depolymerization reactions are believed to start at the unstable $-CF{=}S$ end. Though the chemistry of depolymerization has not been worked out, a possible mechanism for thermal degradation is



Amine degradation could involve the same reactions and would be expected to proceed more readily because the amine can assist hydrolysis.



The copolymer undoubtedly would undergo the same reactions, except a chain-stopping fluoride elimination could occur at the comonomer site.



Of course, the homopolymer can eliminate fluoride ion also, but if it does, a ~CF=S group would be formed that could start the degradation sequence over again. Hydrolysis of the -CF=S end group is known to occur. Glass containers in which homopolymers and copolymers are stored eventually become etched by the HF evolved by this hydrolysis.

Copolymers of thiocarbonyl fluoride with perfluorothioacetyl fluoride, $CF_3CF{=}S$, are readily made in ether at -80° using either N-methylmorpholine or tetraisopropyl titanate as initiators. These products contain as much as 13-40% of $CF_3CF{=}S$. They are of relatively low molecular weight and films pressed from them are limp, opaque, and much less elastic than polythiocarbonyl fluoride. Unlike copolymers with chlorofluorothioacetyl fluoride, these copolymers do not melt very much lower than the homopolymer.

Thiocarbonyl fluoride/hexafluorocyclobutanone copolymers are readily prepared at low temperatures in ether using cesium fluoride as a catalyst. The copolymers, which can contain 14% of the cyclobutanone, are of low molecular weight, and have properties intermediate to those of the elastomeric polythiocarbonyl fluoride and the high-melting polyhexafluorocyclobutanone.[4]

EXPERIMENTAL

Polymerization of Thiocarbonyl Fluoride by Initiation with Dimethylformamide. - Thiocarbonyl fluoride was prepared by cracking 2,2,4,4-tetrafluoro-1,3-dithietane.[2] The monomer was purified by distillation through a 2 ft. x 9 mm. vacuum-jacketed column packed with glass helices and having a still-head that was cooled with a solid carbon dioxide-acetone mixture. The fraction boiling at -54° was taken as pure monomer. A glass container cooled in a solid carbon dioxide-acetone mixture and containing 75 ml. of thiocarbonyl fluoride (ca. 100 g.) was connected through glass tubing to a dry polymerization flask fitted with a stirrer and containing 100 ml. of sodium-dried diethyl ether. The contents of both vessels were frozen by cooling with liquid nitrogen, and the system was evacuated. Then the thiocarbonyl fluoride was distilled into the polymerization flask and dry nitrogen added to bring the system back to atmospheric pressure. The liquid nitrogen bath surrounding the polymerization flask was replaced with a solid carbon dioxide-acetone bath. After the contents of the polymerization flask had melted, the stirrer was started and five drops of dimethylformamide was added from a No. 22 hypodermic syringe needle. Polymerization was essentially complete after two hours, but it was usually convenient to hold the polymerization mixture at -78° for 18 hours. The polymer separated as a white spongy mass that was boiled in water containing 5 ml. of 50% nitric acid to destroy dimethylformamide and expel ether. The yield of dry polymer was essentially quantitative. Inherent viscosities determined using 0.5% solutions in chloroform were from 4 to 6.

Films can be obtained by pressing at 150° and 10,000 lb. ram pressure. Because the polymer is of high viscosity and flows slowly, it is desirable to allow two hours in the press to obtain smooth films. As removed from the press, such films are translucent and elastic. On standing at room temperature, they slowly become opaque and plastic because of crystallization of the polymer. The crystallization temperature is 35°. Torsion pendulum measurements indicated a Tg of -118° and a shear modulus of 2 X 10^7 dynes/$cm.^2$

Polymerization of Thiocarbonyl Fluoride by Initiation with Tetraisopropyl Titanate.[4] A. In Petroleum Ether. - Tetraisopropyl titanate (1.07 g., 0.01 mole) was dissolved in 250 ml. of petroleum ether, and the solution was cooled to -80°. Thiocarbonyl fluoride (25 ml., 34.8 g., 0.42 mole) was distilled into this solution with stirring over a period of 45 minutes. Polymer appeared as a white precipitate immediately upon addition of thiocarbonyl fluoride. Stirring was continued for 30 minutes after monomer addition was complete. Thereupon, 250 ml. of methanol was added and the whole allowed to warm to room temperature. The polymer was separated on a filter, washed with methanol and dried in vacuo at 70°. The yield of polymer was 32.5 g. (93%). It was a white, rubbery crumb having an inherent viscosity (0.1% solution in chloroform at 30°) of 2.91.

B. In Ether. - Polymerization was carried out as described above except dry ether was used as a solvent in place of petroleum ether. As indicated in the table below, yields were low and molecular weight could be controlled by addition of isopropyl alcohol to the polymerization mixture.

g. isopropyl alcohol added	Polymer Yield g.	Polymer Yield %	η_{inh}* of Polymer
0.0	19.9	57	2.88
0.15	19.5	56	2.03
0.6	24	69	1.74
1.2	19.5	56	1.13
2.4	17.1	49	1.04

* 0.1% solutions in chloroform.

C. In Chloroform. - To 40 ml. of alcohol-free chloroform was added 1 ml. (0.0035 mole) of tetraisopropyl titanate. The solution was cooled to -27° and to it was added with stirring 6 ml. (8.4 g., 0.1 mole) of thiocarbonyl fluoride over a period of 15 minutes. A white slurry formed that was held at -25° for 20 minutes. It was then allowed to warm to room temperature during which time the polymer dissolved. Addition of 50 ml. of methanol to the clear solution caused the precipitation of a viscous syrup. Ethyl alcohol, isopropyl alcohol, and acetic acid were equally effective as precipitating solvents. The product was washed with methanol, reprecipitated from chloroform with methanol, and dried in a vacuum desiccator containing sodium hydroxide and "Drierite." The product was a colorless syrup weighing 7.4 g. (88%). The infrared spectra of polymers prepared in this way contain a doublet in the region of 7.2 to 7.25 µ, which indicates the presence of isopropyl groups.

Polymerization Initiators. - A number of other materials were tried as initiators for the polymerization of CF_2S in dry ether at -80°. This was essentially the same experiment as described above for dimethylformamide initiation except for use of materials given in the following table.

Initiator	Product
Di(hydrogenated tallow)dimethylammonium methoxide	Tough, high molecular weight polythiocarbonyl fluoride (ηinh=6.9) formed in 30% yield.
Di(hydrogenated tallow)dimethylammonium chloride	Moderate molecular weight polythiocarbonyl fluoride (ηinh=2.0) obtained in 70-75% yield.
Tetraethylammonium chloride	Low molecular weight polymer formed in 40% yield.
$Al(i-OC_3H_7)_3$	High molecular weight polythiocarbonyl fluoride obtained in 58-60% yield.
Diisopropylamine	70-75% yield obtained of tough polymer, ηinh=1.21.
Triethylamine	58% yield of low molecular weight polymer (ηinh=0.80) formed.
Triphenylphosphine	30% yield of moderate molecular weight polymer.

Reaction of Polythiocarbonyl Fluoride with Antimony Pentafluoride. - High molecular weight polythiocarbonyl fluoride (92 g.) was dissolved in 3800 ml. of carbon tetrachloride. Antimony pentafluoride (2.3 ml., 6.9 g.) dissolved in 25 ml. of 1,1,2-trichlorotrifluoroethane was added with stirring. After 15 minutes, the solution was filtered, 4000 ml. of methanol was added, and the mixture was evaporated to about 1500 ml. The oil that separated was washed three times with methanol and then dissolved in 50 ml.

of carbon tetrachloride. The solution so obtained was filtered and solvent was removed from the filtrate. The residue amounted to 85 g. (92%) of colorless oil. This oil dissolved in pyridine or triethylamine without noticeable reaction. The oil was purified by solution in triethylamine followed by precipitation with water, washing with water and dilute hydrochloric acid, and drying.

Anal. Calcd. for $CF_3S(CF_2S\rightarrow_{50}CF_3$: C, 14.6; S, 38.2; F, 47.2; CF_2/CF_3, 25; mol. wt., 4270. Found: C, 14.3, 14.3; S, 38.1, 38.3; F, 47.6; 47.3; CF_2/CF_3 (by NMR), 25; mol. wt. (ebullioscopic in benzene), 2500.

The NMR peaks referred to above are 43.5 ppm. for $-S-CF_2-S-$ and 37.6 ppm. for $-SCF_3$ both at higher field than CCl_3F (external standard)

Lower molecular weight compounds were obtained by refluorination of 231 g. of the above oil dissolved in 185 ml. of trichlorotrifluoroethane by reaction with 5 ml. of antimony pentafluoride for one hour at room temperature. After filtration and removal of solvent there was obtained 198 g. of a pink liquid that was distilled through a short-pass still at very low pressures.

Fraction	b.p.	Molecular Weight NMR	Cryoscopic
I	90-100° (0.005 mm.)	498	460
II	100-110° (0.005 mm.)	990	675
III	110-150° (0.005 mm.)	1810	935

The infrared spectra of all three fractions were identical and showed absorption at 4.75 μ for the CF overtone, at 7.65 μ, which is associated with CF_3-S-C, at 8.9 μ for CF, at 12.25 μ for CS in $-CF_2S-$, and at 13.13 μ for CS in CF_3S-. Nuclear magnetic resonance showed only two kinds of fluorine and the NMR molecular weights were calculated from the ratios for the areas for CF_2 and CF_3. Mass spectroscopic analysis of Fraction II indicated the main constituent to be $C_4F_{10}S_3$. Fraction I was separated by gas chromatography into two components denoted A and B.

<u>A</u>. Calcd. for $CF_3S(CF_2S)_4CF_3$: C, 14.5; F, 53.4; S, 32.1; mol. wt., 498. Found: C, 14.65; F, 53.32; S, 32.74; mol. wt., 510.

<u>B</u>. Calcd. for $CF_3S(CF_2S)_5CF_3$: C, 14.5; F, 52.4; S, 33.1; mol. wt., 580. Found: C, 15.04; F, 52.41; S, 33.99; mol. wt., 580.

<u>End-Group Determination Using Methanol-C^{14}</u>. - Polythiocarbonyl fluoride was prepared by initiation with DMF in dry ether at -60°. After a 2-hour polymerization period, the polymer was washed with cold ether and purified by two consecutive reprecipitations from carbon tetrachloride solution with petroleum ether. The number average molecular weight of this polymer was found to be 335,000 by osmotic pressure measurements on a chloroform solution. To a solution of 1.5 g. of this polymer in 75 ml. of carbon tetrachloride was added 0.20 g. of methanol-C^{14} that had a specific activity of 8.24×10^8 disintegrations per minute per gram. After 4 hours at 43-48°, the polymer was isolated by precipitation with petroleum ether. Then the polymer was

purified by six consecutive reprecipitations from very dilute carbon tetrachloride solutions with petroleum ether. The polymer was dried and found to have an activity of approximately 78500 disintegrations per minute per gram. Therefore,

$$\frac{78500 \times 335000}{8.24 \times 10^9} = \text{approximately 32 g. (1 mole) methanol-}C^{14}\text{ per mole of polymer}$$

Thus, there is, on the average, one group per chain capable of reacting with methanol.

Initiation of Polymerization with Dimethylformamide-C^{14}. - Dimethylformamide tagged with C^{14} in the carbonyl group (DMF-C^{14}) and having a specific activity of 1.55×10^9 disintegrations per minute per gram was dissolved in ether to give a 1.96% solution. To a solution of 3 ml. of thiocarbonyl fluoride in 20 ml. of ether cooled to -50° was added 0.5 ml. of the DMF-C^{14} solution (total activity = 1.516×10^7 disintegrations per minute). Polymerization was allowed to proceed for 2 hours at -50 to -52°. The polythiocarbonyl fluoride that formed separated as an amorphous white polymer. It was washed with ether and purified by several reprecipitations from chloroform with petroleum ether. Contact with water was avoided to minimize the possibility of replacing any bound dimethylformamide by hydroxyl groups. Purified polymer was dissolved in m-xylene for counting and found to have no activity above background.

The inherent viscosity of 0.1% chloroform solutions of the polymer was 2.03, which corresponds to a $\bar{M}_n$ of 300,000-400,000. Since a polymer having a kinetic chain length of 5×10^6 would have a count of 70-100 disintegrations per minute if a DMF-C^{14} residue remained with every kinetic chain, it is apparent that less than one in ten chains contain such a residue. Indeed, there is no evidence for any of the chains containing DMF-C^{14}.

Polymerization of Hexafluorothioacetone.[6] - The polymerization of hexafluorothioacetone was initiated by BF_3·etherate at very low temperatures. A dry glass trap containing 1 ml. of BF_3·etherate was immersed in liquid nitrogen and evacuated. Perfluorothioacetone (5 ml.) was distilled into the trap. The trap was then removed from the liquid nitrogen bath and allowed to warm to the point where the frozen contents slowly melted. When the blue color of the hexafluorothioacetone disappeared, 15 ml. of acetone was added. The insoluble product was separated, washed with acetone, and dried. The yield of polyhexafluorothioacetone was 1.7 g.

Anal. Calcd. for C_3F_6S: S, 17.16. Found: S, 17.28.

The polymer was a white, rubbery elastomer insoluble in most common organic solvents. It was pressed into a film by use of a Carver press with the platens heated to 50° and under a ram pressure of 10,000 lb. The film was elastomeric. However, when the film was kept for several days at room temperature, the polymer gradually degraded. After sufficiently long storage, it spontaneously changed to hexafluorothioacetone dimer.

The polymer of hexafluorothioacetone was also obtained by initiation with dimethylformamide. In this case, a solution of 2 drops of dimethylformamide and 5 ml. of ether in a glass trap was frozen by immersion of the trap in liquid nitrogen. The trap was evacuated and 2 ml. of hexafluorothioacetone was distilled into it. The contents of the trap were then warmed until about one-half melted. Materials in the trap were refrozen by reimmersion into liquid nitrogen and then remelted. This procedure was repeated until the blue color of the thioketone disappeared. Then the trap and its contents were warmed to room temperature and 25 ml. of acetone was added. The polymer that separated was washed with acetone and dried. It weighed 0.7 g. and was similar to the product described above.

Polymerization of Chlorodifluorothioacetyl Chloride.[7] - The monomer is a deep-red liquid.[3] A solution of 4 g. of this monomer in 20 ml. of dry ether was cooled in a trap immersed in a solid carbon dioxide-acetone bath. One drop of dimethylformamide was added, and the resulting solution was kept cool for 4 hours. After this time, most of the red color had faded. Polymer was precipitated by addition of methanol, separated, washed with methanol, and dried in vacuo. The yield was essentially quantitative. The polymer was pressed into a film in a Carver press at 80° and 10,000 lb. ram pressure. The film was tough, white, and flexible. In contrast to the thiocarbonyl fluoride polymer, it was not elastomeric.

Anal. Calcd. for $C_2Cl_2F_2S$: C, 14.56; Cl, 42.98; F, 23.03; S, 19.40. Found: C, 14.92; Cl, 42.97; F, 23.79; S, 19.79.

Polymerization of Fluorothioacyl Fluorides by Dimethylformamide Initiation. - Most fluorothio acid fluorides polymerize quite well by the procedure described for dimethylformamide initiation of thiocarbonyl fluoride. Some examples are given in the following table.

Thioacid Fluoride	Type of Polymer	Analysis
$HCF_2CF{=}S$[8]	82% yield of a tough somewhat elastic polymer	Calcd. for C_2HF_3S: S, 28.1 Found: S, 28.2.
$CF_3CF{=}S$[3]	Quantitative yield of a rubbery polymer	Calcd. for C_2F_4S: C, 18.19, F, 57.54; S, 24.27. Found: C, 18.21; F, 57.31; S, 24.01.
$ClCF_2CF{=}S$[3]	A flexible, crystalline polymer that becomes rubbery when heated above 50°, and tacky above 100°	Calcd. for C_2ClF_3S: C, 16.17; Cl, 23.87; F, 38.24; S, 21.58. Found: C, 16.46; Cl, 24.06; F, 38.24; S, 21.51.
$CF_3CF_2CF{=}S$[3]	65% yield of a light pink, tacky solid. Soluble but not in alcohol	Calcd. for C_3F_6S: C, 19.79 F, 62.61; S, 17.61. Found: C, 19.57; F, 62.41; S, 17.42.

Polymerization of Pentafluoro-3-butenoyl Fluoride. - This compound[3] polymerized when it was stored at room temperature in a sealed glass tube for two weeks. The polymer is elastomeric and retains rubbery character when heated to 240°, the temperature at which it decomposes. It is insoluble in such solvents as acetone, alcohol, and hydrocarbons.

Anal. Calcd. for C_4F_6S: C, 24.75; F, 58.73; S, 16.52. Found: C, 24.63; F, 58.58; S, 16.82.

Copolymerization of Thiocarbonyl Fluoride and Chlorofluorothioacetyl Fluoride. - A solution of 7.5 g. of thiocarbonyl fluoride, 0.3 g. of chlorofluorothioacetyl fluoride,[8] and 20 ml. of anhydrous ether was cooled to -80°. Polymerization was initiated by addition of 0.05 g. of dimethylformamide dissolved in 6 ml. of anhydrous ether. After 5 hours at -80°, at which point the yellow color of the chlorofluorothioacetyl fluoride had disappeared and much polymer had precipitated, the reaction mixture was poured into hexane. Copolymer obtained by filtration amounted to 4.4 g. It was purified by reprecipitation from chloroform with methanol. Hot-pressing at 150° and 10,000 lb. ram pressure gave a clear, snappy film. The copolymer, η_{inh} (0.1% in chloroform) = 1.89, does not crystallize at 15°, can be cold drawn below 0°, and retains flexibility at -80°.

Anal. Found: C, 15.08; H, 0.59; Cl, 0.66; S, 40.40.

This copolymer contained approximately 2 mole % of chlorofluorothioacetyl fluoride. The composition of the copolymer formed can be adjusted between 1 and 3 mole % by the ratio of monomers used in the polymerization.

Copolymerization of Thiocarbonyl Fluoride with Perfluorocyclobutanone. - An 86:14 CF_2S/C_4F_6O copolymer was prepared from 7.5 g. of thiocarbonyl fluoride and 3 g. of perfluorocyclobutanone[9] dissolved in 10 ml. of anhydrous ether cooled to -80° and initiated with 0.05 g. of cesium fluoride. After 3 hours at -80°, the reaction mixture was poured into water. The polymer that precipitated was washed with acetone and purified by reprecipitation from chloroform solution by addition of methanol. The yield of dry product, η_{inh} (0.1% in chloroform) = 0.40, was 3.1 g. Hot-pressing gave a soft, opaque film that is only slowly attacked by triethylamine.

Anal. Found: C, 17.92; F, 51.31; S, 29.15.

Copolymerization of Thiocarbonyl Fluoride and Trifluorothioacetyl Fluoride.[10] - An 85:15 CF_2S/CF_3CFS mixture was polymerized by dissolving 10.5 g. of thiocarbonyl fluoride and 3 g. of trifluorothioacetyl fluoride in 25 ml. anhydrous ether, cooling to

-80° and adding 2 drops of N-methylmorpholine. After 5 hours, the reaction mixture, which contained precipitated polymer, was poured into 18% hydrochloric acid. The solid polymer obtained, after washing with water and acetone and drying, amounted to 9.7 g. It was purified by reprecipitation from chloroform with methanol. This was an 88:12 CF_2S/CF_3CFS copolymer, η_{inh} (0.1% $CHCl_3$) = 1.19, that could be pressed at 150° and 10,000 lb. ram pressure to an opaque, limp film. It slowly crystallized at 28° to an opaque plastic.

Anal. Calcd. for $[CF_2S]_8[CF_3CFS]$: C, 15.3; F, 48.2; S, 36.5. Found: C, 15.36; F, 48.78; S, 36.53.

A 60:40 CF_2S/CF_3CFS copolymer that does not crystallize at 28° was prepared from a 62:38 monomer mixture. To a solution of 4.5 g. of thiocarbonyl fluoride and 4.5 g. of trifluorothioacetyl fluoride in 10 ml. of anhydrous ether that was cooled to -80° was added 0.1 g. of tetraisopropyl titanate[11] dissolved in 5 ml. of anhydrous ether. After five hours, the reaction mixture was poured into methanol. The polymer that separated was purified by reprecipitation from chloroform with methanol and dried. The yield was 5.1 g. of polymer, η_{inh} (0.1% in chloroform) = 1.01, that could be hot-pressed at 150° to a limp film.

<u>Anal</u>. Calcd. for $[CF_2S]_3[CF_3CFS]_2$: C, 16.5; S, 31.4; F, 52.1. Found: C, 16.20; S, 31.84; F, 50.14.

<u>Acknowledgment</u>. - The authors have had many helpful discussions with Drs. A. L. Barney and W. E. Mochel of this laboratory, and their assistance is gratefully acknowledged.

mac
110*
3-17-65

References

1. Middleton, W. J., J. Org. Chem., ___, 0000 (1965), is the fourth paper in this series.
2. Middleton, W. J., E. G. Howard, and W. H. Sharkey, J. Am. Chem. Soc., 83, 2589 (1961).
3. Middleton, W. J., E. G. Howard, and W. H. Sharkey, J. Org. Chem., ___, 0000 (1965).
4. England, D. C., U. S. Patent 3,039,995 (June 19, 1962).
5. Walter, H. C., U. S. Patent 3,032,537 (May 1, 1962).
6. Middleton, W. J., U. S. Patent 3,069,396 (Dec. 18, 1962).
7. Middleton, W. J., U. S. Patent 3,113,936 (Dec. 10, 1963).
8. Harris, J. F., and F. W. Stacey, J. Am. Chem. Soc., 85, 749 (1963).
9. England, D. C., J. Am. Chem. Soc., 83, 2205 (1961).
10. Middleton, W. J., U. S. Patent 3,069,395 (Dec. 18, 1962).
11. Putnam, R. E., and H. C. Walter, U. S. Patent 3,032,536 (May 1, 1962).
12. Goodman, H. H., and L. T. Sherwood, U.S. Patent 2,994,687 (Aug. 1, 1961).