

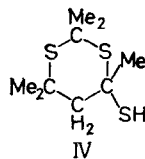
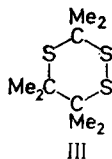
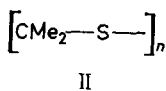
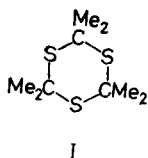
Polythioacetone

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Polythioacetone was prepared by spontaneous polymerization of the monomer in the liquid and solid phases, and in solution. Solid phase polymerization was initiated by sunlight. Fractionation gave a polymer with 27 000 molecular weight. Unlike trioxan and trithian, trithioacetone did not undergo ring opening polymerization. Thermodynamic calculations confirm that trithioacetone is more stable than linear polythioacetone. The polymer was unstable even at room temperature, but was more stable after reacting with ethyl isocyanate. The main decomposition product was trimer. Thermal decomposition began with some chain scission, and was followed by a monomolecular unzipping with an activation energy of 26.6 kcal mole⁻¹. Evidence was obtained suggesting that, during polymerization, about one monomer unit in fifty reacted in the thioenol form, interrupting the carbon-sulphur sequence, and resulting in pendant thiol groups. Some disulphide groups may also occur in the chain.

SEVERAL polythioacetals, with a backbone of alternating carbon and sulphur atoms, have been reported recently. Thus, polythioformaldehyde has been obtained from bis(chloromethyl) sulphide and sodium sulphide¹; from hydrogen sulphide and formaldehyde under pressure or from bis(mercapto-methyl) sulphide²; from methane dithiol using amine initiators³; and from trithian by X-ray initiated solid state polymerization^{4,5} or by ring opening polymerization^{6,7}. Thiocarbonyl fluoride⁸, hexafluorothioacetone⁹ and several other perfluorocarbonyl compounds¹⁰ have also been polymerized to linear polythioacetals.

Aliphatic thioketones such as thioacetone normally exist as stable cyclic trimers, e.g. (I), and although some physical properties of the monomers have been given¹¹⁻¹³, the formation of linear polymers has not been recorded. Recent work in these laboratories¹⁵ has shown that substantially pure monomeric thioacetone spontaneously polymerizes to linear polymer (II). Hence these earlier products were of questionable purity. Linear polythioacetone (II), of molecular weight 2 000 was first reported by Bailey and Chu¹⁴, who found that pyrolysis of allyl isopropyl sulphide gave, among other products, monomeric thioacetone, which polymerized spontaneously. Ettingshausen and Kendrick¹⁵ independently prepared monomeric thioacetone by pyrolysis of the trimer *in vacuo*, and polymerization in the liquid phase gave polymers of molecular weight up to 14 000.



Ettingshausen and Kendrick showed, by mass spectrometry and n.m.r. measurements, that trithioacetone prepared from acetone, hydrogen sulphide and an acid catalyst contained small amounts of isomers (III) and (IV), and that benzoquinone removed the latter. They also showed that trithioacetone did not undergo ring opening polymerization to give (II), thus differing from trioxan and trithian.

EXPERIMENTAL

Special precautions were adopted to avoid disseminating the very offensive and unpopular odours of thioacetone and other products formed during this work. Reactions were carried out in a glove box containing a reservoir of alkaline permanganate for decontaminating apparatus. Small quantities of nitrogen dioxide released into the box destroyed unpleasant vapours presumably by catalysing oxidation.

Polymer molecular weights were determined in benzene solution, using a vapour pressure osmometer (mol. wt < 20 000) or by osmometry (mol. wt > 20 000).

Liquid-phase polymerization of thioacetone

Trithioacetone was purified by partial crystallization, recrystallization from methanol, or treatment with sodium plumbite ('Doctor' solution). The purified product, still unexpectedly containing (III) (see *Table 1*) melted at 21.8°C. This mixture was used in the following experimental work, and is implied when the term 'trimer' or 'trithioacetone' is used. Bailey and Chu¹⁴ give a melting point of 22°C and Fromm and Baumann¹⁶ one of 24°C. We found that the melting point fell to 17.2°C after the trimer was kept at 65°C for 3 h, but that it was restored to 21.8°C after a further 48 h at room temperature. This phenomenon was not investigated further.

Table 1. Mass spectra of trithioacetone samples. Peak intensities relative to M/e 222 = 100

M/e	Isomer characterized	Initial product	Crystalline fraction	Methanol recryst.	Na plum-bite treated
83	(III)	14.7	20.9	20.1	15.0
138	(III)	91.0	120.2	112.8	90.0
157	(III)	4.5	5.6	5.8	5.0
188	(IV)	1.0	← 0.002 →		

Ettingshausen and Kendrick generated thioacetone in a conventional Keten apparatus modified to function at reduced pressure. In the present work this was simplified. A Pyrex reaction tube, 30 cm high 5.5 cm in diameter, contained a loose coil, made from 175 cm s.w.g. 22 Chromel A wire, which extended down two-thirds of the tube [*Figure 1(a)*]. At 17.5 V (31.5 W) very little cracking occurred. At 20 V (40 W) or above, 5 to 6 g of trimer was cracked per hour, but increased voltage led to a decrease in molecular weight of the subsequent polymer. Cracking conditions were therefore standardized at 20 V and 1 mm of mercury pressure. Under these conditions the coil had a long life, and little deposit formed on the walls of

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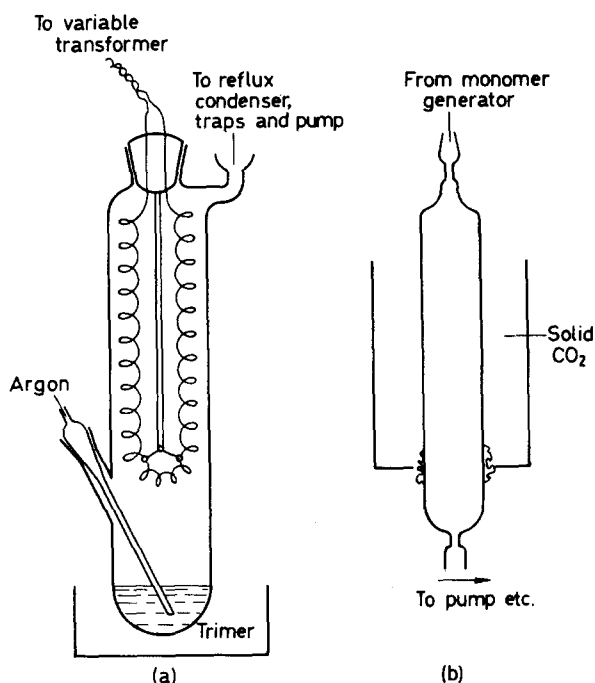


Figure 1—(a) Monomer generator; (b) Reaction tube

the reaction tube. It was calculated that the residence time in the reaction zone was less than ten seconds.

Thioacetone monomer prepared in this way was collected at -78°C and allowed to polymerize under various conditions. Results are summarized in Table 2. Where polymerization temperature is described as 'low', the reaction mixture in the -78°C trap was allowed to warm up undisturbed over two days. The solutions remained clear until the temperature reached -30° to -25°C , hence polymerization probably occurred in this tempera-

Table 2. Polymerization of thioacetone

Run No.	Solvent or comonomer*	Initiator	Polymerization temp. $^{\circ}\text{C}$	Polymer yield, percentage of trimer cracked	M.pt of polymer, $^{\circ}\text{C}$
1	None	—	low	72	119–120
2	Ether	—	low	81	124–5
3	Ether	BF_3 etherate	low	82	101–4
4	Ether	Sodium	low	86	111–6
5	Ether	Ph_3N	low	86	122–3
6	Chloroform	—	0°	20	108–9
7	Ethylene oxide	—	0°	86	120–2
8	Ethylene oxide	—	low	90	122–3
9	Epichlorhydrin	—	0°	57	122–3
10	Propylene oxide	—	0°	80	122–3
11	Solid state	Light	-78°	42	122–4

*The monomer was dissolved in an equal volume of solvent or comonomer.

ture range. Polymerization in solution was not observed after two days at -78°C in light, contrasting with the solid state polymerization in Run 11, discussed later. No copolymers were isolated, all the products being homopolythioacetone.

Solid-state polymerization of thioacetone

Some of the thioacetone monomer condensed on the wall of the -78°C trap as a thin layer of deep orange fernlike crystals. After a brief exposure to daylight the colour of the crystals slowly faded, and when warmed to room temperature some 24 hours later a film of polymer could be stripped from the wall, retaining the original form of the crystals (*Figure 2*). The molecular weight of this film could be as high as 33 000, but the polymer was not very stable in solution and results were erratic. The polymer film did not dissolve in benzene below 40°C .

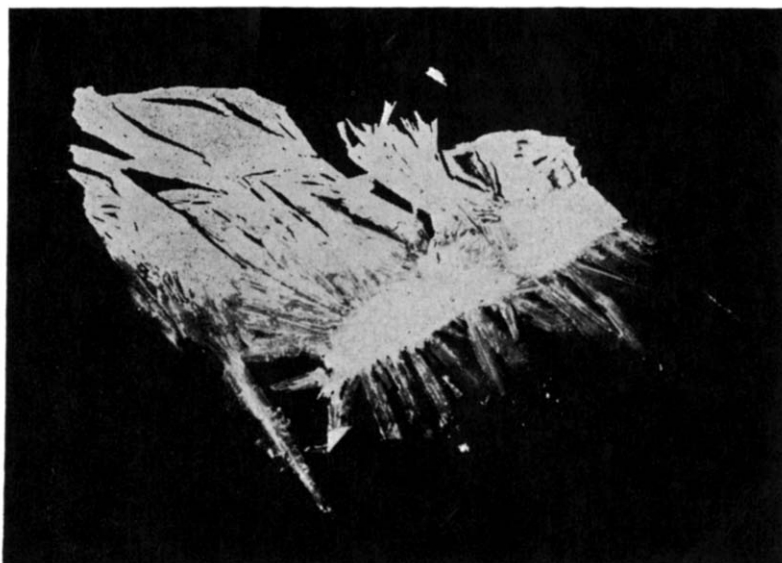


Figure 2—Solid phase polymerization of thioacetone

When the -78°C trap was protected from light by wrapping in aluminium foil, no polymerization of the crystalline monomer occurred in 24 hours. On exposure to light for about a minute, polymerization was initiated. After a further 48 hours at -78°C , acetone was added, and after warming to room temperature 42 per cent of polymer was isolated (*Table 2*, Run 11), molecular weight 13 700. A second run gave a 45 per cent yield. The distilled acetone washings gave a liquid of b.pt 100° to 115°C at 20 mm of mercury pressure in 39 per cent yield. This liquid was mainly trimer, hence under these conditions approximately equal amounts of polymer and trimer are produced.

This appears to be the first record of solid state polymerization initiated by radiation in the visible region.

Pyrolysis of trithioacetone at atmospheric pressure

The apparatus shown in *Figure 1(a)* was used without the reflux condenser, and 30 V was applied to the coil. Reaction products were collected in two traps, the first at 0°C and the second at -78°C. Argon was passed through the trimer at 175°C to 200°C, giving a trimer evaporation rate of between 2 and 5 g/h. Under these conditions about equal volumes of products collected in each trap. The brown condensate at 0°C, amounting to 43 to 51 per cent of the trimer cracked, contained 35 to 48 per cent of thioacetone as determined by the conventional hydroxylamine hydrochloride method for ketones. The very unpleasant smelling liquid collected at -78°C was not examined further.

The trimer was also pyrolysed, under an argon blanket, by direct heating in a flask fitted with a fractionating column. When the trimer was heated to 200° to 250°C it darkened and after 15 min appeared to boil, giving a brown distillate of b.pt 80° to 90°C. Mayer, Morgenstein and Fabian¹¹ report thioacetone to boil at 80°C. As distillation continued, the brown colour of the distillate diminished and the boiling point increased. The undistilled trimer was converted to a black tar. Using cracking temperatures of between 200° and 250°C, distillate yields were 60 to 70 per cent and their thioacetone content (hydroxylamine method) 38 to 41 per cent giving an overall yield of 20 to 30 per cent monomeric thioacetone. The results were unchanged when a length of Chromel A wire was immersed in the trimer, showing that the wire exerted no catalytic effect on the cracking.

The brown liquids obtained in these experiments did not deposit crystals at -78°C, although the monomer prepared by the vacuum process melted at -40°C. They reacted with 2,4-dinitrophenylhydrazine, however, with evolution of hydrogen sulphide, to give acetone-2,4-dinitrophenylhydrazone, confirming the presence of monomer. Attempts to prepare pure monomer by redistillation of the brown liquids were not successful. Heating converted monomer to trimer, the colour diminished, and the new distillates contained only 20 to 40 per cent of monomer. The product of one direct distillation pyrolysis at 250°C deposited five per cent of its weight of linear polymer on standing at room temperature. Otherwise none of the above products gave linear polymer, spontaneously or with possible catalysts. Storing at 0° or -78°C with boron trifluoride etherate, tertiary amines, or triphenyl phosphine led to fading of the colour at varying rates ($\text{BF}_3 > \text{R}_3\text{N} > \text{Ph}_3\text{P}$) but trimerization occurred. The colour was rapidly discharged by u.v. light, less rapidly by daylight.

PROPERTIES OF POLYTHIOACETONE

Polythioacetone, (II), was a white unpleasant-smelling powder of density 1.21. When of high molecular weight (above 10 000) it melted sharply at 124°C to a pink liquid, which on cooling resolidified to a brittle opaque mass. It was soluble in a variety of solvents, being very easily soluble in chloroform and tetrahydrofuran (*Table 3*). The polymer separated as a powder from cooled dioxan solutions.

Films of polythioacetone were prepared by evaporating solutions or by pressing between glass plates above the melting point for a very short time.

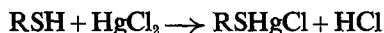
Table 3. Solubility of polythioacetone

<i>Solvents at room temperature</i>	<i>Solvents at 50°C</i>	<i>Non-solvents</i>
Chloroform	Trithioacetone	Alcohols
Carbon tetrachloride	Dioxan	Acetone
Ethyl isocyanate	Ethylene chlorhydrin	Ether
Benzene and other aromatics	Dimethylformamide	Ethylene oxide
Tetrahydrofuran		Paraffins
		Dimethyl sulphoxide

The films were glossy, translucent, or almost clear, and had no strength. In some cases they folded without breaking but were usually brittle. Threads drawn from a melt were initially elastic and transparent, but became brittle and opaque in a few minutes.

STABILITY OF TRITHIOACETONE AND POLYTHIOACETONE TO CHEMICAL REAGENTS

Attempts were made to estimate the thiol isomer (IV) in trithioacetone by reacting with mercury(II) chloride and estimating the hydrogen chloride formed¹⁷.



Instead of the expected reaction, cold aqueous mercury(II) chloride slowly hydrolysed the trimer to acetone, identified by its 2,4-dinitrophenylhydrazone, the yellow precipitate formed having a composition approximating to $\text{HgCl}_2 \cdot \text{HgS}$. Acetone-2,4-dinitrophenylhydrazone was isolated in 47 per cent yield from the distillate from the reaction of trimer, mercury(II) chloride and aqueous alcohol.

Following this observation, the effects of other salts were investigated. Aqueous silver nitrate and copper(II) chloride both decomposed trimer in the cold, giving acetone and quantitative yields of metal sulphide. Aqueous iron(II) and iron(III) salts and nickel salts did not react with trimer, but with solid iron(III) or mercury(II) chloride in the absence of water it gave the metal sulphide with evolution of hydrogen chloride and hydrogen sulphide. The trimer was stable to sodium plumbite ('Doctor' solution) even after 24 h at 100°C, the product recovered by steam distilling the reaction mixture being free of thiol (IV).

Solid polythioacetone was less stable to these reagents, whether ground together in the solid state or treated with aqueous reagent. In the latter case, metal sulphide and acetone were formed. Distillation of the polymer with aqueous alcoholic mercury(II) chloride gave a 67 per cent yield of acetone as the 2,4-dinitrophenylhydrazone. Splitting of the sulphide link by metal salts is not unknown^{18,19}, but polythioacetone reacted very easily.

The effects of various reagents are summarized in Table 4.

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Table 4. Stability of thioacetone trimer and polymer to metal salts at room temperature

<i>Reagent</i>	<i>Trimer</i>	<i>Polymer</i>
BF ₃ etherate	Stable	Unstable
Aq. sodium plumbite ('Doctor' solution)	Stable	Unstable
HgCl ₂ , anhydrous	Unstable	Unstable
HgCl ₂ , aqueous	Unstable	Unstable
FeCl ₃ , anhydrous	Unstable	Unstable
FeCl ₃ , aqueous	Stable	Unstable
CuCl ₂ , hydrate	Unstable	Unstable
CuCl ₂ , aqueous	Unstable	Unstable
NiCl ₂ , hydrate and aqueous	Stable	Stable
FeCl ₂ , hydrate and aqueous	Stable	Stable
AgNO ₃ , aqueous	Unstable	Unstable

Polythioacetone was unstable to hydrochloric acid and hot alcoholic potash. It was more stable to aqueous sodium hydroxide, but probably only because the reagent did not wet the polymer (*Table 5*).

Table 5. Stability of polythioacetone to acids and alkalis. Reaction conditions: 3 h at reflux

<i>Reagent</i>	<i>Polymer decomposed, per cent</i>
1% Hydrochloric acid	50
Conc. hydrochloric acid	(100% in 1 min)
20% aqueous NaOH	10
10% ethanolic KOH	56

ATTEMPTS TO PREPARE POLYTHIOACETONE SULPHONES

Cold alkaline permanganate slowly oxidized trithioacetone to the previously unreported monosulphone, m.pt 102°C (Found: C 42.3, H 7.0, S 38.0 per cent; C₉H₁₈S₃O₂ requires C 42.5, H 7.1, S 37.8 per cent). Warm alkaline permanganate (100°C) gives the disulphone, m.pt 209°C, yields in each case being about 80 per cent.

Further oxidation of the disulphone (hydrogen peroxide in acetic acid) gave a poor yield of trisulphone, m.pt 316°C. These sulphones are stable crystalline solids, and unsuccessful attempts were made to convert them to polysulphones by ring opening polymerization, using methods known to function with trithian.

Molten monosulphone, just above its melting point, was decomposed by a trace of boron trifluoride etherate and did not resolidify on cooling, and prolonged heating at 80°C gave no polymeric product. At 120°C, the mixture began to evolve a volatile product and the refluxing vapour was brown, characteristic of monomeric thioacetone. The condensate, on distillation, was unpleasant-smelling and almost colourless, and unexpectedly was shown by infra-red spectroscopy to consist mainly of acetone. This was confirmed by conversion to the 2,4-dinitrophenylhydrazone. The reaction was not continuous, but recommenced each time a drop of boron trifluoride

etherate was added. The mechanism by which the acetone was produced must have involved a ring opening and transfer of oxygen from sulphur to carbon. The monosulphone was unaffected by dimethyl sulphate until the temperature exceeded 175°C, when decomposition set in (cf. ref. 6).

The disulphone was unaffected by cationic catalysts in dimethyl formamide solution up to 170°C and was recovered unchanged. The molten disulphone decomposed above 215°C, and the decomposition was accelerated by boron trifluoride etherate, iron(III) chloride and mercury(II) chloride.

Bailey and Chu¹⁴ claimed that hydrogen peroxide in acetic acid oxidized polythioacetone to a polysulphone, m.pt 295°C (yield unstated). Under the same conditions, our polymer gave a 12 per cent yield of crystalline material, m.pt 300° to 310°C, which recrystallized from acetic acid as needles, m.pt 316°C. These were identical with authentic trithioacetone trisulphone. The polymer not converted to sulphone was found to have been quantitatively oxidized to sulphuric acid. Thus, Bailey and Chu's claim was not confirmed.

Addition of nitrogen dioxide or nitric acid to polythioacetone or trimer gave green complexes, which on heating gave only black tars. Polythioacetone was slowly but completely decomposed by permanganate.

THE THERMAL STABILITY OF POLYTHIOACETONE

Polythioacetone always emitted an unpleasant odour. When placed in the reservoir of a mass spectrometer at room temperature trimer was first desorbed, presumably the accumulated product of decomposition previous to the experiment, and then followed a steady evolution of monomer and trimer. At an inlet temperature of 250°C the products also included hydrogen sulphide, small amounts of $C_3H_6SC_3H_4$ ($M=114$), $C_6H_{10}SC_3H_4$ ($M=154$) and $C_3H_6SC_3H_6SC_3H_4$ ($M=188$) with minor amounts of a series $(C_3H_4)_n-SC_3H_6$.

The main decomposition product of polythioacetone is the relatively non-volatile trimer, b.pt 130°C at 13 mm pressure. In measuring the thermal decomposition of the polymer, it was important to establish that the observed rate of loss of weight was not, in fact, the rate of evaporation of accumulating trimer. To test this, polymer samples (0.2 g) of very different stabilities, and a sample of trimer were heated at 100°C in identical tubes (5 cm high \times 1.5 cm diameter). The trimer evaporated steadily at 7 mg/h, while the rates of weight loss of the polymer decreased with time and ranged from 2 to 50 mg/h. If trimer evaporation were the controlling factor, the rates of weight loss of the polymers would have increased until a steady value for trimer was reached, and would then have remained constant. The residues never contained more than one per cent of acetone-soluble material, proving that trimer did not accumulate.

The rate of thermal decomposition of unstabilized polythioacetone does not change appreciably with varying molecular weight. The rate usually increased until about 20 per cent had decomposed, after which there was an apparently first-order decomposition until about 30 per cent remained (Figure 3).

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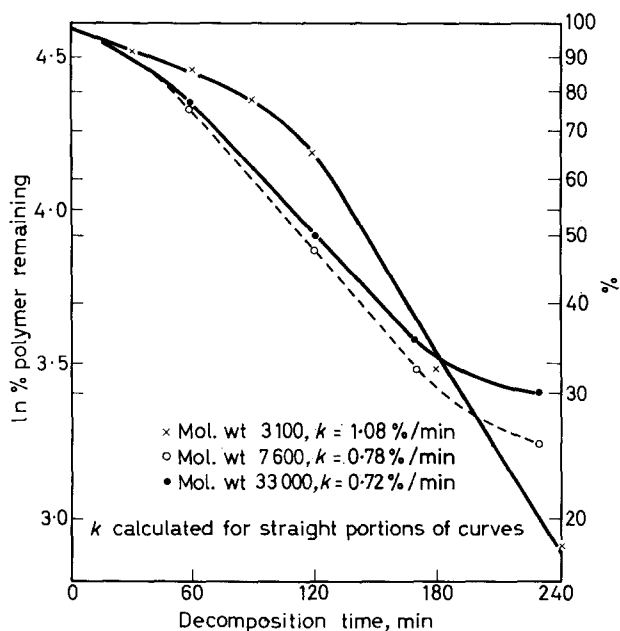


Figure 3—Effect of molecular weight on the thermal decomposition of unstabilized polythioacetone at 100°C in air

As with polyformaldehyde, polythioacetone could be stabilized with suitable end-capping reagents. Refluxing for one hour with acetic anhydride containing one per cent sodium acetate resulted in a 50 per cent loss of polymer. The product, however, had better initial thermal stability than the starting material, but the decomposition rate accelerated until it approached that of the initial polymer. Standing at room temperature with acetic anhydride and benzene had little effect on stability, but ethyl isocyanate (not phenyl isocyanate) gave considerably improved stability over a wide range of decomposition (Table 6).

Table 6. Decomposition rates of stabilized polythioacetone at 100°C

Stabilization procedure	Decomposition rate, per cent/min	Range of decomposition, per cent
None	0.26	0-20
None	1.1	20-80
Refluxing Ac_2O , NaOAc	0.05	0-20
Refluxing Ac_2O , NaOAc	0.8	20-80
EtNCO in benzene	0.043	10-85

For a more detailed investigation of stability, 100 g of polymer (Table 2, Run 2) was reacted with 50 ml of ethyl isocyanate in 200 ml of chloroform for one week at 0°C. The polymer was recovered by acetone precipitation and fractionated at 25°C by extracting with acetone-chloroform mixtures of increasing chloroform content. After extracting more soluble fractions,

17 g of polymer, of molecular weight 20 000, was obtained (which was soluble in a mixture of chloroform and acetone 13:7 v/v, but insoluble in a 12:8 v/v mixture) and 16 g of a higher fraction, molecular weight 27 000, insoluble in the 13:7 v/v mixture.

The polymer of molecular weight 27 000 was heated to between 110° and 115°C in a stream of argon, and was sampled at intervals. Each sample was washed with acetone to remove occluded trimer (the loss in weight in acetone washing proved to be less than one per cent), and finally pumped out for 6 h at 0.1 mm pressure. The molecular weight of the polymer fell rapidly at first, but reached a steady value of about 10 000 (*Figure 4*).

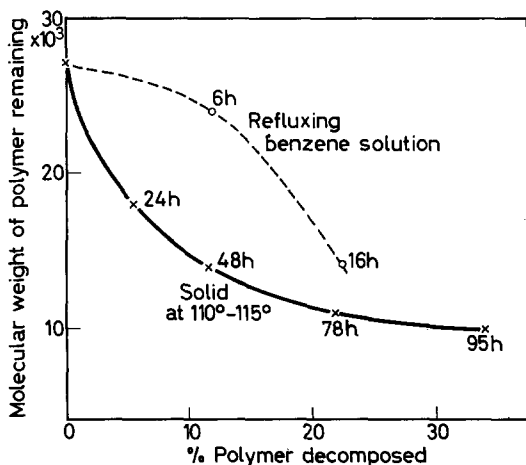


Figure 4—Molecular weight changes in polythioacetone during thermal decomposition at 110°C to 115°C or in refluxing benzene

The molecular weight in refluxing benzene (1 g of polymer to 3 ml of benzene) fell more slowly. The polymer was recovered from the benzene by acetone precipitation. Again the molecular weight was approximately 10 000 (see *Figure 4*).

The thermal decomposition of the polymer of molecular weight 20 000 was studied between 105° and 145°C. At 125°, 135° and 145°C the polymers were liquid and a first-order decomposition rate was followed from 10 to 90 per cent decomposition (*Figure 5*). Below the melting point (125°C) the results were erratic (*Figure 6*). At 118°C initial decomposition was rapid, this corresponding to the chain breaking stage. This was followed by a short first-order decomposition ($k=0.186$ per cent/min), but signs of melting then appeared. The rate of decomposition increased as melting progressed, and when melting was complete a further first-order decomposition was observed ($k=0.55$ per cent/min). Later, the rate decreased ($k=0.37$ per cent/min). At 105°C the polymer did not melt, and the first half of the decomposition, excluding a short initial faster reaction, was first order ($k=0.049$ per cent/min). This increased to about 0.1 per cent/min towards the end of the reaction.

When the logarithms of the rates of decomposition of the liquid polymer at 125°, 135° and 145°C, and those for the early stages of the solid decom-

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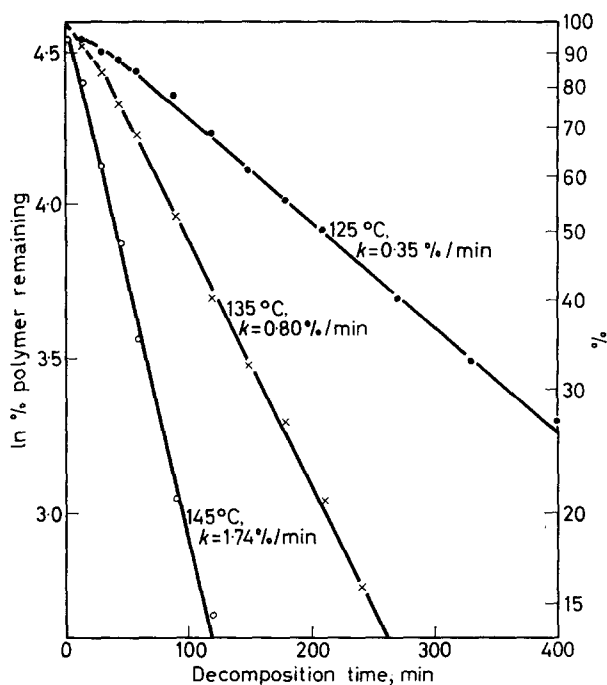


Figure 5—Thermal decomposition of polythioacetone, mol. wt 20 000, ethyl isocyanate stabilized in argon

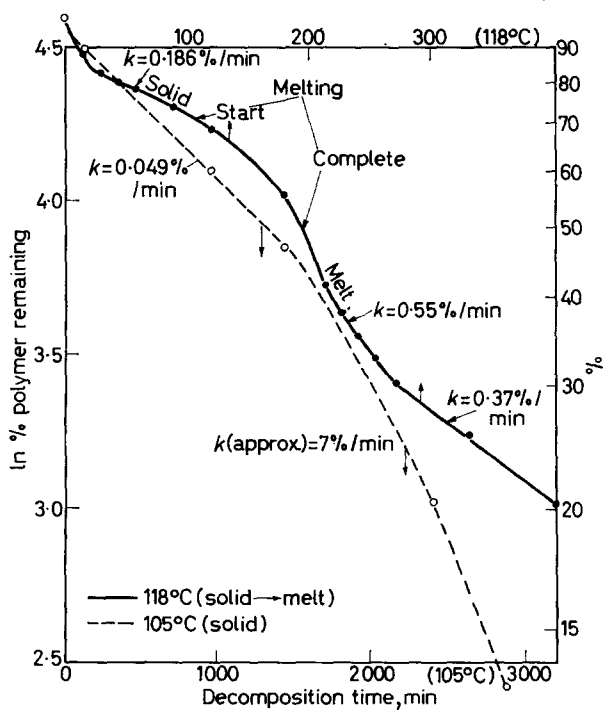


Figure 6—Thermal decomposition of polythioacetone, mol. wt 20 000, ethyl isocyanate stabilized in argon

position at 118° and 105°C, were plotted against the reciprocal of the decomposition temperature, a straight line was obtained corresponding to an activation energy of decomposition of 26.6 cal/mole.

THE STRUCTURE OF POLYTHIOACETONE

The properties of polythioacetone suggest that its structure is mainly that of the polythioacetal (II). Thus it decomposes in a first-order manner to monomer and trimer, has a simple n.m.r. spectrum¹⁵, and the i.r. spectrum is similar to that of the trimer, apart from the expected broadening of the bands (*Figure 7*). Decomposition with desulphurization gives acetone. Other evidence, however, indicates irregularities in the polymer chain.

The improved thermal stability of the polymer after reacting with acetic

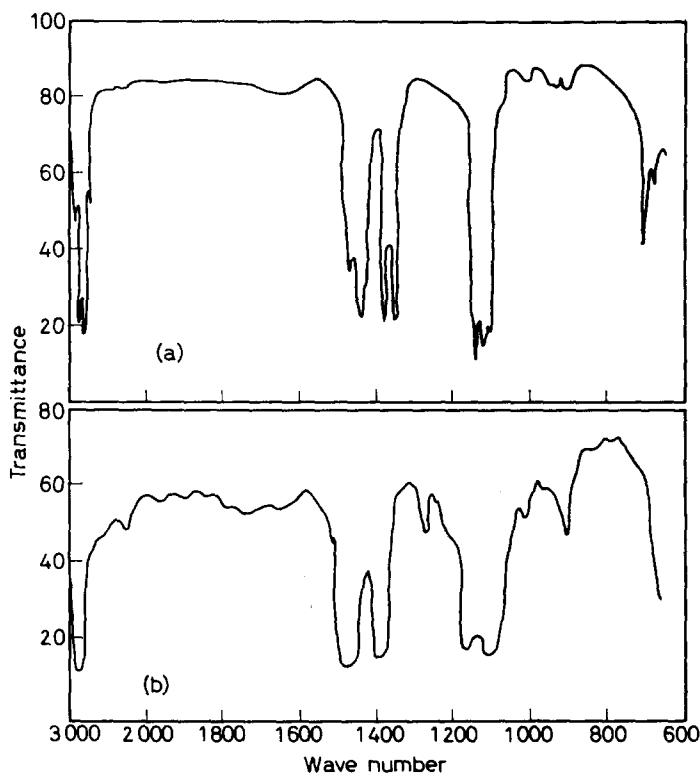


Figure 7—Infra-red spectra of thioacetone trimer and polymer:
(a) trithioacetone (liquid); (b) polythioacetone (film)

anhydride and especially with ethyl isocyanate suggested the presence of esterifiable end groups, possibly —SH. The nitrogen contents of ethyl isocyanate stabilized polymers, however, were not consistent with the presence of two nitrogen atoms per molecule, as shown in *Table 7*.

The nitrogen contents of the polymers prepared by the two methods followed different patterns. For polymers prepared in solution they were

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Table 7. Nitrogen contents of ethyl isocyanate stabilized polythioacetones

Polymer mol. wt	Preparative method	Nitrogen found, per cent	Nitrogen calculated for end groups, per cent	% N found minus % N calc.
9×10^3	In ether	0.66	0.31	0.35
20×10^3	In ether	0.55	0.14	0.41
27×10^3	In ether	0.45	0.10	0.35
3×10^3	Solid state	0.35	1.00	(-0.65)
14×10^3	Solid state	0.38	0.21	0.17

about 0.37 per cent in excess of the value required for end groups. The two polymers prepared in the solid state had nitrogen contents of about 0.38 per cent, unrelated to molecular weight or the number of chain ends. A possible explanation is that the solution-prepared polymer has terminal thiol groups whereas these are absent in the solid-state polymerization.

One terminal thiol group may be derived from hydrogen sulphide which is a byproduct of the monomer preparation and therefore available in the solution polymerization but not readily available in the solid phase. The nitrogen content of the stabilized solid-state polymerized product and the excess nitrogen in the stabilized polymer prepared in ether, which are virtually the same, 0.37 per cent, must therefore be due to pendant thiol groups. The poly-acetal sequence of alternating carbon and sulphur atoms is therefore interrupted by an occasional $-\text{CH}_2-\text{CMe}(\text{SH})-$ group (about 1 in 50) derived from the thioenol form of the monomer, $\text{CH}_2=\text{CMeSH}$. The rapid fall of molecular weight to 10 000 during thermal degradation suggested that the polymer contained a few very unstable links. They may be disulphide links, attached to tertiary carbon atoms: $-\text{CMe}_2-\text{S}-\text{S}-\text{CMe}_2-$. Absence of terminal thiol groups in the polymer would have been expected to give improved thermal stability. This was not observed. The anomalous groups in the polymer may therefore be analogous to the unsymmetrical isomers (III) and (IV) which occur in the trimer.

Unequivocal proof of the presence of these groups in polythioacetone has not been found, probably because their effects are slight and are masked by the preponderance of the main structure. The trimer obtained by decomposing the polymer contained the isomers (III) and (IV) and if the decomposition occurred by a backbiting process, this would constitute a proof. If the primary decomposition product is monomer, however transient its existence, these data are irrelevant to the structure of the polymer. Thermal decomposition of the polymer in the mass spectrometer gave a $\text{C}_6\text{H}_{10}-\text{S}-\text{C}_3\text{H}_5$ fragment, but the simultaneous appearance of a series of minor peaks $(\text{C}_3\text{H}_5)_n-\text{S}-\text{C}_3\text{H}_5$ (which may very well be formed in the apparatus by recombination reactions) introduces the suspicion that the C_6H_{10} group may also be an artefact.

THERMODYNAMIC CONSIDERATIONS

Before postulating a mechanism for thioacetone polymerization, the relevant thermodynamics will be considered.

An interesting fact emerging from this work is that cyclic trithioacetone

is the most stable component of the monomer-trimer-linear polymer system. This contrasts with the formaldehyde system in which linear polymer is the most stable. Theoretical confirmation of this seemed desirable and calculation of the relevant ceiling temperatures has therefore been attempted. Thermodynamic calculations as rigorous as those applied to formaldehyde were not possible, as the necessary bond energy E ($C=S$) is not accurately known. It was not possible to obtain this by thermochemical measurements on di-*t*-butylthione. Attempts to prepare this thioketone by published methods²¹ did not give a pure stable monomer.

Accordingly, the ceiling temperature has been estimated from the available data. To provide a check, consideration was given to formaldehyde and acetone. The heats of reaction for each system were calculated from estimates of the heats of formation of monomer, cyclic trimer and polymer obtained from additive bond energy relationships and heats of fusion and vaporization. Entropy changes for the polymerizations have been estimated in a similar way.

Enthalpy changes

These were calculated for the C, H, O compounds by using the bond energy scheme of Allen²⁸ with the revised parameters reported by Skinner and Pilcher²⁹. For the thioacetone problem one additional parameter, the bond energy E ($C=S$) = 110 kcal mole⁻¹ bond⁻¹ was estimated from a comparison of published heats of formation of CO₂, CS₂, (NH₂)₂CS, and Me₂CO. Strain energies introduced by steric hindrance in linear chains or cyclization have been estimated by a method introduced by Skinner²⁹. Heats of fusion of the polymers were estimated from literature values for similar polymers. Heats of vaporization were estimated from the cohesive energy densities of similar polymers and cross-checked by calculating the cohesive energy density using Small's additivity relationship²⁷.

Entropy changes

As far as possible, entropy changes were calculated from absolute values estimated by use of the method of chemical groups introduced by Benson and Buss²⁴. In addition, the following approximations have been made:

- (i) For the change 3 monomer \rightarrow cyclic trimer ΔS was assumed to be the same as 3 ethylene \rightarrow cyclohexane.
- (ii) For the polymerization monomer \rightarrow linear polymer ΔS_p is assumed to be the same as for the corresponding olefin polymerization, as given by Dainton and Ivin²⁵.

For monomer and trimer the entropy of vaporization is assumed to follow Trouton's rule, i.e. to be 21 cal mole⁻¹ (deg. K)⁻¹. For the linear polymer we assume from the data for polyethylene given by Dainton and Ivin²⁵

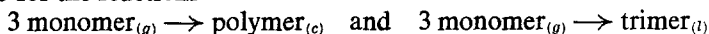
$$\Delta S_{c \rightarrow g} = 7 \text{ cal mole}^{-1} (\text{deg. K})^{-1} \quad \Delta S_{t \rightarrow g} = 4 \text{ cal mole}^{-1} (\text{deg. K})^{-1}$$

referred to the repeat unit of the polymer. Walden's rule applied to fusion of monomer and trimer gives $\Delta S_{c \rightarrow t} = 13 \text{ cal mole}^{-1} (\text{deg. K})^{-1}$ and consideration of the known heats of fusion of polymers suggests for a linear polymer that

$$\Delta S_{c \rightarrow t} = 3 \text{ cal mole}^{-1} (\text{deg. K})^{-1}$$

POLYTHIOACETONE

Enthalpy and entropy changes have been estimated and are shown in Table 8 for the reactions



The data for thioacetone in Table 8 assume that polymerization occurs through the thione form. The ceiling temperature for each reaction is estimated from the relationship

$$T_c = \Delta H / \Delta S$$

This is the temperature above which the free energy change for the reaction becomes positive. If we consider the free energy changes at some lower temperature T , then the higher T_c the more negative will be ΔG in the reaction. Thus comparison of T_c for polymer and trimer formation is a useful guide to their relative stabilities.

Table 8. Comparison of CH_2O and Me_2CS

$\text{Monomer}_{(g)} \rightarrow \text{Polymer}_{(c)}$				$\text{Monomer}_{(g)} \rightarrow \text{Trimer}_{(t)}$		
Sample	$-\Delta H$ kcal mole ⁻¹	$-\Delta S$ cal mole ⁻¹ (deg. K) ⁻¹	T_c °K	$-\Delta H$ kcal mole ⁻¹	$-\Delta S$ cal mole ⁻¹ (deg. K) ⁻¹	T_c °K
CH_2O	36.6	91.8	400	36.1	111	325
Me_2CS	135.3	144	940	136.6	107	1275

These results are consistent with the known experimental facts that polyformaldehyde may be formed from either the trimer or the monomer because the free energy of the polymer is always lower than that of the trimer. This is not so for thioacetone. Here, the thermodynamic functions show that the trimer is more stable than the polymer, and hence the reaction



would have a positive free energy change. This supports the observation that polythioacetone cannot be obtained directly from the trimer, but only after it has been converted to monomer.

These results also have some bearing on the comparative stabilities of polyformaldehyde and polythioacetone below the ceiling temperature ($\text{monomer}_{(g)} \rightarrow \text{polymer}_{(c)}$). Any decomposition of polyformaldehyde could give monomer or trimer in equilibrium with undecomposed polymer. Decomposition of polythioacetone would not give this equilibrium and trimer would result from an irreversible reaction. In fact, we have observed that unstabilized polythioacetone, on keeping in a sealed tube for 18 months at room temperature, was converted to the trimer in 28 per cent yield. Mass spectrometry showed the main decomposition product to be the trimer containing proportions of (III) and (IV), since its mass spectrum resembled those in Table I.

The ceiling temperature was measured by collecting 1 g portions of thioacetone monomer in thin-walled glass tubes at -78°C [Figure 1(b)]. The tubes were immediately plunged into constant temperature baths held at various temperatures. After one hour any polymer was washed out and weighed. The results are shown in Figure 8. A ceiling temperature of about 370°K is indicated.

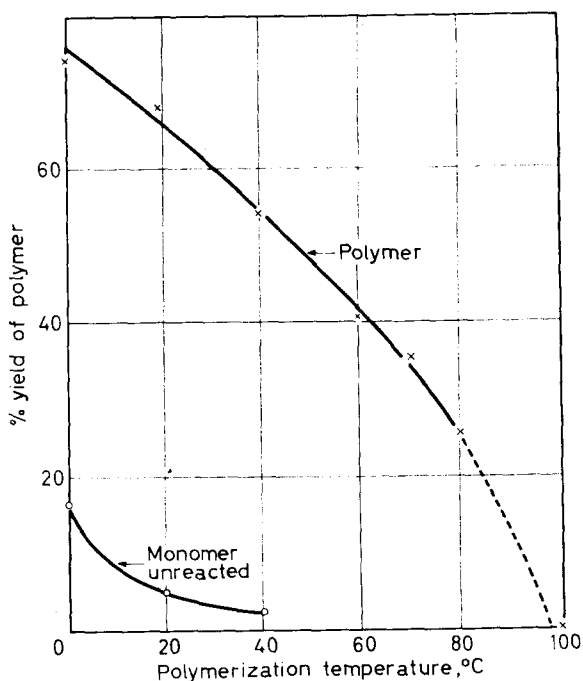


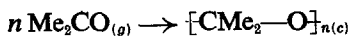
Figure 8—Variations in yield of polythioacetone from thioacetone monomer at various temperatures. Reaction duration, 1 h

The predicted ceiling temperatures for formaldehyde are acceptable, but for thioacetone the calculated 940°K is very high, the experimental estimate being 370°K . The uncertainty in the value of $E(\text{C}=\text{S})$ may be the sole cause of this discrepancy. On the other hand, polymerization may occur through the thioenol form and this assumption gives a lower estimate of ceiling temperature, viz. 540°K . If $E(\text{C}=\text{S})=110 \text{ kcal mole}^{-1} \text{ bond}^{-1}$ is correct, the indications are that polymerization proceeds through the thioenol form.

Table 9. Polymerization of thioacetone–thioenol form

	$-\Delta H$ kcal mole^{-1}	$-\Delta S$ cal mole^{-1} $(\text{deg. K})^{-1}$	$T_c^{\circ}\text{K}$
$\text{monomer}_{(g)} \longrightarrow \text{polymer}_{(c)}$	81	150	540

The acetone system differs from both thioacetone and formaldehyde. Reported preparations of polyacetone have been questioned²⁶ and the only products isolated were those of a reversible aldol type condensation, namely diacetone alcohol and triacetone dialcohol. For the reaction



$\Delta H = -7.2 \text{ kcal mole}^{-1}$, $\Delta S = -55 \text{ kcal mole}^{-1} (\text{deg. K})^{-1}$ and $T_c = 120^{\circ}\text{K}$.

For polymerization from liquid monomer, $\Delta H = 0$, hence $T_c = 0^\circ\text{K}$, that is polymerization is impossible.

For the observed reactions, the calculated thermodynamic functions are:



$$\Delta H = -9.9 \text{ kcal mole}^{-1}, \Delta S = -20 \text{ cal mole}^{-1} (\text{deg. K})^{-1}, T_c = 495^\circ\text{K}.$$



$$\Delta H = -18.5 \text{ kcal mole}^{-1}, \Delta S = -36.5 \text{ cal mole}^{-1} (\text{deg. K})^{-1}, T_c = 510^\circ\text{K}.$$

The calculations do not exclude other possible products but they confirm that aldol condensation is more favourable than polyacetal formation.

THE MECHANISM OF THIOACETONE POLYMERIZATION
Theories of the mechanism of thioacetone polymerization must account for the following:

(1) Addition of boron trifluoride etherate to polymerizing thioacetone reduced the molecular weight relative to that of spontaneously formed polymer without reducing yield (Table 3). It may therefore have induced polymerization.

(2) Boron trifluoride etherate initiates depolymerization of polythioacetone above 12°C .

(3) The polymer contains pendant thiol groups and a few disulphide linkages.

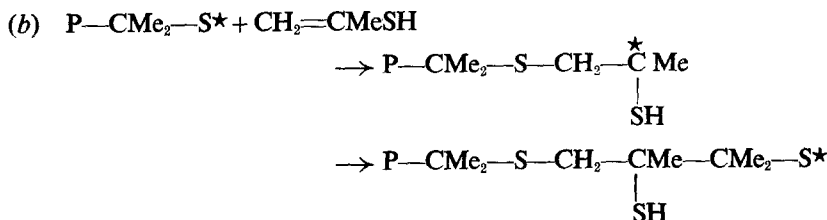
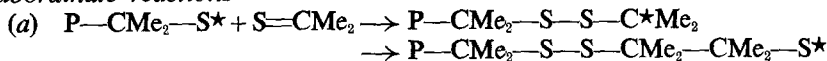
(4) Thioacetone would be expected to exist as an equilibrium between thione and substantial amounts of thioenol form¹¹, but n.m.r. measurements at -78°C in chloroform suggested no more than one per cent enol. Reactions are therefore possible which do not have to be considered in aldehyde polymerizations.

As both forward and reverse reactions are boron trifluoride etherate catalysed, thioacetone polymerization may be cationic. Initiation in the solid phase by light may also be ionic. The colour of monomeric thio-ketones has been attributed to diradicals, but this is debatable^{11,20}.

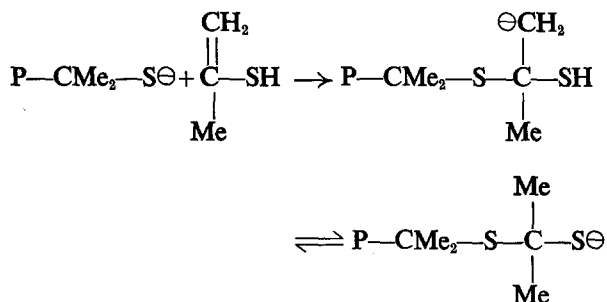
Whether free radical or ionic, propagation is probably as follows:



Subordinate reactions—

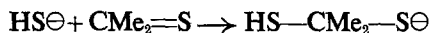


An alternative anionic mechanism can be devised in which the polymer can be derived from the thioenol:

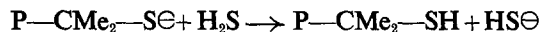


Initiation of anionic polymerization in solution may be similar to that postulated for linear polyformaldehyde, with hydrogen sulphide replacing water as a contributing factor. This would give a polymer terminated at each end by thiol groups.

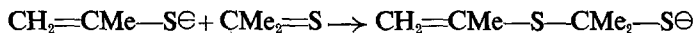
Initiation—



Termination—



A similar role could be played by the thioenol form to give an isopropylidene end group. This could occur in the solid phase.



CONCLUSIONS

Liquid thioacetone spontaneously polymerizes. Light induces polymerization in the crystalline phase.

The polymer is linear and comprises $[-\text{CMe}_2-\text{S}-]_n$. This repeat unit is interrupted by $-\text{CMe}_2-\text{S}-\text{S}-\text{CMe}_2-$ and by $-\text{CH}_2-\text{CMe}-\text{CMe}_2-\text{S}-$
 $\quad \quad \quad \text{SH}$

The polymer irreversibly decomposes to the cyclic trimer.

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