

## Polymerization of Trithiane

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### Synopsis

The catalytic solid-state polymerization of trithiane to polythiomethylene has been studied. The polymerization can be initiated by wide varieties of substances such as metal salts, halogen, and active organic halides. The polymerization proceeds in solid-state without topochemical process. The catalytic irreversible degradation of polythiomethylene to dimethyl sulfide and carbon disulfide has been observed.

### INTRODUCTION

Polythiomethylene (PTM) could be an interesting polymeric substance as the sulfur analog of polyoxymethylene. The synthesis of PTM was first reported by Wohl<sup>1</sup> by means of polycondensation. Recently, Gipstein<sup>2</sup> reported the ring opening polymerization of trithiane (Ts), cyclic trimer of thioformaldehyde, using boron trifluoride, methyl iodide or dimethyl sulfate as catalyst. Stannett<sup>3</sup> reported gamma ray induced solid-state polymerization of Ts, including topochemical propagation. Very recently Russo<sup>4</sup> synthesized cyclic tetramer and pentamer of thioformaldehyde and polymerized them to PTM. This paper deals with a solid-state catalytic polymerization of Ts on which Ohama<sup>5</sup> has first reported preliminarily in patent.

### Experimental

**Trithiane:** Commercial Ts was recrystallized twice from anhydrous toluene solution, mp 216–217°C. (Found: C, 26.23; H, 4.62; S, 69.86%;  $C_3H_6S_3$ : C, 26.1; H, 4.3; S, 69.6.)

**Reagents:** Commercial analytical-grade reagents were used with or without purification according to their properties with careful removal of water.

**Polymerization:** In general, solid-state bulk polymerization was carried out in an evacuated glass ampoule, at 180°C in the presence of catalyst (0.5 to 2 mol % on monomer). The polymerized masses were

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extracted by boiling toluene to remove unreacted monomer until constant weight was achieved.

For example, Ts was polymerized by adding 0.5 mol % of stannic chloride as catalyst at 180°C for 2 hr and a polymer of mp 243–245°C was obtained in 58.6% yield after extraction with boiling toluene for 3 hr. (Found: C, 27.66; H, 5.14; S, 67.05; Cl, 0.97%.)

## Results

### Catalyst

It is well known that the sulfides can form stable addition compounds with metal halides.<sup>6</sup> Thus the catalytic activity of metal halides on the solid-state polymerization of Ts was tested. Results are listed in Table I.

TABLE I  
Polymerization of Trithiane by Metal Halides\*

Salts	Yield	Salts	Yield	Salts	Yield
HCl	1.5%	CdCl <sub>2</sub>	0	SbCl <sub>3</sub>	86.2
LiCl	0	CdBr <sub>2</sub>	Trace	BiCl <sub>3</sub>	57.3
KCl	0	CdI <sub>2</sub>	0	BiOCl <sub>3</sub>	48.9
CuCl	0	HgCl	11.7	CrCl <sub>3</sub>	Trace
CuBr	0	HgCl <sub>2</sub>	50.4	S <sub>2</sub> Cl <sub>2</sub>	43.0
CuI	0	HgBr <sub>2</sub>	70.4	MnCl <sub>2</sub>	0
CuCl <sub>2</sub>	16.0	HgI <sub>2</sub>	0	" 3H <sub>2</sub> O	0
" 2H <sub>2</sub> O	7.1	BCl <sub>3</sub>	71.0	FeCl <sub>3</sub>	86.3
CaCl <sub>2</sub>	0	AlCl <sub>3</sub>	60.7	RuCl <sub>3</sub> H <sub>2</sub> O	8.9
SrCl <sub>2</sub>	0	CCl <sub>4</sub>	4.4	CoCl <sub>2</sub>	Trace
BaCl <sub>2</sub>	0	SiCl <sub>4</sub>	7.3	RhCl <sub>3</sub> 3H <sub>2</sub> O	4.3
ZnCl <sub>2</sub>	48.1	SnCl <sub>4</sub>	58.6	IrCl <sub>3</sub>	0
ZnBr <sub>2</sub>	50.0	PbCl <sub>2</sub>	0	NiCl <sub>2</sub>	Trace
ZnI <sub>2</sub>	61.4	VOCl <sub>3</sub>	77.9	PdCl <sub>2</sub>	7.6
				PtCl <sub>4</sub> 5H <sub>2</sub> O	15.1

\* Polymerizations were carried out at 180°C for 2 hr without solvent using 1 mole % of salt. Hot toluene-insoluble parts are recorded as yield.

Metal halides such as halides of copper, zinc, mercury, boron, aluminum tin, antimony, bismuth, vanadium, sulfur, platinum, and iron are active catalysts. As shown in Table II, polymerization were carried out also with the catalysts including metal salts other than halides, halogen, hydrogen halides, organo halogen compounds, onium compounds, and donor-acceptor systems with free radical initiators.

Weak acid salts of mercury showed activity, but those of zinc, cadmium, lead, and sodium were observed to be inactive for the polymerization of Ts, in which the anion part of the salts such as acetate or benzoate was found to be incorporated into the resultant polymer, as determined from infrared analysis.

Hydrogen halide was inactive for the polymerization of Ts while it had a catalytic activity for the polymerization of trioxane, *i.e.*, oxygen analog of

TABLE II

Compound	Amount mole %	Yield	Compound	Amount mol %	Yield				
Salts other than halides*									
HgNO <sub>3</sub> H <sub>2</sub> O	2	0	Zn(OAc) <sub>2</sub> H <sub>2</sub> O	1	0				
Hg(NO <sub>3</sub> ) <sub>2</sub> ·1/2H <sub>2</sub> O	2	Trace	Zn(OAc) <sub>2</sub>	1	0				
HgOAc	2	20.6	Cd(OAc) <sub>2</sub> ·2H <sub>2</sub> O	1	Trace				
Hg(OAc) <sub>2</sub>	2	20.9	Cd(OAc) <sub>2</sub>	1	0				
Hg(OCOØ) <sub>2</sub>	1	13.0	Pb(OAc) <sub>2</sub> ·3H <sub>2</sub> O	1	0				
Hg(OCOCH <sub>2</sub> ) <sub>2</sub>	1	24.7	Pb(OAc) <sub>2</sub>	1	0				
Hg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1/3	40.8	NaOAc	2	0				
Hg(CN) <sub>2</sub>	2	0	HgS	2	0				
HgSO <sub>4</sub>	2	Trace	HgO (yellow)	2	0				
HgO(red)	2	0							
Halogen and hydrogen halides									
Cl <sub>2</sub>	1	26.5	ICI	0.5	69.3				
Br <sub>2</sub>	1	52.1	HCl	1	1.5				
I <sub>2</sub>	1	85.7	HBr	1	8.0				
Organo halogen compounds									
CCl <sub>4</sub>	1	4.4	ClCH <sub>2</sub> OCH <sub>3</sub>	2	27.5				
CBr <sub>4</sub>	1	48.6	BrCH <sub>2</sub> SCH <sub>2</sub> Br	1	42.0				
C <sub>2</sub> Cl <sub>6</sub>	1	2.8	φCH <sub>2</sub> Cl	2	28.7				
CH <sub>3</sub> I	1	15.6	φCH <sub>2</sub> Br	2	59.0				
n-C <sub>4</sub> H <sub>9</sub> Cl	1	0	CH <sub>2</sub> =CHCH <sub>2</sub> Br	2	11.6				
n-C <sub>4</sub> H <sub>9</sub> Br	1	1.0	ClCH <sub>2</sub> CH <sub>2</sub> OAc	1	Trace				
n-C <sub>4</sub> H <sub>9</sub> I	2	7.7	(ClCH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> PO	1	13.7				
t-C <sub>4</sub> H <sub>9</sub> Cl	2	0	(2,4-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )Cl	0.5	0				
t-C <sub>4</sub> H <sub>9</sub> Br	2	Trace	φCOCl	1	29.0				
ClCH <sub>2</sub> Br	2	Trace	C <sub>2</sub> H <sub>5</sub> OCOCl	2	4.2				
N-halogen compounds									
(CH <sub>2</sub> CO) <sub>2</sub> N-Br	2	44.8	AcNH-Br	2	18.4				
(CH <sub>2</sub> CO) <sub>2</sub> N-Cl	2	41.7	NCQ	2	Trace				
Onium compounds									
(n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	1	10.5	φN <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> Br <sup>-</sup>	1	9.7				
(CH <sub>3</sub> ) <sub>3</sub> S <sup>+</sup> I <sup>-</sup>	1	18.2	(CH <sub>3</sub> ) <sub>3</sub> S-HgCl <sub>2</sub>	1	70.0				
(CH <sub>2</sub> ) <sub>4</sub> S-HgCl <sub>2</sub>	2	29.3							
Free radical initiators									
AIBN	1	0	S <sub>8</sub>	1	0				
TMTD	1	0	CBr <sub>4</sub>	1	48.6				
C <sub>2</sub> Cl <sub>6</sub>	1	2.8	(CH <sub>2</sub> CO) <sub>2</sub> N-Br	2	47.8				
Donor-acceptor									
Ac- ceptor	Mole %	Radical source	Yield	Acceptor	Radical source	Yield			
MAH	10	AIBN	1	10.3	Quinone	10	S <sub>8</sub>	1	5.3
MAH	10	S <sub>8</sub>	1	84	Naphtho-Q	10	S <sub>8</sub>	1	5
MAH	10	TMTD	1	5	Anthra-Q	10	S <sub>8</sub>	1	0
MAH	10	—	—	2.5	DEM	10	S <sub>8</sub>	1	0
φ <sub>2</sub> NH <sup>a</sup>	1	S <sub>8</sub>	—	Trace	DEF	10	S <sub>8</sub>	1	0
φ <sub>2</sub> NH <sup>a</sup>	1	—	—	0	DEM	10	TMTD	1	0
					DEF	10	TMTD	1	0

\* Polymerizations were carried out at 180°C for 2 hr. Hot toluene insoluble parts are recorded as yield. Ac, Acetyl; φ, Phenyl; NCQ, N-chloroquinone imine; AIBN, Azo bisisobutyronitrile; TMTD, Tetramethylthiuramdisulfide; MAH, Maleic anhydride; Q, Quinone; DEM, Diethyl maleate; DEF, Diethyl fumarate (a) electron donor, sulfur would be an acceptor in this case.

Ts. As for halogen itself, the activity was just opposite for these two cases.

*N*-halogen imides, some sulfonium and ammonium compounds were also active. Usual free radical initiators could not initiate the polymerization. Ts can be polymerized, however, with a radical initiator in the presence of an acceptor such as maleic anhydride.

### *Rate of Polymerization*

Time-conversion curves of the solid-state polymerization of Ts are shown in Figures 1 and 2.

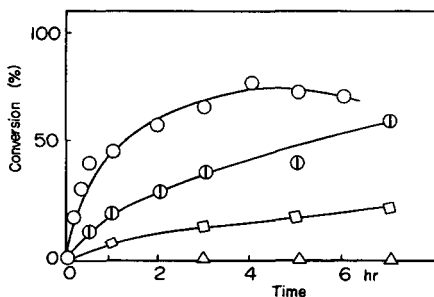


Fig. 1. Rate of polymerization: (O) SnCl<sub>4</sub>, 0.5 mole % 180°C; (⊕) Benzyl chloride, 2 mole % 180°C; (□) SnCl<sub>4</sub>, 0.5 mole % 150°C; and (Δ) SnCl<sub>4</sub>, 0.5 mole % 100°C.

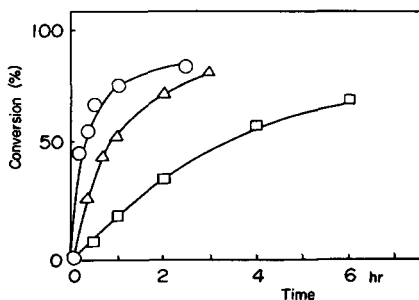


Fig. 2. Rate of polymerization: (O) 190°; (Δ) 180°; and (□) 170°. HgCl<sub>2</sub>, 1 mole %.

An apparent activation energy was calculated to be 48 kcal/mole for the heterogeneous solid-state polymerization catalyzed by mercuric chloride. A large value of activation energy here obtained means that the reaction proceeds in the solid-state. The polymerization did not occur at 100°C using a strong catalyst such as stannic chloride.

### *Terminal Groups*

It was found that polymers polymerized by halogen compounds contained halogen, and mercury when mercury salts had been used as catalyst. The elemental analysis data are listed in Table III.

TABLE III  
Terminal Analyses

Catalyst	Amount mole %	Con- version	Hg	Cl	Cl/Hg	CH <sub>2</sub> S/Cl	DP
HgCl <sub>2</sub>	1	46%	1.21	0.43	2.01	—	—
HgCl <sub>2</sub>	1	68	1.24	0.57	2.83	—	—
HgCl <sub>2</sub>	1	71 <sup>a</sup>	0.95	0.34	2.02	—	—
Hg(OCOCH <sub>3</sub> ) <sub>2</sub>	2	21	4.22	—	—	—	—
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	2	29	—	0.60	—	125	42
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	4	62	—	1.01	—	75	25
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	6	87	—	1.08	—	70	23

Cat- alyst	Amount	C	H	S	Br	N	DP
BAA	1	25.66	4.30	59.26	5.67	0.98	10
		C/N 30	H/N 61	S/N 26	Br/N 1		
NBS	2	—	—	—	0.48	1.69	—
					Br/N 0.6		
NBS	3	—	—	—	0.63	2.05	—
					Br/N 0.6		

<sup>a</sup> Extracted by ethanol instead of toluene.

BAA: N-Bromoacetoamide; NBS: N-Bromosuccinimide.

From the infrared spectra of polymers, absorption bands associated with carbonyl group were observed at 1740–1745 cm<sup>-1</sup> and 1700 cm<sup>-1</sup> for the polymers obtained by mercuric acetate and benzoate, respectively. Also, carbonyl group absorption at 1680 and perhaps thioester absorption at 1290 cm<sup>-1</sup> for the polymer obtained by *N*-bromoacetoamide, and carbonyl group absorption at 1710 cm<sup>-1</sup> (imide) by *N*-bromo and chlorosuccinimide were observed. For the terephthalic acid chloride initiated polymers, the content of carbonyl group calculated from the intensity of the band at

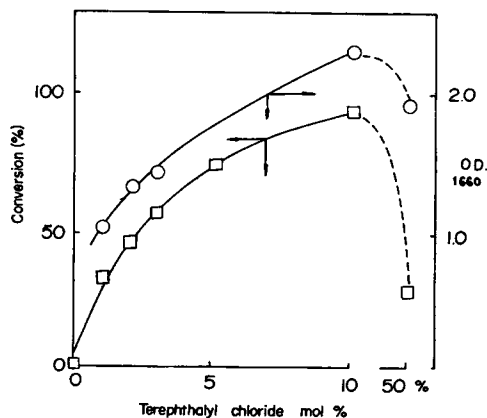


Fig. 3. Carbonyl group in the polymer.

1660  $\text{cm}^{-1}$  (thioester) increases with the increase of initiator as shown in Figure 3.

The facts above mentioned indicate that the moiety of initiator might be incorporated into the polymer end.

### *X-Ray Analysis*

An oscillation photograph of polymerized solid obtained by chlorine, bromine, boron trifluoride etherate, stannic chloride, benzyl bromide, or chloromethyl ether shows only unoriented Debye-Scherrer-ring corresponding to PTM, and on the other hand unreacted monomer gives oriented spots corresponding to orthorhombic unit cell reported by Stannett.<sup>3</sup>

### *Infrared*

The infrared spectra of polymers obtained by catalytic solid-state polymerization of Ts show typical absorption corresponding to PTM at 705, 730, 740, 875, 880, 1175, 1185, 1350, 1360, 1370, 2905, and 2960  $\text{cm}^{-1}$ . Among all the bands, the bands at 1185, 1175, 880, and 875  $\text{cm}^{-1}$  were observed to be sensitive to physical or mechanical treatment such as heating or compression.

The thermal effect on their relative intensities expressed in terms of OD 1185/1175 and OD 875/880 is shown in Figure 4.

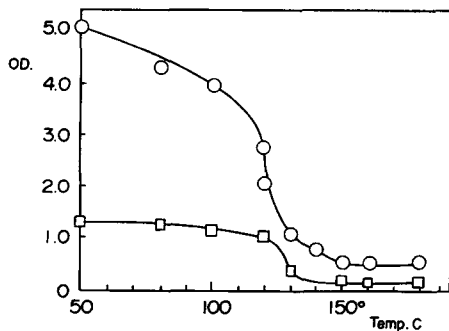


Fig. 4. Thermal change on infrared absorption intensity: (○) OD 875/880; and (□) OD 1185/1175.

With elevating temperature, a marked transition is observed at a temperature from 120° to 130°C by infrared spectra. While, by lowering temperature, no change in the spectra is observed at this temperature. But, by applying a compressional force (200  $\text{kg}/\text{cm}^2$ ), the quenched specimen shows the above mentioned transition from the spectra being characteristic of a high temperature type to that of a low temperature type. This cycle of the transitional change is reproducible by the same temperature and pressure change.

*Degradation of Polymer*

During the polymerization of Ts, it has been observed that high polymerization temperature or the presence of excess catalyst produces liquid by-products which have been analyzed to be carbon disulfide and dimethyl sulfide by infrared, NMR and gas chromatography.

Conversion of Ts to PTM is measured by infrared method and shown as a function of time in Figure 5.

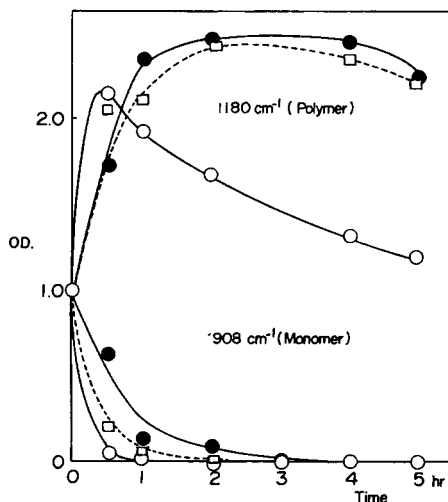


Fig. 5. Time conversion curve by infrared method: (●)  $\text{SnCl}_4$ , 1 mole %; (◻)  $\text{HgCl}_2$ , 1 mole %; and (○)  $\text{HgCl}_2$ , 12 mole %. Reaction temp.,  $180^\circ\text{C}$ . 100% conversion to polymer: OD 1180 = 2.54; and OD 908 = 0.

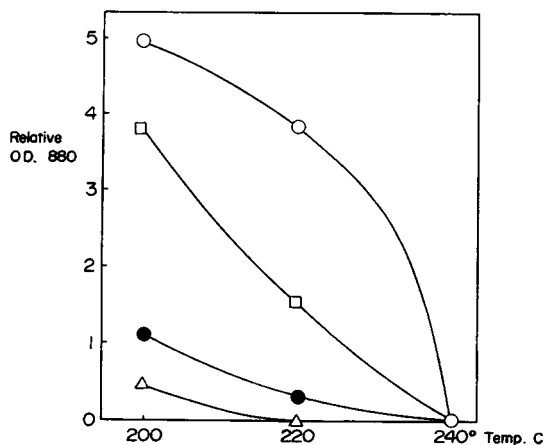


Fig. 6. Degradation of polythiomethylene: (○) Polytrithiane by  $\text{HgCl}_2$ ; (◻) Polytrithiane by benzyl bromide or polythiomethylene by condensation method; (●) Polytrithiane by  $\text{SnCl}_4$ ; and (Δ) Polythiomethylene (condensation) with  $\text{SnCl}_4$ . Heated for 1 hr, in KBr disk under reduced pressure.

The time-conversion curve gives a maximum showing decrease of conversion after this point. Nevertheless, the depolymerization of polymer to monomer has not been observed, by which it indicates an occurrence of side reaction mentioned above. Actually the increase in the intensity of absorption band at  $1500\text{ cm}^{-1}$  corresponded to C=S group has been observed with the progress of degradation of polymer. The degradation of PTM was also accelerated with strong catalyst or elevating temperature (Fig. 6).

## Discussion

### Catalytic Activity

It is difficult to predict the catalytic activity of metal salts on the polymerization of Ts. However, the heat of complex formation for a certain sulfide with metal salts might be useful as a measure for finding whether a salt would be active or not. Table IV shows the heat of complex formation between dimethylethane-1,2-dithiol and metal salts, and also the catalytic activities on the polymerization.

TABLE IV  
Heat of Complex Formation,  $\text{MX}_n$  with Dimethylethane-1,2-dithiol<sup>a</sup>

Salts	Heat of formation	Cat. activity	Salts	Heat of formation	Cat. activity
CuCl <sub>2</sub>	14.85	+	CdBr <sub>2</sub>	11.27	-
CuI	5.88	-	CdI <sub>2</sub>	9.96	-
ZnCl <sub>2</sub>	13.19	+	HgCl <sub>2</sub>	13.23	+
ZnBr <sub>2</sub>	15.35	+	HgBr <sub>2</sub>	11.33	+
ZnI <sub>2</sub>	14.18	+	HgI <sub>2</sub>	4.83	-
CdCl <sub>2</sub>	12.16	-	SnCl <sub>4</sub>	28.06	+

<sup>a</sup> From *J. Chem. Soc.*, **1925**, 1917.

TABLE V  
Melting Point and Vapor Pressure of Salts<sup>a</sup>

Salts	mp	Vp <sub>100</sub>	Way of feed	
			Powder yield	Solution yield
HgCl <sub>2</sub>	265°C	237°C	52.1%	55.7%
FeCl <sub>3</sub>	300	273	77.0	75.0
BiCl <sub>3</sub>	230	343	33.0	87.5
ZnCl <sub>2</sub>	275	610	27.3	78.3
CdCl <sub>2</sub>	568	797	0	19.3
CdBr <sub>2</sub>	557	—	Trace	26.6
CdI <sub>2</sub>	387	640	0	Trace
NiCl <sub>2</sub>	973 <sub>sub</sub>	866 <sub>sub</sub>	Trace	31.5
LiCl	614	1129	0	0

<sup>a</sup> Powder: Finely divided powder of salt was used as catalyst. Solution: Salt was used in ethanolic solution.



The active salts have a larger value than about 11 with an exception of cadmium salts. Cadmium salts have a rather high melting point and a low vapor pressure. Therefore, the heterogeneity of reaction system could reduce the apparent activity because the polymerizations have started from mixtures of the powdered monomer and a salt without any solvent. In the following experiments the salts which did not degrade in alcohol were fed in anhydrous ethanolic solution followed by complete removal of ethanol. Results are listed in Table V.

Apparent catalytic activity of a salt of a high melting point and a low vapor pressure was changed to increase by employing this method. Cadmium chloride and bromide yielded the polymer in this way and cadmium iodide (heat of complex formation is smaller than 11) showed no increase in activity.

A qualitative relationship may be expected between the catalytic activity of metal salts on the polymerization and the above mentioned heat of complex formation.

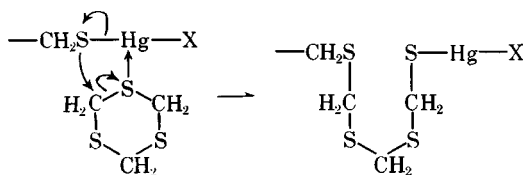
#### Role of Catalysts

The role of catalysts on the polymerization of Ts is not yet clear. Catalysts can be classified into five groups according to their properties as (1) Friedel-Crafts type:  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{SnCl}_4$ , and  $\text{FeCl}_3$ ; (2) weak acceptors:  $\text{HgCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{PtCl}_4$ ; (3) neutral or basic salts:  $\text{HgCl}$ ,  $\text{HgOAc}$ ,  $\text{Hg}(\text{OAc})_2$ , and  $\text{BiOCl}$ ; (4) alkylation or acylation agents:  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ ,  $\text{ClCH}_2\text{OCH}_3$ ,  $\text{C}_6\text{H}_5\text{COCl}$ , and  $\text{CH}_3\text{I}$ ; and (5) others: NBS,  $\text{CBr}_4$ , and maleic anhydride-sulfur.

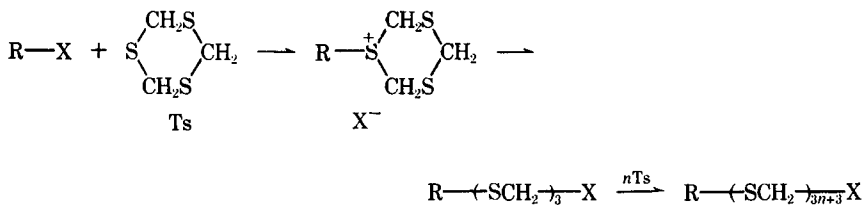
With Group 1 catalysts the polymerization would proceed cationically. However, rather high reaction temperature changes cationic nature of the reaction, for example water does not inhibit the polymerization by stannic chloride. The fact that hydroquinone can not inhibit the polymerization and free radical initiators will not initiate the polymerization, implies that Ts polymerizes not via free radical mechanism.

The second type of catalysts is difficult to elucidate the role. Ts-mercuric chloride complex decomposes at  $189^\circ\text{C}$  to give mercuric sulfide.<sup>6</sup> Chlorine might migrate on carbon atom to form chloromethyl sulfide derivatives which are homolog of Group 4 catalysts.

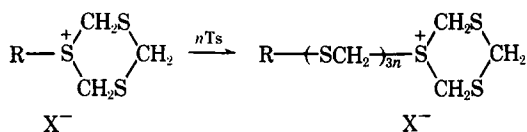
Formation of mercaptide would be plausible with Group 3 or also 2 salts. Coordination of sulfur atom of Ts to metal mercaptide followed by ring opening is probable propagation step. However, no experimental result has been obtained to support this mechanism.



Stepwise, alkylation of sulfide followed by ring cleavage or propagation including sulfonium ion may be a suitable reaction scheme for the polymerization by Group 4. The mechanism mentioned below shall be proposed from the terminal analysis and the properties of catalysts.



or



The polymers obtained by Group 4 catalysts such as acid chloride or benzyl halide are living polymer. Namely, the polymer even after remained catalyst being carefully removed could act as initiating species. Thus 286 mg and 180 mg of polymer was obtained by heating of Ts (1 g) at 180°C for 1 hr with the polymer (100 mg) polymerized by terephthaloyl chloride and benzyl bromide, respectively. On the contrary mercuric chloride (Group 2) initiated polymer produced no new polymer by heating with Ts but the degradation of parent polymer took some extent. Therefore the propagating species of Group 4 and 2 initiated systems might not similar.

Although, *N*-bromo succinimide and carbon tetrabromide are known to be a free radical source, they may act in different way. Bromine or chlorine reacts with Ts to produce halogenated fragments including dihalomethyl sulfide<sup>7</sup> known as Group 4.

Polymerization of Ts in the presence of maleic anhydride and sulfur affords an acid anhydride containing polymer so that the radical-cation mechanism would be plausible which has been recommended in trioxane-maleic anhydride-radical source system.<sup>8</sup> Actually sulfur can abstract the hydrogen from Ts above 150°C, in which the evolution of hydrogen sulfide is confirmed.

#### *Solid-state Polymerization*

Judging from the rather high activation energy, x-ray analysis on single crystal polymerization and the high melting point of Ts, it is valid that the propagation involves the solid-state reaction. In contrast to the fact that the topotactic propagation has been observed in gamma ray-induced solid-state polymerization Ts by Stannet,<sup>3</sup> the catalytic solid state polymerization of the same monomer at the same temperature only results unoriented

polymer independently of the size of catalyst used. Recently Stannet<sup>9</sup> has reported that the very traces of impurities in the monomer would be the active species in the gamma ray-induced polymerization.

Russo<sup>4</sup> reported that the cyclic tetramer and pentamer of thioformaldehyde were soluble in common organic solvents and of the low melting point in contrast with the high melting Ts, and that they were polymerizable at room temperature by boron trifluoride in solution.

The solid-state propagation commonly requires high activation energy. No polymer has been obtained in 5% solution of Ts in toluene or dichloroethane at 110° or 83°C, with large amount of stannic chloride up to 10 mole % on monomer. The result might be related to the stability of six-membered ring to the ring cleavage.

### *Molecular Weight*

Since the PTM is hardly soluble in common organic solvents even at an elevated temperature, it is difficult to determine the molecular weight by viscometry. Difference between the melting temperature of polymers, as shown in Table VI, might be related to the difference in molecular weight.

TABLE VI  
Polymer Melting Temperature of Polythiomethylene

Catalyst	Amount	PMT
Benzyl bromide	0.5 mole %	258-260°C
"	1.0	247-252
"	2.0	246-250
"	3.0	240-245
"	4.0	240-244
Benzyl chloride	2.0	251-253
"	4.0	240-242
"	6.0	238-241
Bromine	1.0	249-252
Mercuric chloride	1.0	256-260
Zinc chloride	1.0	228-232
Bismuth chloride	1.0	260-268

Apparent number average molecular weight can be determined from terminal analysis of polymers, and one of the samples in the table is estimated to be Ca. 5700.

### *Degradation*

As mentioned before, excess of catalyst, high reaction temperature, or long polymerization time caused irreversible degradation of PTM chain to carbon disulfide and dimethyl sulfide. This degradation may be far from the expectation and has never been reported.

*Infrared Spectra*

Although the fact that the intensities of infrared absorption at 1185 and 1175 or at 875 and 880  $\text{cm}^{-1}$  are reversed by elevating temperature or by compression implies that the transition of molecular conformation might occur, neither change in x-ray diffraction pattern nor in thermal analysis by differential scanning calorimeter has been observed under similar condition and also no relation has been found out between the above mentioned phenomenon and the irreversible endotherm at 150°C reported by Stannett<sup>8</sup> which could not be found at about 150° in our experiments, and the irreversible crystalline transition of condensation polymers to hexagonal at 153°C suggested by Russo.<sup>10</sup>

**Conclusion**

Solid-state polymerization of Ts has been found to be catalyzed by wide varieties of substances including metal halides, mercury salts, halogen, active organic halides, *N*-halogen imides, onium salts, and maleic anhydride with radical source. The molecular weight of resultant polymers was rather low. Polymerization proceeds in solid-state without topochemical process. The irreversible degradation of PTM chain occurs under severe conditions producing carbon disulfide and dimethyl sulfide as major products.

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