

# Haloaldehyde polymers: 16. Stabilization of anionically-prepared polychloral by end-capping with decomposable cations and other additives

L. S. Corley and O. Vogl

*Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, USA*

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Completely or partly stable polychloral was obtained by anionic cryotachensic polymerization of chloral in the presence of alkylating or acylating agents, notably dimethyl sulphate. Stabilization was also achieved when the polymerization was carried out with specific salts as anionic initiators whose cations could be thermally decomposed at slightly elevated temperatures. Sulphonium salts (particularly trimethylsulphonium and dimethylbenzylsulphonium) and also iodonium salts were found to be effective, although quantitative stabilization of polychloral could not be achieved. Polychloral with improved stability was also obtained with selected amide acetals as initiators.

## INTRODUCTION

Stabilization of polyformaldehyde has become necessary for its commercialization and practical use. It has been accomplished by end-capping, a post-reaction which changes the unstable end-groups (primarily hydroxyl end-groups) to stable ester or ether end-groups.<sup>1-5</sup> This kind of endcapping stabilization has also been demonstrated to be effective for the polymers of higher aliphatic aldehydes.<sup>6</sup>

Polymers of haloaldehydes, although qualitatively similar in their behaviour and their end-groups to polyformaldehyde or polymers of higher aliphatic aldehydes, are nevertheless substantially different in the details of the reaction of their end-groups. The preparation and polymerization of haloaldehydes have been studied and described in a series of papers and patents.

Of particular interest in studies of haloaldehyde polymers are the polymers of chloral.<sup>7-18</sup> It was found that the yield in polychloral preparation depended very much on the type of initiation and subsequent polymerization, the polymerization mechanisms by which the polymer was obtained and also the type of end-group which was produced by individual polymerization conditions.

Cationic polymerization of chloral with protonic acids was found to produce primarily hydroxyl end-groups which can be acylated.<sup>7,11,19</sup> Certain Lewis acid initiators gave polymers with equal and even higher stability whose end-groups have, however, not been identified as the polymers have no characteristic end-groups on which specific reactions could be carried out.<sup>19</sup>

Polychloral is insoluble and infusible; however, it degrades readily above 200°C to monomer. Because of the insolubility, infra-red spectroscopy and thermogravimetric analyses (which gives chloral monomer as the only degradation product), were the only practical characterization techniques for chloral polymers. Differential thermogravimetric analysis (d.t.g.) is by

far the most useful method for end-group analysis of polychloral samples of varying thermal stabilities which infra-red spectra of polymers with widely ranging differences in stability showed as the only identifiable end-groups, hydroxyl end-groups, or on relatively rare occasions, carbonyl end-groups.<sup>20,2</sup> In the identification of carbonyl end-groups, care had to be taken not to mistake for ester end-groups carbonyl groups of chloral monomer which is present often in small amounts as an impurity in the polymer. Reaction products of chloral with acylating agents can also be mistaken for acyl end-groups from successful end-capping reactions.<sup>22</sup> In actual fact, very rarely have acetate end-groups been introduced into chloral polymers by end-capping reactions other than with cationically-prepared chloral polymer.

In anionic chloral polymerization, especially when cryotachensic polymerization techniques were used, the end-groups have been identified to be primarily alkoxide end-groups which could be transformed into hydroxyl end-groups by treatment of the polymers with HCl in methanol.<sup>21</sup> Although alkoxide end-groups were the normal end-groups, some side reactions could occur when the reaction products of the anionic polymerization were allowed to stand for extended periods of time; small amounts of stable polychloral fractions were sometimes obtained. The amount of stable polymer depended on the type of counteraction that was used for the anionic polymerization and on side reactions of alkoxide end-groups with excess chloral.

Stable chloral polymer portions have been observed with both Ph<sub>3</sub>P initiation and lithium tertiary butoxide (LTB) initiation. In general, most treatments which are normally known to accomplish end-capping with acylating and alkylating<sup>1-6</sup> agents have proven to be relatively fruitless.<sup>24</sup> The only effective treatment of anionically-prepared polychloral was treatment with PCl<sub>5</sub>.<sup>21-24</sup> This post-treatment provided polymer of high thermal stability.

One of the problems that plagued the stabilization of

polychloral samples was caused by the incompleteness of most post-treatment reactions. Even when stabilization of polychloral was successful, only partial stabilization was achieved as determined by d.t.g. evaluation of the stabilized polymer samples. Each type of polymer sample gave a characteristic thermal degradation spectrum but only in those cases where a single maximum degradation rate temperature (*MDT*) above 300°C was observed without a lower *MDT* peak, could stabilization be called successful.<sup>19,21</sup>  $\text{PCl}_5$  treatment of anionically-prepared polychloral powders or thin films gave completely stabilized polymer.<sup>21-24</sup> Although this technique was excellent, it was not effective for thick polymer sections or for materials from which desirable mechanical properties were expected as degradation of internal parts of the polymer caused the formation of voids.

One of the reasons why post-treatment was not always believed to be effective was the limited swellability of the polychloral sample, with the result that the post-treatment reagent could not effectively diffuse to the end-group reaction site. Furthermore, the alkoxide end-groups of the anionically prepared polychloral are in an environment of high steric hindrance and consequently few reactions, with the exception of protonation to form hydroxyl end-groups were expected to occur at such sites. Failure of other reactions to occur made it probable that many simpler bimolecular reactions could not be achieved for steric reasons.

Anionic polymerization of chloral had been achieved in the presence of chain transfer or chain termination reagents<sup>20</sup> such as acetyl and benzoyl chloride. A substantial portion of the polychloral obtained was of increased thermal stability; this reaction however was not quantitative, and chain transfer was found to occur only to a minor extent with most acylation taking place after the polymerization had been completed.

Our objective in this work was to attempt the stabilization of polychloral by carrying out anionic polymerization in the presence of reactive reagents of two types: (a) neutral but reactive compounds which are generally known to be capable of alkylating or acylating alkoxy groups; (b) cations (particularly sulphonium ions) which were to be used as counter ions in anionic chloral polymerization and whose stability was such that they could alkylate alkoxide end-groups of the chloral polymer at a somewhat elevated temperature which was hoped to be below the depolymerization temperature of the polychloral sample.

## EXPERIMENTAL

### Materials

*Chloral* (Montrose Chemical Company) was heated to reflux overnight over  $\text{P}_2\text{O}_5$  (about 20 g l<sup>-1</sup> of chloral) and distilled slowly from  $\text{P}_2\text{O}_5$  in a distillation apparatus with a column packed with glass helices. After desired monomer purity was reached, chloral was distilled and used immediately thereafter. The impurity level as determined by gas chromatography was below 0.3% in all experiments and below 0.03% in most.<sup>18,25</sup>

*Bromacetyl bromide* (Aldrich Chemical Company) was stirred overnight over dry 4 Å molecular sieves to adsorb HBr, a possible impurity. It was then distilled; the middle fraction was distilled directly into a Schlenk tube for storage: b.p. 56–57°C/20 mm.

*2,2-Dimethoxypropane* (Aldrich Chemical Company) was dried for 2 days over liquid NaK alloy with stirring. It was

then distilled under nitrogen at atmospheric pressure and the last 15 ml of a 70 ml charge was taken: b.p. 80°C. Gas chromatography showed the distillate to contain 2% of a single impurity with the same retention time as acetone.

*Dimethyl sulphate* (Eastman Kodak Company) was dried over anhydrous  $\text{K}_2\text{CO}_3$  for 4 days, decanted and distilled under nitrogen at reduced pressure; b.p. 84–85°C/20 mm. A centre fraction equal to about half the charge was taken.

*Dimethyl sulphide* (Phillips Petroleum Company), for the reaction with bromoacetyl bromide and for attempted chloral initiation, was dried for 5 h over  $\text{K}_2\text{CO}_3$  and then for 4 days over  $\text{CaH}_2$ . It was then distilled at atmospheric pressure under nitrogen: b.p. 37°–38°C. Gas chromatography (25°C, Carbowax 20 M) showed less than 0.05% impurity. For other sulphonium salt syntheses, the dimethyl sulphide was used as received.

*Lithium tertiary butoxide* (LTB) (Ventron Alfa Products) was sublimed at 135°–145°C/0.1 mm.

*Methyl iodide* (Pfaltz and Bauer, Inc.) for use as a polymerization additive was dried overnight over  $\text{CaH}_2$  and distilled under nitrogen at atmospheric pressure: b.p. 42°–43°C. Methyl iodide for sulphonium and oxosulphonium salt syntheses was used as received.

*Pyridine* (Aldrich Chemical Company) was dried over  $\text{CaH}_2$  for 4 days and distilled at atmospheric pressure under nitrogen.

*Trimethyl orthoformate* (Aldrich Chemical Company) was dried for 4 days, with stirring, over liquid NaK alloy. It was then distilled under nitrogen at atmospheric pressure: b.p. 98°C.

*2, 4, 6-Trimethylpyridine* (Aldrich Chemical Company) was used as received; gas chromatography showed less than 0.05% impurity.

*Triphenylphosphine* ( $\text{Ph}_3\text{P}$ ) (Aldrich Chemical Company) was recrystallized from methanol or from acetone/Skelly B.

*Acetonitrile* (Eastman Kodak Company), for use as a solvent for initiators, was dried overnight over  $\text{CaH}_2$  and then distilled under nitrogen at atmospheric pressure.

*Benzene and cyclohexane* (Eastman Kodak Company) were dried for one day over  $\text{CaH}_2$ , distilled under nitrogen at atmospheric pressure, and stored over liquid NaK alloy. Gas chromatography revealed less than 0.05% impurity.

*Carbon tetrachloride* (Fisher Scientific Company) was used after standing overnight over 4 Å molecular sieves.

*Chloroform* (Fisher Scientific Company) was allowed to stand over  $\text{P}_2\text{O}_5$  for several days to remove ethanol; it was then filtered through a medium porosity glass filter and stored over 4 Å molecular sieves. Gas chromatography revealed less than 0.05% impurity.

*Dichloromethane* (Fisher Scientific Company) was dried over  $\text{P}_2\text{O}_5$  and distilled under nitrogen at atmospheric pressure.

*Diethyl ether* was Fisher Electronic Grade and was used as received.

*N, N-Dimethylacetamide* (DMAc) (Aldrich Chemical Company) was dried for 2 days over  $\text{P}_2\text{O}_5$  with stirring and was then distilled from the  $\text{P}_2\text{O}_5$  at reduced pressure under nitrogen: b.p. 67°C/20 mm. A middle fraction was taken

Table 1 Extraction stability of polychloral samples prepared with additives in the polymerization mixture

Initiator (mol %) <sup>b</sup>	Additive (mol %)	Wt % of polymer remaining after extraction <sup>a</sup>								
		0	0.2	0.4	0.8	1.6	3.2	6.4	12.8	25.2
Ph <sub>3</sub> P (0.2)	BrCH <sub>2</sub> COBr		4	0	8	15	10	5		
LTB (0.1)	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> <sup>c</sup>		37				(48)	33		
Ph <sub>3</sub> P (0.2)	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> <sup>c</sup>		2(11)	2(3)	1(3)	1(2)	0(2)	2(1)		
LTB (0.1)	CH <sub>3</sub> I <sup>d</sup>	37	20	10	36	50	33	38	62	50
	Additive (mol %)							5.6	11.1	22.2
LTB (0.1)	HC(OCH <sub>3</sub> ) <sub>3</sub> <sup>e</sup>							25(21)	34(25)	46(33)
Ph <sub>3</sub> P (0.2)	HC(OCH <sub>3</sub> ) <sub>3</sub> <sup>e</sup>							75(25)	31(7)	14(4)
LTB (0.1)	(CH <sub>3</sub> ) <sub>2</sub> C(OCH <sub>3</sub> ) <sub>2</sub> <sup>e</sup>							12(22)	64(26)	48(26)
	Additive (mol %)							3.4	6.9	13.8
Ph <sub>3</sub> P (0.2)	Sulpholane							74	79	80

<sup>a</sup> Extraction with methanol in Soxhlet extractor for 3 days

<sup>b</sup> LTB was 0.3M in benzene or cyclohexane; Ph<sub>3</sub>P was 1 M in toluene

<sup>c</sup> In examples in parentheses, dimethyl sulphate was added to initiated chloral; otherwise initiator was added to warm chloral—dimethyl sulphate mixture. See text

<sup>d</sup> Tubes were kept 17 days at room temperature before opening

<sup>e</sup> In examples in parentheses, polymer sample was treated with a solution of 0.5 ml. or BF<sub>3</sub>.Et<sub>2</sub>O in 50 ml of additive at 80°C for 3 days before extraction

Table 2 Thermal stability of polychloral samples prepared with stabilizing additives<sup>a</sup>

Additive (mol %)	Weight per- cent of poly- mer remain- ing after ex- traction (CH <sub>3</sub> OH in Soxhlet, 3 days)	D.t.g. Parameters (heating rate 20°C/min)	
		Onset of decomposition (°C)	Degradation rate maxima (°C) (% of total area under peak)
None	4 <sup>c</sup>	110	224 (100)
	37	130	214 (100)
CH <sub>3</sub> COC1 (0.55) <sup>b</sup>	81 <sup>d</sup>		230 (30), 290 (70)
(CH <sub>3</sub> CO) <sub>2</sub> O (0.65) <sup>b</sup>	72 <sup>d</sup>		230 (87), 290 (13)
C <sub>6</sub> H <sub>5</sub> COC1 (0.85) <sup>b</sup>	78 <sup>d</sup>		230 (65), 290 (35)
BrCH <sub>2</sub> COBr (1.6) <sup>b</sup>	15	160	254 (74), 350 (26)
(0.2)	37	120	157 (42), 287 (58)
(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (3.2)	48	120	180 (13), 289 (87)
	33	205	277 (100)
HC(OCH <sub>3</sub> ) <sub>3</sub> (22)	46	140	195 (60), 317 (40)
(CH <sub>3</sub> ) <sub>2</sub> C(OCH <sub>3</sub> ) <sub>2</sub> (20)	48	180	262 (100)
(12.8)	62	130	212 (100)
CH <sub>3</sub> I (25.2)	50	150	229 (100)

<sup>a</sup> Initiator: LTB (0.1 mol % with respect to chloral)

<sup>b</sup> Initiator: Ph<sub>3</sub>P, 0.2 mol % (first three values from ref 20)

<sup>c</sup> Extracted with CH<sub>3</sub>OH at room temperature for 3 days

<sup>d</sup> Extracted with acetone in Soxhlet for 2 days

and stored over 4 Å molecular sieves. Gas chromatography revealed less than 0.05% impurity.

*Dimethyl sulphoxide* (DMSO) (Aldrich Chemical Company) was dried and refluxed over CaH<sub>2</sub> for 2 h and then distilled at reduced pressure: b.p. 70°C/10 mm. Gas chromatography revealed less than 0.05% impurity.

*Sulpholane* (Aldrich Chemical Company) was dried over NaOH/CaCl<sub>2</sub> for 2 h and then distilled: b.p. 110°C/0.7 mm. The distillate was stored over 3 Å molecular sieves; a gas chromatogram taken shortly before use showed water content to be less than 0.03%.

*Toluene* (Fisher Scientific Company) was refluxed over molten sodium for several days, distilled from the sodium at

atmospheric pressure under nitrogen, and stored over fresh sodium wire.

Reagents and solvents not listed in one of the above procedures were used as received. Solvents or other liquids for use as eventual components of chloral polymerization mixtures were stored in Schlenk tubes (topped with stopcocks) which had been dried overnight at at least 120°C and purged with dry nitrogen. Transfer of solvents to and from these tubes was via syringes under continuous nitrogen blanketing. Transfer of solids was carried out inside a glove bag filled with dry nitrogen.

#### Stabilization of Chloral Homopolymers:

*Stabilization of polychloral by use of additives in the polymerization mixture.* A number of 15 × 125 mm test tubes were dried overnight at 120°C, with rubber serum stoppers, wired and purged with dry nitrogen. Chloral (8 ml, 12.1 g, 82 mmol) and the respective additives in the amounts given (Table 1) were then injected into each test tube with dry syringes. The tubes were then placed in a 70°C oil bath for 5 to 10 min, injected with initiator solution (LTB or Ph<sub>3</sub>P) and shaken to mix the solution components.

In the case of the tubes in which CH<sub>3</sub>I was used as an additive, it was added after the initiator solution. The tubes were then placed into an ice bath to polymerize the chloral. After the polymerization was complete, the polymer plugs were removed from the tubes.

The plugs of polymers prepared with bromoacetyl bromide, dimethyl sulphate, CH<sub>3</sub>I, trimethyl orthoformate and 2,2-dimethoxypropane as stabilizing additives were extracted for 2 days with methanol in a Soxhlet extractor and then dried for 1 day at room temperature and 20 mm pressure. The weights of plugs before and after extraction and drying were compared. D.t.g. spectra of appropriate samples prepared with each stabilizing additive were then determined (Tables 1 and 2).

#### Syntheses of sulphonium and oxosulphonium salt initiators for chloral polymerization.

*General procedure for synthesis of sulphonium and oxosulphonium salts by nucleophilic displacement<sup>25</sup>.* The

alkyl halide, dialkyl sulphide or sulphoxide and reaction solvent used were combined in a glass-stoppered flask and allowed to stand at room temperature (reflux in the case of oxosulphonium salts) until crystals no longer appeared to be forming at a detectable rate. The crystals were then filtered, washed with solvent and dried overnight over  $P_2O_5$  at room temperature and 0.1 mm pressure; if the compounds were to be used as chloral initiators, they were recrystallized from appropriate solvents.

*General procedure for synthesis of sulphonium and oxo-sulphonium chlorides by metathesis*<sup>25</sup>. Silver nitrate and concentrated aqueous HCl were each dissolved in 50–100 ml of water in separate flasks and heated to 80°C. The solutions were then mixed with stirring. The AgCl precipitate was removed by filtering through a medium porosity glass filtering funnel and washed with water until the eluate was neutral.

The sulphonium bromide or iodide was dissolved in water, with a minimum amount of methanol added to increase solubility if necessary. The precipitated silver chloride was then added to the sulphonium salt solution with a ceramic spatula. The suspension was stirred overnight and filtered. The filtrate was evaporated in a rotary evaporator at 30–40°C/20 mm and then placed in a vacuum desiccator at room temperature and 0.1 mm pressure over  $P_2O_5$  until crystallization occurred. The crystals were washed and, in most cases, recrystallized from appropriate solvents.

The molar ratio of sulphonium bromide (or iodide), silver nitrate and HCl used in these experiments was 1:2:4.

Two compounds not previously isolated were prepared in this study; in addition, a known compound was prepared by a previously unreported method. Their synthesis are detailed as follows.

*Synthesis of tert-butyl dimethylsulphonium iodide*. Di(tert-butyl) sulphide (13.9 g, 0.095 mol), methyl iodide (14.1 g, 0.1 mol) and diethyl ether (20 ml) were combined in a glass-stoppered flask and allowed to stand at room temperature for 10 weeks. The reddish-brown reaction mixture was filtered and the solid was washed with  $CH_2Cl_2$  to yield 4.0 g (33%) of white crystals which decomposed without melting at 150–160°C; lit m.p.<sup>37</sup> 160°C (dec.). Infra-red and  $^1H$  n.m.r. spectra<sup>25</sup> confirmed the identity of the compound.

*Synthesis of tert-butyl dimethylsulphonium chloride*. Tert-butyl dimethylsulphonium iodide (3.0 g, 0.012 mol) was dissolved in 50 ml of water in which 0.025 mol of freshly prepared AgCl was then suspended. The suspension was stirred overnight and then filtered. Evaporation of the filtrate followed by recrystallization from methanol–acetone yielded 1.9 g (56%) of white crystals which decomposed at 140–144°C without melting. The infra-red spectrum (KBr) showed absorptions at 3450  $cm^{-1}$  (m, b,  $H_2O$ ), 2290  $cm^{-1}$  (s), 2920  $cm^{-1}$  (m), 2650  $cm^{-1}$  (w), 1480  $cm^{-1}$  (m), 1455  $cm^{-1}$  (m), 1435  $cm^{-1}$  (m), 1380  $cm^{-1}$  (s), 1340  $cm^{-1}$  (m), 1175  $cm^{-1}$  (m), 1060  $cm^{-1}$  (m), 1050  $cm^{-1}$  (m), 1020  $cm^{-1}$  (s), 980  $cm^{-1}$  (w), 950  $cm^{-1}$  (w), and 800  $cm^{-1}$  (w). The  $^1H$  n.m.r. spectrum ( $CF_3COOH/1\%$  TMS) showed resonances at  $\delta$ : 1.4 (singlet, 9H,  $(CH_3)_3C-$ ) and 2.9 (singlet, 6H,  $-S(CH_3)_2$ ). Analysis calculated for  $C_6H_{15}ClS$ : C, 46.58%; H, 9.77%; Cl, 22.92%. Found: C, 46.29%; H, 10.27%; Cl, 22.18%. The salt was stored in a vacuum desiccator over  $P_2O_5$ .

*Synthesis of carbethoxymethyl dimethylsulphonium chloride*. Carbethoxymethyl dimethylsulphonium bromide (5.0 g, 0.022 mol) was dissolved in 50 ml of water in which 0.044 mol of freshly prepared AgCl was then suspended. The

suspension was stirred overnight and then filtered. The filtrate was evaporated, poured into a crystallizing dish and allowed to stand for 1 week at room temperature. The resultant crystals were washed with 9/1 (v/v) acetone/methanol and dried over  $P_2O_5$  in a vacuum desiccator: yield 0.30 g (7%). The material could not be successfully recrystallized from any solvent tested. The infra-red spectrum (KBr) showed absorptions at 3450  $cm^{-1}$  (w, b,  $H_2O$ ), 3000  $cm^{-1}$  (s), 2930  $cm^{-1}$  (s), 2890  $cm^{-1}$  (s), 1730  $cm^{-1}$  (vs, C=O stretching), 1470  $cm^{-1}$  (m), 1455  $cm^{-1}$  (m), 1440  $cm^{-1}$  (m), 1420  $cm^{-1}$  (m), 1400  $cm^{-1}$  (s), 1375  $cm^{-1}$  (m), 1370  $cm^{-1}$  (m), 1335  $cm^{-1}$  (m), 1310  $cm^{-1}$  (vs), 1200  $cm^{-1}$  (vs, b), 1100  $cm^{-1}$  (m), 1055  $cm^{-1}$  (s), 1035  $cm^{-1}$  (s), 1010  $cm^{-1}$  (s), 945  $cm^{-1}$  (m), 905  $cm^{-1}$  (m), 865  $cm^{-1}$  (s), 805  $cm^{-1}$  (w), 765  $cm^{-1}$  (w), 690  $cm^{-1}$  (w) and 670  $cm^{-1}$  (w). The  $^1H$  n.m.r. spectrum ( $CF_3COOH/1\%$  TMS) showed resonances at  $\delta$ : 1.4 (triplet, 3H,  $CH_3CH_2O-$ ), 3.2 (singlet, 6H,  $-S(CH_3)_2$ ) and 4.5 (multiplet, 4H,  $CH_3CH_2OCOCH_2S-$ ). Analysis calculated for  $C_6H_{13}O_2ClS$ : C, 39.02%; H, 7.31%; Cl, 19.20%. Found: C, 39.05%; H, 7.10%; Cl, 18.91%. The salt was stored in a vacuum desiccator over  $P_2O_5$ .

#### *Syntheses of miscellaneous salt and ylide initiators for chloral polymerization*

*Synthesis of diphenyliodonium chloride*. This compound was prepared by the condensation of benzene with potassium iodate in acetic acid–acetic anhydride–sulphuric acid<sup>26</sup>.

*Synthesis of 3,3'-dinitrodiphenyliodonium chloride*. This compound was prepared by the condensation of nitrobenzene with iodyl sulphate (prepared by oxidation of iodine in a mixture of fuming  $HNO_3$  and  $H_2SO_4$ ).<sup>27</sup>

*Synthesis of tropylium chloride*. Tropylium bromide was prepared by bromination of 1, 3, 5-cycloheptatriene in  $CCl_4$  followed by dehydrobromination at 60°C and recrystallization from absolute ethanol.<sup>28</sup> Tropylium chloride was prepared from tropylium bromide and HCl gas in absolute ethanol.<sup>29</sup>

*Synthesis of ethyl(dimethylsulphuranylidene) acetate*. This compound was prepared by dehydrohalogenation of carbethoxymethyl dimethylsulphonium bromide with NaOH in saturated  $K_2CO_3$  solution and isolated as a light yellow oil.<sup>30</sup>

*Synthesis of dimethylsulphonium phenacylide*. This compound was prepared by dehydrohalogenation of phenacyl dimethylsulphonium bromide with aqueous NaOH.<sup>31</sup>

#### *Syntheses of amide acetal initiators for chloral polymerization*

*Synthesis of 1,1-dimethoxytrimethylamine (dimethylformamide dimethyl acetal)*. This compound was prepared by *O*-methylation of dimethylformamide with dimethyl sulphate and reaction of the resultant salt with  $NaOCH_3$  in  $CH_3OH$ .<sup>32</sup>

*General procedure for synthesis of higher 1, 1-dialkoxytrimethylamines (dimethylformamide acetals)*. These compounds were prepared by alcohol exchange of the 1, 1-dimethoxytrimethylamine with an excess of the alcohol containing the desired alkoxy group.<sup>32</sup> The reactions were conducted in the pot of a spinning band column with the methanol (or methanol–dimethylamine mixture) distilled out as it was formed. In some cases, 1, 1-dimethoxytrimethylamine which contained 60% of trimethyl orthoform-

mate was used as a reactant. The trimethyl orthoformate was distilled from the system after the methanol and did not take part in the reaction.

*Synthesis of 1-(dimethoxymethyl)-3, 5-dimethylpyrazole.* This compound was prepared from trimethyl orthoformate and 3, 5-dimethylpyrazole with *p*-toluensulphonic acid as catalyst.<sup>33</sup>

*Chloral polymerizations with initiators which cause potential stabilization of the polymer*

*Preparation of polychloral films and plugs with previously prepared potentially stabilizing initiators.* This section describes the general procedure used for chloral polymerization with a number of potentially stabilizing initiators of different types and is a composite of the work of several experiments. Deviations from the general procedure in specific cases are mentioned either in the text of this section or in the data tables.

A number of pairs of 250 mm × 250 mm × 3 mm Pyrex glass plates were dried overnight at 120°C, fitted with clamps and spacers of 3 mm rubber tubing, and returned to an oven at 70°C for about 2 h until needed for preparation of polychloral films. For chloral polymerization in cylindrical or plug form, a number of 15 × 125 mm or 25 × 200 mm test tubes were flamed out or heated overnight at 120°C, cooled under dry nitrogen, fitted with rubber serum stoppers and wired.

Initiator solutions of 0.1, 0.3 or 1 M concentration were prepared in DMSO, DMAc, CHCl<sub>3</sub>, or CH<sub>3</sub>CN.

Chloral (5 or 8 ml for plug preparation; 30 or 50 ml for film preparation) was then injected into the test tubes with a syringe. The tubes were placed into an oil bath at 70°C and allowed approximately 10 min to come to oil bath temperature. The appropriate amount of initiator solution to obtain the specified initiator concentration was then injected into each tube and the tubes were shaken to obtain homogeneous mixtures.

If films were to be prepared, part of each solution (or suspension) was withdrawn from the tube with a 70°C syringe and placed in one of the polychloral film moulds. Plates and tubes were then placed into an ice-water bath at 0°C and kept there for from 16 to 24 h. (Chloral polymerization proceeded rapidly with most initiators, with gelation occurring within 5 to 10 min after cooling.) The film moulds were then removed from the ice bath, allowed to air dry, and opened; the polychloral plugs were similarly removed from the test tubes with the test tubes being broken if necessary. The films and plugs of polychloral were each divided into two or more parts which were each weighed and given one of a variety of treatments which included heating for 1 or 2 h at 100° or 120°C in an air oven, soaking for one day in a 9:1 (v:v) mixture of methanol and concentrated aqueous HCl, and extraction with methanol for 2 days in a Soxhlet extractor.

The treated films and plugs were then dried for 1 to 3 days at 20 mm pressure and weighed again. Percentage weight retention after work-up and drying was calculated for each sample and is given in *Tables 3* and *4*. D.t.g. spectra were determined for a number of the samples treated in various ways; important parameters from these spectra are listed in *Table 5*.

#### Measurements

Infra-red spectra were obtained on a Perkin-Elmer 283 Infrared Spectrometer (4000–200 cm<sup>-1</sup>) with a scan time

of 12 min or on a Perkin-Elmer 727 Infrared Spectrometer (4000–600 cm<sup>-1</sup>) at a 'normal' scan rate. Polymer films were used as such. Solid low molecular weight compounds were generally incorporated into KBr pellets, while the infra-red spectra of liquids were usually measured on neat samples between NaCl plates. Polymer powders were sometimes used as KBr pellets, but better results were obtained when polymer powder spectra were measured on mulls of the polymer in CCl<sub>4</sub> between NaCl plates. The polystyrene band at 1601 cm<sup>-1</sup> was used as the calibration standard.

Differential thermogravimetric (d.t.g.) spectra were recorded on a Perkin-Elmer TGS-1 Thermobalance under nitrogen at a heating rate of 20°C/min. The heating rate was regulated by a Perkin-Elmer UU-1 Temperature Program Control.

Gas chromatograms were obtained with Varian Associates Model 920 gas chromatograph, generally with a 2 m column packed with Chromosorb W (100/120 mesh) coated with 36% by wt diisodecyl phthalate.

## RESULTS AND DISCUSSION

Partial or extensive stabilization of anionically-prepared polychloral homopolymers has been achieved by three routes: (a) addition of potential end-capping reagent to chloral polymerizations initiated with LTB and Ph<sub>3</sub>P; (b) use of 'decomposable' cations, particularly sulphonium, as the counterions for anionic polymerization; (c) use of nitrogen-containing compounds, such as, for example, amide acetals which would act as initiator and capping agent at the same time.

#### *Stability of polychloral prepared with end-capping additives in the polymerization mixture*

In previous work, acid chlorides or anhydrides were added to warm chloral initiated with LTB or Ph<sub>3</sub>P prior to cryotachensic polymerization.<sup>20</sup> The best stabilizing results obtained from this work are summarized in the first part of *Table 2*. Acetyl chloride, when used at a concentration of 0.55 mol % with respect to chloral, produced a polymer with a d.t.g. peak at 300°C with 70% of the total area under the d.t.g. spectrum. When the acetyl chloride concentration was increased in an attempt to obtain complete stabilization, however, reduction in polymer yield resulted and the percentage of stable fraction in the polymer was not increased.<sup>20</sup> Acetic anhydride and benzoyl chloride were considerably less effective stabilizing agents than acetyl chloride.

In an attempt to extend this work to acylating agents of higher reactivity, bromoacetyl bromide was used in several concentrations in chloral polymerization mixtures initiated with LTB and Ph<sub>3</sub>P (*Table 1*). At all concentrations used, bromoacetyl bromide inhibited chloral polymerization with LTB, as did acetyl chloride.<sup>20</sup> Chloral polymerizations initiated with Ph<sub>3</sub>P in the presence of bromoacetyl bromide gave only low yields of polymer stable to methanol extraction. Probably much of the tetrachloroethoxide initiating species was acylated by the highly reactive acid bromide before it could initiate chloral polymerization, although we did not attempt to determine the presence of tetrachloroethyl bromoacetate in the polymer samples produced. Although yields of chloral polymer were very low, some of the polymer was stabilized since a peak with an *MDT* at 350°C included 26% of the area in the d.t.g. spectrum.

**Table 3** Stability to heating and extraction of polychloral samples prepared with sulphonium, oxosulphonium, iodonium, and tropylium salt and sulphonium ylide initiators<sup>a</sup>

Initiator mol % with respect to chloral	Percent weight retention after		
	Heating 2 h/100°C in air	Heating in air 2 h/100°C followed by methanol extraction 2 days in Soxhlet	Methanol ex- traction 2 days in Soxhlet (no prior heating)
(CH <sub>3</sub> ) <sub>3</sub> S I (1 M in DMSO) (film) 0.77	42	b	26
(CH <sub>3</sub> ) <sub>3</sub> S I (satd. solution in DMAc) 0.5 ml. solution/5 ml. chloral	66	b	15b
(CH <sub>3</sub> ) <sub>3</sub> SCl (0.3M in DMSO)			
0.1	79	56	69
0.2	75	48	68
0.4	73	31	62
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Br (0.3M in DMSO) (polymers nearly transparent)			
0.1	79	54	54
0.2	84	54	46
0.4	82	46	59
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Br (satd solution in DMAc) 0.5 ml solution/5 ml chloral	64	b	8b
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> C1 (0.3M in DMSO) (polymers nearly transparent)			
0.1	89	c	60 <sup>c</sup>
0.2	85	c	44 <sup>c</sup>
0.4	86	c	44 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Br (0.5M in DMAc)			
0.2	50	b	2b
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Br (0.5M in CH <sub>2</sub> Cl <sub>2</sub> )			
0.5	No polymerization		
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Br·LiOC(CH <sub>3</sub> ) <sub>3</sub> (0.19M in CH <sub>2</sub> Cl <sub>2</sub> )			
0.046	32	(powder) <sup>c</sup>	
0.18		low <sup>c</sup>	
p-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> C1 (0.3M in DMSO) (polymers nearly transparent)			
0.1	84	57	45
0.2	81	50	46
0.4	72	29	44
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Br (satd. solution in DMAc) 1.0 ml. solution/8 ml. chloral	35	b	1 b
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> C1 (0.3M in DMSO)			
0.1	67	43	33
0.2	72	34	39
0.4	65	22	39
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> S(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Br (0.5M in CH <sub>2</sub> Cl <sub>2</sub> )			
0.5	No polymerization		
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> S(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Br·LiOC(CH <sub>3</sub> ) <sub>3</sub> (0.19M in CH <sub>2</sub> Cl <sub>2</sub> )			
0.046	93	c	51 c
0.18	33	c	3 c
CH <sub>3</sub> CH <sub>2</sub> OCOCH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Cl (0.3M in DMSO)			
0.1	69	34	29
0.2	70	33	40
0.4	44	6	17
(CH <sub>3</sub> ) <sub>3</sub> CS(CH <sub>3</sub> ) <sub>2</sub> Cl (0.3M in DMSO) (two experiments)			
0.1	57, 24	28, 2	20, 23
0.2	74, 69	39, 23	35, 30
0.4	68, 65	24, 19	55, 62
(CH <sub>3</sub> ) <sub>3</sub> SOI (satd. solution in DMSO) 3 ml solution/30 ml chloral	61	b	2
(CH <sub>3</sub> ) <sub>3</sub> SOI (satd. solution in DMAc) 0.5 ml solution/5 ml. chloral	60	b	6
(CH <sub>3</sub> ) <sub>3</sub> SOCI (satd. solution in DMSO) 3 ml solution/30 ml chloral	75	b	
(CH <sub>3</sub> ) <sub>3</sub> SOCI (satd. solution in DMAc) 0.5 ml. solution/5 ml chloral	60	b	12 b
(CH <sub>3</sub> ) <sub>3</sub> SOCI (0.3M in DMSO)			
0.1	78	51	51
0.2	75	35	58
0.4	65	15	56
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ICI (satd. solution in DMSO) 3 ml solution/30 ml chloral	31	b	33
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ICI (0.3M in DMAc) 0.5 ml solution/5 ml chloral	59	b	14 b
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ICI (0.3M in DMSO)			
0.1	67	43	50
0.2	77	43	59
0.4	80	38	57
Tropylium bromide (0.3M in DMSO)			
0.1	36	6	0
0.2	20	3	0
0.4	43	9	0
Tropylium bromide, 0.3M in DMSO + LTB, 0.3M in benzene			
0.2	47	7	48

**Table 3** Stability to heating and extraction of polychloral samples prepared with sulphonium, oxosulphonium, iodonium, and tropylium salt and sulphonium ylide initiators<sup>a</sup>

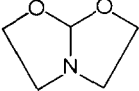
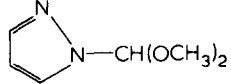
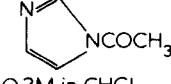
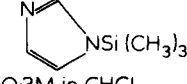
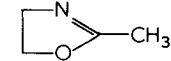
Initiator mol % with respect to chloral	Percent weight retention after		
	Heating 2 h/100°C in air	Heating in air 2 h/100°C followed by methanol extraction 2 days in Soxhlet	Methanol ex- traction 2 days in Soxhlet (no prior heating)
Tropylium chloride, satd. solution in CH <sub>3</sub> CN (approx. 0.3M)	(parenthesized numbers in third column are for samples treated with CH <sub>3</sub> OH/10% HCl for one day before extraction)		
0.1	24 <sup>c</sup>	15 <sup>c</sup>	20 (19)
0.2	59 <sup>c</sup>	35 <sup>c</sup>	43 (35)
0.4	78 <sup>c</sup>	60 <sup>c</sup>	70 (57)
LTB, 0.1, + tropylium chloride, 0.3M in CH <sub>3</sub> CN (same as above) (mole%)			
0.1	52 <sup>c</sup>	8 <sup>c</sup>	31 (25)
0.2	35 <sup>c</sup>	8 <sup>c</sup>	25 (27)
0.4	88 <sup>c</sup>	56 <sup>c</sup>	72 (65)
C <sub>6</sub> H <sub>5</sub> COCH=S(CH <sub>3</sub> ) <sub>2</sub> , 0.3M in CHCl <sub>3</sub>			
0.1	30 <sup>c</sup>	0 <sup>c</sup>	0
0.2	70 <sup>c</sup>	5 <sup>c</sup>	2
0.4	88 <sup>c</sup>	6 <sup>c</sup>	5
CH <sub>3</sub> CH <sub>2</sub> OCOCH=S(CH <sub>3</sub> ) <sub>2</sub> , 0.3M in CHCl <sub>3</sub>			
0.1	67 <sup>c</sup>	11 <sup>c</sup>	3
0.2	29 <sup>c</sup>	5 <sup>c</sup>	17

<sup>a</sup> Samples were cylindrical, about 12 mm in diameter and weighing 2 to 5 g, except as noted.

<sup>b</sup> Heated at 120°C for 1 h

<sup>c</sup> Heated at 100°C for 1 h

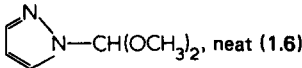
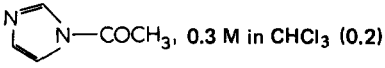
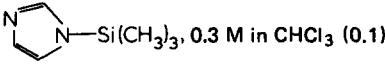
**Table 4** Heating and extraction stability of polychloral prepared with miscellaneous potentially stabilizing initiators<sup>a</sup>

Initiator, mole % with respect to chloral (b)	Percent weight retention after			
	Heating, 1 h/100°C in air	Heating in air 1 h/100°C. followed by methanol extraction, 2 days in Soxhlet	Methanol/10% HCl 1 day at room temperature followed by methanol extraction, 2 days in Soxhlet	Methanol extraction 2 days in Soxhlet
(CH <sub>3</sub> ) <sub>2</sub> NCH(OCH <sub>3</sub> ) <sub>2</sub>	0.8	8–29		
	1.6	14		
(CH <sub>3</sub> ) <sub>2</sub> NCH(OCH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub>	0.8	3		
(CH <sub>3</sub> ) <sub>2</sub> NCH/(O-cyclo-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	0.8	46		
(CH <sub>3</sub> ) <sub>2</sub> NCH(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.8	31		
	0.8	No polymerization		
	0.1	42	20	
	0.2	56	24	
	0.4	61	29	
	0.8	67	30	
	1.6	71, 77	23, 27	
	0.1	67	13	65
	0.2	65	7	69
	0.4	48	4	42
0.3M in CHCl <sub>3</sub>				5
	0.1	57	1	55
	0.2	49	0	59
	0.4	6	0	31
0.3M in CHCl <sub>3</sub>				0
	0.1–100	< 1		

<sup>a</sup> Samples were cylindrical, about 12 mm in diameter, weighing 3–10 g

<sup>b</sup> Initiator used as neat liquid unless otherwise specified

Table 5 D.t.g. spectra of polychloral samples prepared with 'onium' salt and other potentially stabilizing initiators

Initiator (mol%)	Percent of initial weight remaining in sample used after treatment given	D.t.g. parameters <sup>d</sup>	
		Onset of decomposition (°C)	Degradation rate maxima (°C) (% of total area)
(CH <sub>3</sub> ) <sub>3</sub> SI, 1M in DMSO (0.77)	42 <sup>a</sup>	160	220 (47), 272 (53)
(CH <sub>3</sub> ) <sub>3</sub> SI, satd. in DMAc (Table 3)	15 <sup>b</sup>	140	244 (60), 320 (40)
(CH <sub>3</sub> ) <sub>3</sub> SCl, 0.3M in DMSO (0.1)	56 <sup>b</sup>	100	237 (87), 283 (13)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Br, 0.3M in DMSO (0.1)	54 <sup>b</sup>	100	210 (100)
	54 <sup>c</sup>	110	231 (100), 170 (sh)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Br, satd. in DMAc (Table 3)	8 <sup>b</sup>	135	210 (90), 310 (10)
	60 <sup>b</sup>	130	209 (70), 327 (30)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> C1, 0.3M in DMSO (0.1)	62 <sup>c</sup>	110	191 (40), 322 (60)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Br, 0.5M in DMAc (Table 3)	2 <sup>c</sup>	130	205 (100)
p-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> C1, 0.3M in DMSO (0.1)	57 <sup>b</sup>	110	224 (100)
	45 <sup>c</sup>	120	250 (100), 180 (sh)
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> Br, satd. soln. in DMAc (Table 3)	1 <sup>b</sup>	120	200 (100)
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> C1, 0.3M in DMSO (0.1)	43 <sup>b</sup>	100	215 (100)
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> S(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Br·LiOC(CH <sub>3</sub> ) <sub>3</sub> 0.19M in CH <sub>2</sub> Cl <sub>2</sub> (0.18)	51 <sup>b</sup>	110	175 (100)
CH <sub>3</sub> CH <sub>2</sub> OCOCH <sub>2</sub> S(CH <sub>3</sub> ) <sub>2</sub> C1, 0.3M in DMSO (0.1)	34 <sup>b</sup>	120	226 (100)
(CH <sub>3</sub> ) <sub>3</sub> CS(CH <sub>3</sub> ) <sub>2</sub> C1, 0.1	28 <sup>b</sup>	130	230 (100)
0.3M in DMSO 0.2	23 <sup>b</sup>	130	210–225 (100)
(CH <sub>3</sub> ) <sub>3</sub> SOI, satd. soln. in DMSO (Table 3)	61 <sup>a</sup>	120	194 (94), 250 (6)
(CH <sub>3</sub> ) <sub>3</sub> SOI, satd. soln. in DMAc (Table 3)	6 <sup>b</sup>	130	197 (100), 267 (sh)
(CH <sub>3</sub> ) <sub>3</sub> SOC1, satd. soln. in DMSO (Table 3)	75 <sup>a</sup>	130	210 (100), 247 (sh)
(CH <sub>3</sub> ) <sub>3</sub> SOC1, satd. soln. in DMAc (Table 3)	12 <sup>b</sup>	140	220 (100), 300 (sh)
(CH <sub>3</sub> ) <sub>3</sub> SOC1, 0.3M in DMSO (0.1)	51 <sup>b</sup>	110	219 (100)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ICl, satd. soln. in DMSO (Table 3)	31 <sup>a</sup>	120	180 (100)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ICl, satd. soln. in DMAc (Table 3)	14 <sup>b</sup>	140	225 (80), 320 (20)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ICl, 0.1M in DMSO (0.1)	43 <sup>b</sup>	120	205 (83), 283 (17)
Tropylium bromide, 0.3M in DMSO (0.1)	6 <sup>b</sup>	140	215 (100)
Tropylium bromide, 0.3M in DMSO (0.2) + LTB, 0.3M in benzene (0.1)	7 <sup>b</sup>	130	202 (100)
Tropylium chloride, approx. 0.3M in CH <sub>3</sub> CN (0.4)	78 <sup>b</sup>	130	217 (100)
	70 <sup>c</sup>	120	196 (100)
Tropylium chloride ~0.3M in CH <sub>3</sub> CN (0.2) + LTB, 0.3M in benzene (0.1)	8 <sup>b</sup>	120	202 (100), 252 (sh)
C <sub>6</sub> H <sub>5</sub> COCH=S(CH <sub>3</sub> ) <sub>2</sub> , 0.3M in CHCl <sub>3</sub> (0.2)	5 <sup>b</sup>	130	230–310 (broad)
C <sub>2</sub> H <sub>5</sub> OCOCH=S(CH <sub>3</sub> ) <sub>2</sub> , 0.3M in CHCl <sub>3</sub> (0.2)	5 <sup>b</sup>	130	212 (100)
 N-CH(OCH <sub>2</sub> ) <sub>2</sub> , neat (1.6)	77 <sup>a</sup>	50	162 (87), 264 (13)
 N-COCH <sub>3</sub> , 0.3 M in CHCl <sub>3</sub> (0.2)	7 <sup>b</sup>	110	212 (100)
 N-Si(CH <sub>3</sub> ) <sub>3</sub> , 0.3 M in CHCl <sub>3</sub> (0.1)	1 <sup>b</sup>	110	195 (100), 152 (sh)

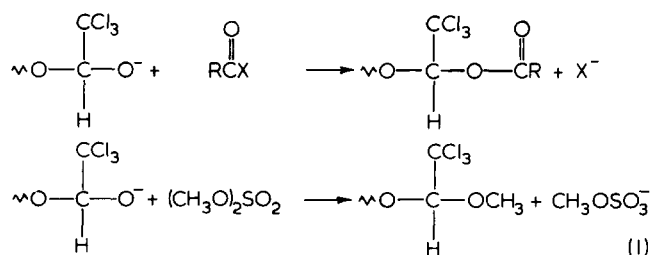
<sup>a</sup> Heated without extraction (1 or 2 h at 100–120°C in air; see Tables 24 and 25 for details).

<sup>b</sup> Heated followed by Soxhlet extraction with methanol.

<sup>c</sup> Soxhlet extracted with methanol without prior heating.

<sup>d</sup> D.t.g. data for sample after heating or extraction (listed in weight percentage column).

Dimethyl sulphate was also added to LTB- and Ph<sub>3</sub>P-initiated chloral polymerization mixtures as a potential stabilizing agent. It was thought that dimethyl sulphate could methylate the alkoxide-terminated polychloral chain just as acyl halides could acylate it (equation 1). In Ph<sub>3</sub>P-



initiated chloral polymerization over a range of dimethyl sulphate concentrations, very low yields of polymer stable to methanol extraction (1–10%) were obtained. This was the case regardless of whether the Ph<sub>3</sub>P or the dimethyl sulphate was added first to the warm chloral. Perhaps a mechanism operated here similar to that which lowered polymer yield when bromoacetyl bromide was used as an additive.

In sharp contrast to the situation with Ph<sub>3</sub>P initiation, addition of dimethyl sulphate to LTB-initiated chloral polymerization mixtures led to highly irreproducible results. In the experiment shown in Table 1 twelve test tubes were dried and capped under identical conditions and filled with chloral from the same distillation cut. The tubes were warmed to 70°C and injected with LTB solution and the





with bromide or iodide salts. For this reason, a number of the sulphonium and oxosulphonium bromides and iodides were converted to chlorides by metathesis. Bromide and iodide salts were allowed to react in water with a substantial excess of freshly precipitated AgCl. Water instead of methanol or ethanol solutions was used for these metathesis reactions, because a number of sulphonium salts were found to be more susceptible to solvolysis in alcoholic than in aqueous solutions.<sup>37,38</sup> A number of sulphonium bromides could not be converted to crystalline chlorides by the above metathesis procedure.

Some of the sulphonium salts had melting points which differed markedly from the literature values. However, since all sulphonium salts melt with decomposition, the 'melting' point is often quite dependent on heating rate; when more than one melting or decomposition point for a salt is given in the literature, the temperatures listed often vary considerably. Infra-red and <sup>1</sup>H n.m.r. spectra, and where indicated, elemental analyses were determined to verify the identity of the compounds prepared.<sup>25</sup>

The salts were dissolved in appropriate solvents and used as initiators for chloral polymerization. Unfortunately, the only satisfactory aprotic solvent for many of the salts was DMSO, which tends to undergo side reactions above 80°C. However, DMSO was the only available aprotic solvent which would dissolve many of the initiators to a concentration of > 0.1 M, and therefore was in most cases used as the carrier solvent for dissolving the initiators in the warm chloral before polymerization.

Polychloral plugs, after polymerization, were generally cut into 2 pieces. One piece was heated at 100°C (or 120°C) for 1 to 2 h in an effort to effect the stabilization reaction between the polychloral alkoxide end-groups and the sulphonium ions. The other piece was extracted with methanol in a Soxhlet extractor without preheating as a control sample. After heating, the sample was divided into 2 parts, one of which was also Soxhlet extracted with methanol. Heating and extraction stability data for polychloral prepared with the various initiators are shown in Table 3, while d.t.g. data are given in Table 5

As can be seen from Table 3, most of the polychloral samples prepared with sulphonium initiators were at least 65% stable to the heat treatment and at least 40% stable to extraction with or without the heat treatment. The heat treatment generally had little effect on subsequent extraction stability (with the pre-work-up sample as a base) and in most cases the amount of initiator used (from 0.1 to 0.4 mol %) had little effect on extraction stability. Some of the polychloral samples, particularly those prepared with trimethylsulphonium and benzyldimethylsulphonium halides, were thermally stable and were extracted in amounts comparable with that found in Ph<sub>3</sub>P-initiated polychloral.

With regard to stabilization, although initial work with sulphonium salts (Table 5) led to quite promising results, attempts to perfect the stabilization capabilities of the systems did not increase the amount of stable fraction. Trimethylsulphonium iodide and chloride produced polychloral samples sometimes containing over 50% of stable polymer fraction (with a d.t.g. peak near 300°C) in the heated or extracted polymer. However, the 'stabilized' fraction as a percentage of initial polymer weight was low (6–22%) because of extensive degradation of the polymer during heating and extraction.

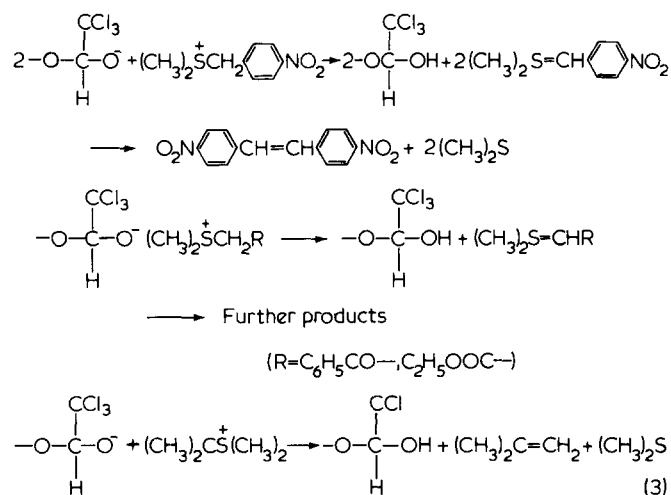
It was thought that the problem hindering stabilization of the polychloral by the trimethylsulphonium cation could

be resistance of the cation to nucleophilic attack by the polychloral alkoxide anion. Hence sulphonium salts were prepared containing substituent groups such as benzyl, *p*-nitrobenzyl, phenacyl, carbethoxymethyl and tert-butyl; it was felt that these groups would be considerably easier to displace nucleophilically than the methyl group. In the thermal decomposition of benzyldimethylsulphonium<sup>36</sup> or phenacyldimethylsulphonium<sup>35</sup> salts, the benzyl or phenacyl and dimethyl sulphide were formed in high yield, showing that attack by the anion occurred preferentially on the benzyl or phenacyl group and not on the methyl group.

When these salts were used as chloral initiators, the benzyldimethylsulphonium chloride produced some significant stabilization of the polychloral, even when used as a solution in DMSO. A polychloral section which was heated and then extracted with methanol contained 30% of a 'stabilized' fraction with a d.t.g. peak temperature above 300°C, but another section from the same sample which was extracted with methanol without prior heating contained 60% of this 'stabilized' fraction (Table 5). (These correspond to 16% and 37% of the original polymer weight respectively). The higher percentage of stabilized fraction in the unheated than in the heated sample suggested that the reaction between the polychloral alkoxide group and the benzyldimethylsulphonium ion had taken place extensively in the polymer before heating, or perhaps that methanol application might have promoted the desired reaction, with application of heat instead causing side reactions. Benzyldimethylsulphonium bromide (as a DMSO solution) when used as an initiator did not appear to cause any end-capping, although a small amount of stabilization was noticeable when a DMAc solution was used as an initiator.

Dimethylsulphonium bromides or chlorides containing *p*-nitrobenzyl, phenacyl, carbethoxymethyl, or tert-butyl substituent groups were effective chloral polymerization initiators, although the yield of polychloral after extraction was lower than for the trimethyl- or benzyldimethylsulphonium salts. However, no end-capping could be detected in the d.t.g. spectra or polychloral initiated with these salts; the d.t.g. spectra of the heated, methanol-extracted polymers resembled that of polychloral containing only hydroxyl end-groups.

Although this result at first appeared very puzzling in light of the observed stabilization of polychloral by trimethyl- and benzyldimethylsulphonium salts, it may be possible that hydroxyl groups (which would not be alkylated by sulphonium ions) are formed from the growing polychloral alkoxide groups by one of the following reactions:





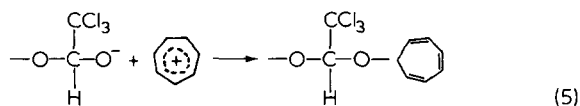
fifth compound did not homopolymerize chloral at all, while the sixth produced a nearly transparent polymer of intermediate stability to heating in air. The d.t.g. spectrum of this polymer (Table 5), however, gave dubious, if any, evidence for end-capping. It seems rather noteworthy that in polychloral initiated with this pyrazole amide acetal initiator, polymer stability to heating and extraction generally increased rather than decreased with increasing initiator concentration. This is in sharp contrast to the behaviour of polychloral initiated with pyridine, triethylamine, or tributylamine.<sup>24</sup> Even though the pyrazole amide acetal contains a basic nitrogen, excess initiator apparently does not catalyse polymer thermal decomposition or methanolysis as is the case with polychloral initiated with other amines.

Because of the tendency of acyl- or silylimidazoles to act as acylating or silylating agents for hydroxyl groups,<sup>45,46</sup> *N*-acetylimidazole and *N*-(trimethylsilyl)-imidazole were also tested as chloral initiators, in the hope that the polychloral end-groups would be acetylated or trimethylsilylated by these materials. However, polychloral prepared with these initiators showed the standard behaviour of amine-initiated polychloral (Table 4), with stability to heating low and decreasing with increasing initiator concentration and stability to methanol extraction very low but markedly increased by acid treatment. The d.t.g. spectra of polychloral prepared with these initiators showed no evidence of end-capping.

2-methyl-2-oxazoline, a member of a class of compounds first prepared and polymerized by Litt<sup>47</sup> and later found by other groups<sup>48</sup> to serve as initiators for, and comonomers with, many electrophilic monomers such as  $\beta$ -propiolactone, was tested as an initiator for cryotachensic polymerization.

2-methyl-2-oxazoline was tested as an initiator for cryotachensic polymerization of chloral over a concentration range from 0.1 mol % to equimolar. At low initiator concentrations, soft, weak polychloral gels were formed which were less than 1% stable to heating 1 h in air at 100°C, followed by methanol extraction. At equimolar initiator concentrations, a crystalline compound was formed which melted at 118°–119°C.

To test further the concept of stabilization by initiators and to explore the limits of initiation in the presence of reactive cations, however, we wished to use an initiator containing a countercation which could react with the polychloral alkoxide anion without the necessity of displacement of a group from the cation. Hence tropylium bromide and chloride were prepared and tested as initiators for chloral polymerization. It was thought that the halide ion would initiate a standard anionic polymerization of chloral, but that the tropylium ion would react with any polychloral alkoxide end-group encountered immediately upon contact to form a cycloheptatrienyl ether end-group (equation 5). This reaction occurs rapidly in methanol with sodium methoxide and tropylium bromide.<sup>29</sup>



Tropylium bromide dissolved in DMSO was a poor initiator for chloral polymerization (Table 4). The resultant polymers have a low stability to heating and methanol extraction. The polymer produced with a mixture of 0.2 mol % tropylium bromide and 0.1 mol % LTB was somewhat more stable to extraction, but neither form of polymer showed

any trace of end-capping by d.t.g. (Table 6). It may be argued that the reason for these results is that much of the tropylium bromide was consumed by a side reaction with DMSO. Tropylium chloride was therefore prepared, dissolved in  $\text{CH}_3\text{CN}$  and used as a chloral initiator. This initiator produced chloral polymers which were much more stable to heating and extraction than those prepared with tropylium bromide in DMSO, but which also showed no peak near 300°C in the d.t.g. spectrum (Table 5). The same results were observed when tropylium chloride was used as an additive to chloral initiated with LTB.

The failure of tropylium salts to end-cap polychloral chains is difficult to explain. Such results might be expected if the polymerization occurred by a cationic, rather than an anionic, mechanism. However, the polymer obtained from chloral by tropylium salt initiation is hard and tough, not powdery like typical cationically-initiated polychloral. Most likely, tropylium ion may undergo a side reaction with chloral (and/or acetonitrile) converting it into a species which cannot end-cap the polychloral chain.

One attempt was made to use as an initiator for chloral polymerization a salt containing an acid bromide group,  $\text{BrCOCH}_2\text{S}^+(\text{CH}_3)_2 \text{Br}$ . However, this salt, or rather the uncharacterized reaction product of bromoacetyl bromide with dimethyl sulphide, as a solution in sulpholane, did not polymerize chloral.  $\text{Ph}_3\text{P}$  in the presence of bromoacetyl bromide (or sulpholane) did cause chloral polymerization.

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