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### Haloaldehyde Polymers. XIX. Degradation Behavior of Chloral Polymers

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## Haloaldehyde Polymers. XIX.\* Degradation Behavior of Chloral Polymers

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### ABSTRACT

Thermal stability of samples of polychloral prepared with different initiators and treated with various endcapping agents was studied using differential thermogravimetric analysis (DTG). Four temperature regions at which maxima of DTG curves occur were identified. On the basis of the known mechanism of initiation and the possible mechanism of termination, the structures of both initial and terminal endgroups of individual polychloral samples were elucidated which enabled the identification of the specific temperature region of thermal degradation of polychloral molecules having a specific type of endgroup. These results were confirmed by studies of the DTG curves of chloral-isocyanate copolymers containing stable terminal fragments with a high content of urethane linkages.

### INTRODUCTION

Since the development of cryotachensic chloral polymerization [1-4], the preparation of films and uniform pieces of polychloral of

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\*Part XVIII, by P. Kubisa, T. Teshirogi, K. Hatada, L. S. Corley, and O. Vogl, is in preparation.

desired shape has become possible. Polychloral as prepared has a rather limited thermal stability [5-14]; polymer stabilization similar to that of other polyacetals is necessary.

The concepts of stabilization of polymers of the polyacetal type were developed in the past for polyoxymethylene [15, 16], as the commercial application of this polymer became possible only after effective methods of stabilization had been developed. In the early work it was recognized that the main factor determining the thermal stability of polyacetals was the structure of the polymer endgroups, and that thermal degradation of polyacetals proceeded by the so-called "unzipping" mechanism [17]. As soon as the degradation process is initiated, polymer is transformed back into its monomer.

The reason for this behavior is that the polymerization of aldehydes and cyclic acetals proceeds with a relatively small enthalpy of polymerization ( $\Delta H_{\text{polym}}$ ), and the entropy factor  $T\Delta S_{\text{polym}}$  may easily outweigh  $\Delta H_{\text{polym}}$  even at relatively low temperatures making the free energy of polymerization  $\Delta G_{\text{polym}}$  positive [18]. Above the

ceiling temperature the polymer is thermodynamically unstable with respect to its monomer and decomposes spontaneously. Before this process can take place the weakest bond within the polymer chain, which is often the endgroup, must be broken either thermally or otherwise in order to produce the active species for depropagation. Thus stabilization of unstable polymers, such as polyacetals, requires the formation of endgroups which are resistant to thermal decomposition.

In order to produce a thermally stable polyacetal it is necessary to know the structure of the endgroups formed by the individual polymerization system. If the thermal stability of these original endgroups obtained at the end of the polymerization is not sufficient, a method must be developed to replace them with more stable endgroups.

The objective of the present work was to study the thermal properties of chloral polymers prepared under conditions (anionic or cationic polymerization) in which the structure of the endgroups may be reasonably predicted. On the basis of our analysis of DTG curves of polychloral samples containing different endgroups, attempts will be made to relate the thermal stability of polychloral samples with the structure of the initial and terminal endgroups.

## EXPERIMENTAL PART

### Preparation of Samples

The procedures for preparation and posttreatment with stabilizing reagents of the samples of polychloral and chloral-isocyanate copolymers used in this work have been given in previous papers in this series [11-14, 19-21].

## Measurements

Differential thermogravimetric analysis (DTG) of polymer samples was carried out in a nitrogen atmosphere (nitrogen flow rate = 30 cc/min) using a Perkin-Elmer TGS-1 Thermobalance at a programmed heating rate of 20°C/min. Degradation of selected polychloral samples was studied at lower heating rates.

Onset temperature of degradation, the beginning of the deviation from the baseline, and maximum degradation temperature, the maximum rate of weight loss, are recorded. We also use expressions peaks of the thermal degradation spectrum to refer to the descriptions of the thermal degradation behavior as recorded in the DTG mode [22].

## RESULTS AND DISCUSSION

The thermal stability of polychloral depends strongly on the nature of the initiator used and on the posttreatment procedure applied. During the thermal degradation of polychloral, chloral monomer is formed exclusively, which leads to the conclusion that thermal degradation is an unzipping reaction (depropagation) with initiation occurring at the chain ends. The same mechanism was also established for other polyaldehydes, especially for polyoxymethylene. Thermally unstable polymers of formaldehyde containing predominantly hydroxyl endgroups have been stabilized by replacing the hydroxyl hemiformal endgroups (from which the unzipping process starts) with stable ester or ether endgroups which increase the activation energy of initiation of depolymerization.

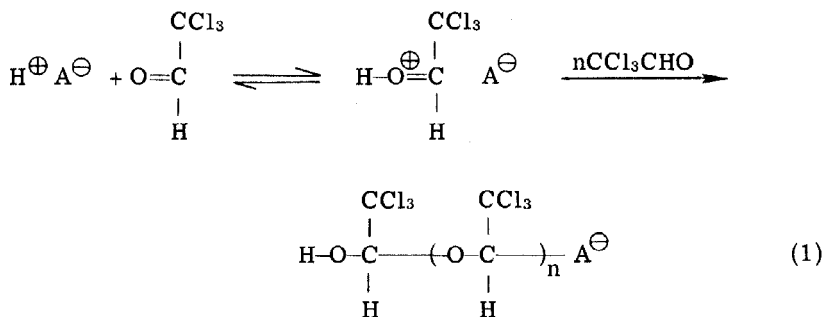
To understand all phenomena related to the thermal stability of polychloral, it was necessary to identify possible endgroups and to study the thermal degradation of polychloral containing different endgroups of well-defined structure. Although some information on this subject has recently been published [10-14], no comprehensive or comparative study of the thermal stability of polychloral and its relation to endgroup structure has been made.

## Endgroup Analysis

Homo- and copolymers of chloral are insoluble and infusible, which limits greatly the scope of analytical approaches which can be used to identify polychloral endgroups. Moreover, because of the insolubility the molecular weight of the polymer cannot be easily determined; the actual concentration of endgroups in polymers cannot be estimated as all presently known analytical methods provide only qualitative or semiquantitative information which is of limited value.

Nevertheless, rather intensive studies to characterize polychloral

samples by IR spectroscopy have been performed [5-7, 9-11]. The typical IR spectrum of a high molecular weight polychloral film prepared by cryotachensic polymerization gave no indication of the presence of any specific endgroups in polymers prepared with a variety of anionic initiators [11]. On the other hand, IR spectra of polychloral prepared by a cationic mechanism with protonic acids as initiators showed a broad peak at  $3400\text{ cm}^{-1}$ , indicative of hydroxyl endgroups [5, 6, 11]. This observation suggested that hydroxyl endgroups were formed as a result of protonation of monomer at the initiation step:



The same peak is found in the IR spectra of low molecular weight polychloral powders prepared with large concentrations of lithium tertiary butoxide (LTB) initiator and subsequently treated with methanolic HCl [11]; its intensity decreases when these polymer powders are stabilized by treatment with  $\text{PCl}_5$ .

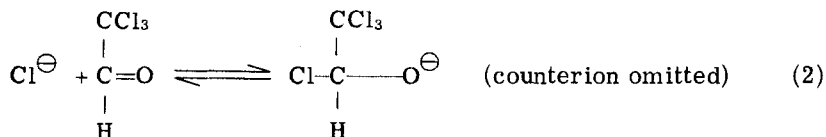
There has been some indication that molecular weights of polymers prepared by cationic and anionic mechanisms may be different, and the DP of polychloral films prepared by standard cryotachensic anionic polymerization is much higher [11]. The absence of hydroxyl group peaks in IR spectra of anionically polymerized polychloral films consequently does not exclude the possibility that these endgroups are formed as terminal endgroups. The concentration of endgroups in high molecular weight polymers would be lower than in polychloral obtained by a cationic mechanism. This possibility is supported by the fact that although different posttreatment procedures (e.g., treatment of polymer samples with solutions of acetyl chloride or phosphorus pentachloride) considerably improve thermal stability of polychloral films prepared by cryotachensic anionic polymerization, which indicates that the nature of the endgroups is affected by this procedure, no change of the IR spectrum of the polymer was observed after the treatment [7, 11], indicating that the concentration of endgroups is below the detection level (although diminution of the hydroxyl peak was observed in low molecular weight polychloral [11]). Consequently, on the basis of IR studies alone it is impossible to draw any definite

conclusions concerning the structure of the endgroups in high molecular weight polychloral prepared by the cryotachensic anionic method.

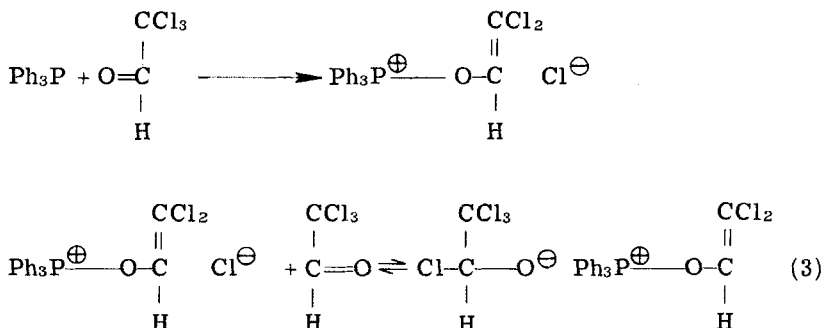
### Studies of Initiation Mechanism

The mechanism of initiation of anionic and cationic polymerization of chloral was extensively studied in this laboratory [11, 19, 20] and it was found that the majority of anionic initiators which were found to be effective for chloral polymerization may be divided into two categories.

(a) Initiators which contain, or are able to produce in situ, a chloride anion  $\text{Cl}^-$ , which initiates polymerization by addition to a monomer molecule:



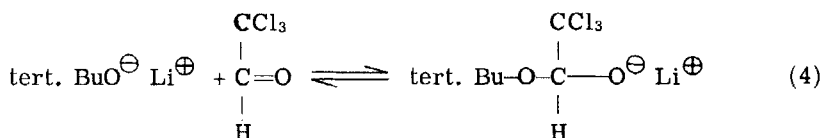
To this group belong stable organic salts containing the  $\text{Cl}^-$  anion: carbenium (e.g., tropylium) chlorides, sulfonium (e.g., trimethylsulfonium) chlorides, and ammonium (e.g., tetraethylammonium) chlorides and also some inorganic salts, e.g., lithium chloride.  $^1\text{H}$  NMR studies of the initiation mechanism of chloral polymerization initiated by tertiary phosphines (e.g., triphenylphosphine) revealed that in this system the true initiator is also a chloride anion which is formed in the preinitiation step in which triphenylphosphine reacts with 1 mole of chloral-forming triphenyl(dichlorovinyl)oxyphosphonium chloride:



Consequently, tertiary aromatic phosphines are also included into this category.

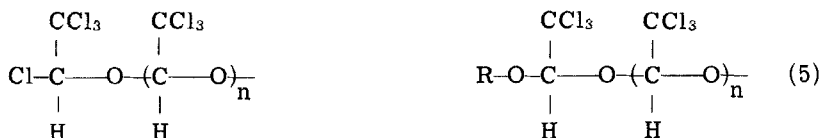
The mechanism of initiation with tertiary amines as initiators is not clear although some results indicate that a zwitterion mechanism may be operating [10]. This system will not be discussed here.

(b) Salts which initiate the polymerization by addition of alkoxide anion. The typical example of this group is LTB which was found to be the most effective initiator of this group:

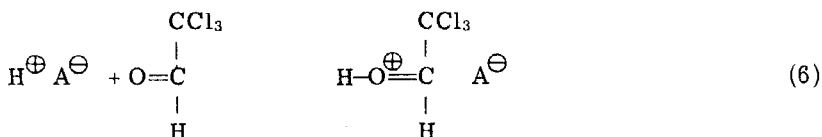


The structure of the first product of addition (shown in Eq. 4) was proven by  $^1\text{H}$  NMR spectroscopy, and it was found that Reaction (4) is fast, its equilibrium being shifted almost completely to the right-hand side.

Thus, by proper choice of initiator, it is possible to obtain by anionic mechanism polymers of chloral containing known endgroups at the beginning of the chain:



The cationic polymerization of chloral has been studied to a lesser extent. It was, however, established that chloral can be polymerized by protonic acids (e.g., trifluoromethanesulfonic or sulfuric acid [5, 6, 20]). Although the mechanism of initiation was not studied specifically, it may be reasonably assumed that initiation involves protonation of the monomer molecule:



This proposition is strongly supported by the results of IR studies indicating the presence of hydroxyl endgroups in those polychloral samples prepared with protonic acids as initiators.

Thus, in addition to two known endgroups which are introduced at the beginning of polychloral chains by anionic polymerization, cationic initiation produces the third well-defined structure



by forming a hydroxyl group by protonation of the carbonyl oxygen of chloral as the initiation step.

### Structure of the Terminal Endgroups

The depolymerization may with equal probability be initiated on both ends of the macromolecule. Thus, in order to relate the thermal stability of polychloral to the structure of its endgroups, it is necessary to know also the structure and stability of the terminal endgroup. As already mentioned, no chemical or spectroscopic method could be reliably and unequivocally applied to determine the structure of the terminal endgroup.

We have analyzed the thermal behavior of chloral polymers prepared with different initiators in an effort to identify the structure of the terminal endgroup. DTG curves of polychloral usually show more than one maximum when the rate of weight loss is plotted against temperature; moreover, the number and positions of maxima of the rate of degradation depend on the initiator used to produce the initial endgroup and the posttreatment procedure used to produce the terminal endgroup. This observation is evidence that degradation indeed starts from the endgroups of the polymers and that the temperatures at which maxima occur are characteristic for specific types of endgroups. The highest temperature of any observed for the DTG maxima indicates that the stability of the main chain has probably been reached. This conclusion is supported by the results of experiments in which the thermal stability of cyclic trimers of chloral was compared with that of the polymer.

### Analysis of DTG Curves

The shape of DTG curves depends not only on the chemical structure of the analyzed material but also on such factors as the heating rate, nitrogen flow rate, and size and physical characteristics of the polymer sample. In order to limit the influence of these factors on the shape of DTG curves and position of maxima, the conditions of measurement were standardized. All DTG curves reported in this paper were obtained with a constant heating rate ( $20^{\circ}\text{C}/\text{min}$ ) and a nitrogen flow rate ( $30\text{ cm}^3/\text{min}$ ), and the sample size used was  $10 \pm 2$  mg. The standardization of sample morphology was more difficult. Generally, polymer films were used and in some cases (when the polymers were prepared with high initiator concentration and only powdery polymer was obtained) the polymers were analyzed as powders. To evaluate the effect of the sample morphology on the position of the maximum in DTG curves, polymer films of different thickness varying from 0.08 to 0.25 mm were prepared under identical experimental conditions from the same solution at the same time and the corresponding DTG spectra were determined. The DTG curves of



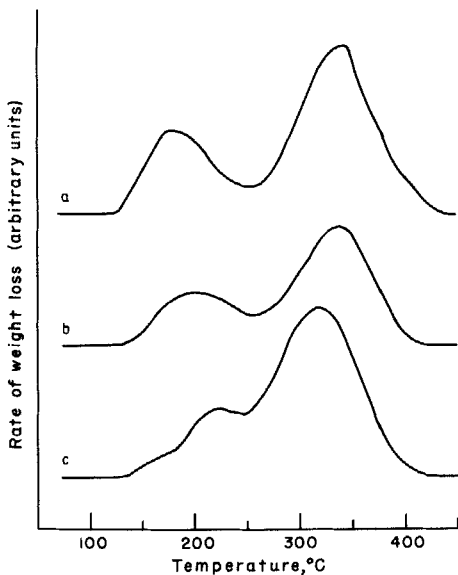


FIG. 1. DTG curves of polychloral films of different thickness prepared under identical conditions.  $\text{Ph}_3\text{P}$ : 0.3% mole, polymers treated with  $\text{PCl}_5/\text{CCl}_4$  and extracted. Film thickness: (a) 0.25 mm, (b) 0.20 mm, (c) 0.08 mm.

polychloral samples of three different thicknesses initiated with  $\text{Ph}_3\text{P}$  are shown in Fig. 1. All three curves are bimodal, the higher temperature maximum decreasing by  $20^\circ\text{C}$  to lower temperatures for the thinner films. This characteristic reflects the more effective heat and mass exchange in thinner sections.

Since the DTG peak position changes slightly with varying film thickness, it is necessary to use films of the same thickness in order to obtain comparable data for different samples. This was achieved by using the spacer of the same thickness to separate the glass plates and applying the same type and number of clamps to hold the plates together. Even when standard experimental techniques were applied, the thickness of films used varied and the positions of DTG maxima also varied with  $\pm 15^\circ\text{C}$  from sample to sample. Nevertheless, separate maxima could be observed clearly for most of the samples at a heating rate of  $20^\circ\text{C}/\text{min}$  and their positions could be fitted within one of four well-defined temperature regions ( $170 \pm 15^\circ\text{C}$ ,  $210 \pm 15^\circ\text{C}$ ,  $300 \pm 15^\circ\text{C}$ , and  $340 \pm 15^\circ\text{C}$ ).

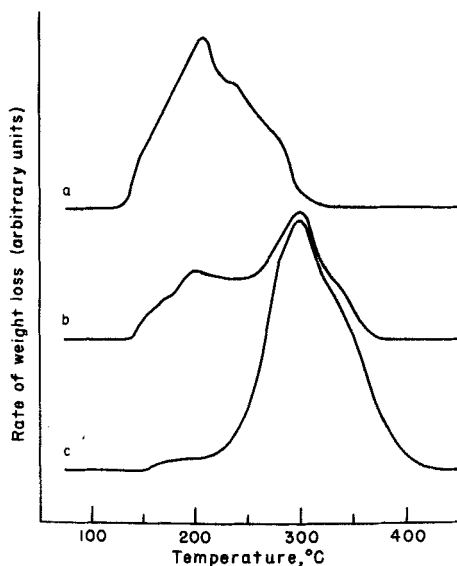


FIG. 2. DTG curves of polychloral showing disappearance of the maximum at  $210 \pm 15^\circ\text{C}$  after  $\text{CH}_3\text{COCl}$  and  $\text{PCl}_5/\text{CCl}_4$  treatment. (a) LTB: 0.1% mole, extracted. (b) LTB: 1.8% mole, refluxed 2 days with  $\text{CH}_3\text{COCl}$ , extracted. (c) LTB: 0.1% mole, refluxed 4 days with  $\text{PCl}_5/\text{CCl}_4$ , extracted.

### Interpretation of DTG Curve Maxima

The maxima of the rate of thermal degradation (MDT) observed for a number of polychloral samples prepared by cationic or anionic polymerization can be fitted within one of four temperature regions, namely:  $170 \pm 15^\circ\text{C}$ ,  $210 \pm 15^\circ\text{C}$ ,  $300 \pm 15^\circ\text{C}$ , and  $340 \pm 15^\circ\text{C}$ .

A maximum at  $210 \pm 15^\circ\text{C}$  appears on essentially all DTG spectra of polychloral prepared by an anionic mechanism, but its intensity decreases after treatment of the samples with  $\text{CH}_3\text{COCl}$  and completely disappears after prolonged treatment with a  $\text{PCl}_5$  solution. This is illustrated in Fig. 2 in which DTG curves of anionically prepared polychloral subjected to different posttreatment procedures are shown. Curve "a" shows the degradation of unstabilized polymer which was extracted for 2 days with methanol. The polychloral sample decomposed within the low temperature region but with a maximum of the decomposition rate at  $210^\circ\text{C}$ . Polymer "b" was subjected to  $\text{CH}_3\text{COCl}$  treatment; the resulting DTG curve is bimodal showing the presence of two fractions with maxima at 210 and  $300^\circ\text{C}$ . Finally, Polymer "c" treated with  $\text{PCl}_5$  shows only one maximum at

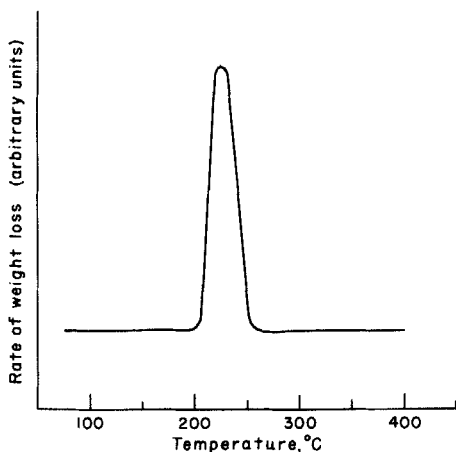
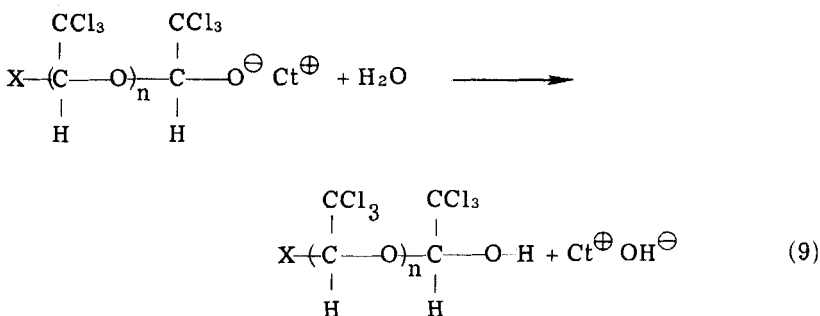
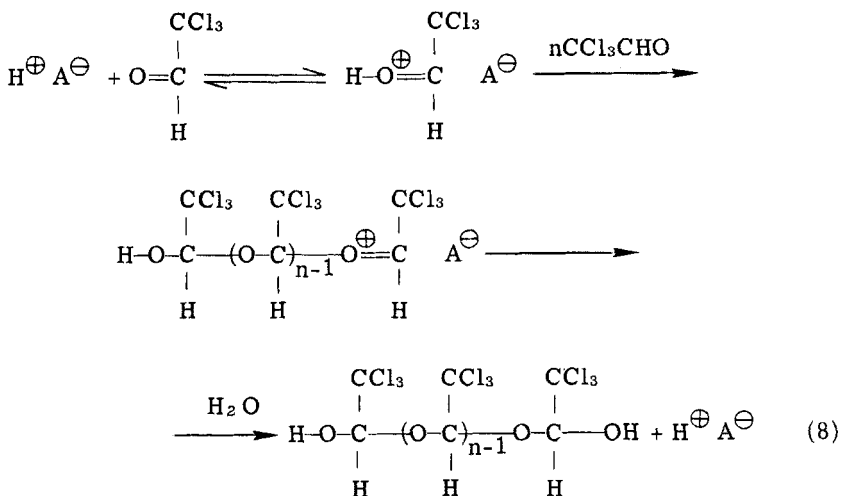


FIG. 3. DTG curve of polychloral prepared by cationic mechanism with  $\text{H}_2\text{SO}_4$  as initiator.  $\text{H}_2\text{SO}_4$ : 2% mole, extracted.

$300^\circ\text{C}$  with only a small shoulder at lower temperatures. These results indicate that upon the action of  $\text{PCl}_5$  or acetyl chloride (which may act either as an acetylating or a chlorinating agent [7, 10-12]), as stabilizing agents, polymer endgroups which are responsible for the presence of fractions decomposing at  $210 \pm 15^\circ\text{C}$  are replaced by endgroups from which degradation starts at a much higher temperature ( $300 \pm 15^\circ\text{C}$ ).

The MDT at  $210 \pm 15^\circ\text{C}$  also appears on DTG curves of polychloral prepared by a cationic mechanism with  $\text{H}_2\text{SO}_4$  as initiator. In this case the degradation peak is sharp and degradation occurs fast and within the narrow temperature range (Fig. 3). These observations indicate that a  $210 \pm 15^\circ\text{C}$  degradation temperature is associated with a polymer with OH endgroups. Polychloral prepared by cationic polymerization probably contains two hydroxyl endgroups, one formed in the initiation step and the other formed either by chain transfer to adventitious water or by hydrolysis of sulfuric acid ester endgroup during workup and extraction of the polymer (extraction was carried out with acetone or methanol without special attention to the extraction conditions, i.e., without drying the solvents). In such cases, degradation may simultaneously start from both ends of the macromolecule. Consequently, once the degradation had started, the rate was expected to be higher than the rate of degradation of polychloral prepared by an anionic mechanism, which normally contains only one terminal hydroxyl group formed in the reaction of alkoxide endgroups with protonic acid or water (Eqs. 8 and 9).

The disappearance of the  $210 \pm 15^\circ\text{C}$  peak of the MDT curves after treatment with  $\text{CH}_3\text{COCl}$  or  $\text{PCl}_5$  is in full agreement with the assumption



X = Cl or RO, Ct<sup>⊕</sup> = Counterion

that this maximum is indicative of the presence of hydroxyl endgroups. Hydroxyl groups should be either acetylated or replaced by chlorine upon this treatment. Thus we conclude that the fraction of polychloral which shows a degradation rate maximum at  $210 \pm 15^\circ\text{C}$  contains hydroxyl endgroups.

As mentioned earlier, in some polychloral samples maxima appear at still lower temperatures ( $170 \pm 15^\circ\text{C}$ ), indicating the presence of a fraction which is less stable than the fraction terminated with hydroxyl endgroups. The maximum at  $170 \pm 15^\circ\text{C}$  was found on MDT curves of raw, unextracted polymer as shown in Fig. 4. This fraction is generally unstable to extraction, partially unstable to heat treatment at  $100^\circ\text{C}$ , and, in most cases, was completely degraded after 3 days of extraction with boiling acetone or methanol. In some samples, however, especially those which were prepared with a high

concentration of LTB as initiator (1-5 mole %), some unstable fraction was still present after the extraction (Fig. 4).

This fraction of low thermal stability (MDT = 170°C), considerably lower than the stability of polychloral terminated with hydroxyl endgroups, may consist of nonterminated alkoxide anions which, although potentially able to participate in both propagation and depropagation processes, are "deactivated" as a result of occlusion within the polychloral gel or else incapable of further reaction because of complete insolubility of the polymeric gel matrix. During the precipitation of the partially crystalline polymer a  $\Delta H_{\text{cryst}}$  of 8-12 kJ/mole had been gained and the depropagation equilibrium shifted to higher temperatures.

The experimental results which strongly support this hypothesis are shown in Fig. 5. DTG curves of polychloral obtained by anionic mechanism with low concentration of LTB initiator show no indication of the presence of the 170 ± 15°C fraction in the polymer. Some, but not all, polymers prepared with high LTB concentration have this polymer fraction clearly present.

In polychloral samples prepared with low initiator concentration (0.1 mole %), the concentrations of growing alkoxide ions and adventitious water may be comparable, thus nearly all polymer molecules could be ultimately terminated with hydroxyl endgroups. For chloral

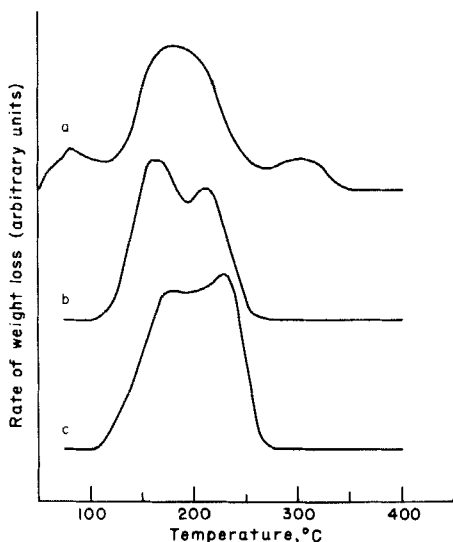


FIG. 4. DTG curves of polychloral showing the presence of a maximum at 170 ± 15°C. (a) Ph<sub>3</sub>P: 0.2% mole, unextracted. (b) LTB: 1.8% mole, extracted. (c) LTB: 2.5% mole, extracted.

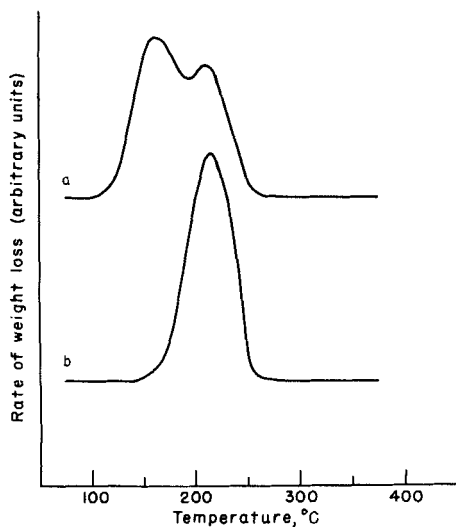


FIG. 5. DTG curves of polychloral prepared with low and high LTB concentration. (a) LTB: 1.8% mole, extracted. (b) LTB: 0.1% mole, extracted.

polymerizations with a higher concentration of LTB ( $> 1$  mole %) as initiator, the concentration of adventitious water was expected to be much lower than the concentration of alkoxide anions; consequently, there could not be enough water molecules present to terminate all growing chains and a fraction of macromolecules remained unterminated (living but dormant), resulting in the presence of the fraction with a  $170^{\circ}\text{C}$  MDT peak as part of the polychloral sample.

Alternatively, the  $170^{\circ}\text{C}$  MDT fractions observed in acid-treated low molecular weight polychloral samples may represent low molecular weight hydroxyl-ended polychloral with considerably lower stability than high molecular weight polychloral having the same endgroups [11].

To increase polymer stability, both types of endgroups with DTG maxima at  $170$  and  $210^{\circ}\text{C}$  should be transformed into more stable ester or halide endgroups by posttreatment. These reactions cannot be realized easily because both alkoxide and hydroxyl endgroups are entrapped within the polychloral gel matrix which does not permit ready access and penetration of the terminating agent.

Nevertheless, for some polymer films, especially those prepared with LTB as the initiator, it was possible to achieve complete stabilization as shown in Fig. 6, and obtain the polymer which shows only one maximum on the DTG curve in the region  $300 \pm 15^{\circ}\text{C}$  after refluxing the polymer sample with  $1\text{ M}$  solution of  $\text{PCl}_5$  in  $\text{CCl}_4$  for 2 days [11]. In all cases where the posttreatment was carried out with a

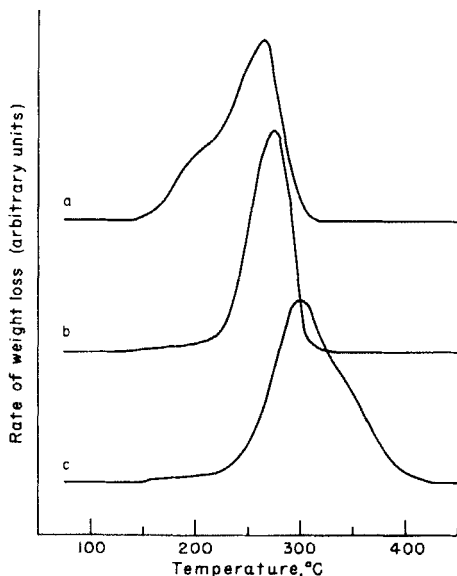


FIG. 6. DTG curves of polychloral after  $\text{PCl}_5/\text{CCl}_4$  treatment. (a) LTB: 7.3% mole, refluxed 2 days with  $\text{PCl}_5/\text{CCl}_4$ , extracted. (b) LTB: 1.8% mole, refluxed 2 days with  $\text{PCl}_5/\text{CCl}_4$ , extracted. (c) LTB: 0.1% mole, refluxed 4 days with  $\text{PCl}_5/\text{CCl}_4$ , extracted.

solution of  $\text{CH}_3\text{COCl}$  in  $\text{CCl}_4$  or neat  $\text{CH}_3\text{COCl}$  as the terminating agent, incomplete stabilization was observed [7, 11, 12]. Separate from the maximum at  $300 \pm 15^\circ\text{C}$  there was also a considerable fraction of polymer showing a maximum at  $210 \pm 15^\circ\text{C}$  (hydroxyl endgroups) left, indicating the lower efficiency of this method of stabilization (Fig. 7).

The same type of DTG curves was also observed when acetylating agents (e.g.,  $\text{CH}_3\text{COCl}$  or  $(\text{CH}_3\text{CO})_2\text{O}$ ) were introduced into the initial mixture of monomer and initiator and polymerization proceeded from the beginning in the presence of acetylating agent [7]. It had been expected that acetyl chloride or acetic anhydride would be uniformly distributed throughout the polychloral gel and would act as a chain transfer agent producing completely stabilized polychloral. This was, however, not the case; DTG curves obtained from polychloral samples obtained in these studies had the same character as those shown in Fig. 7, indicating only partial stabilization.

Similar results were obtained if the polymerization of chloral was initiated with organic salts containing chloride anion as the nucleophilic initiator and cation as a possible alkylating agent. A variety of sulfonium salts with the general formula  $\text{R}'\text{R}''\text{R}'''\text{S}^+\text{Cl}^-$  and also iodonium and tropylium chlorides were used as initiators. Again, the

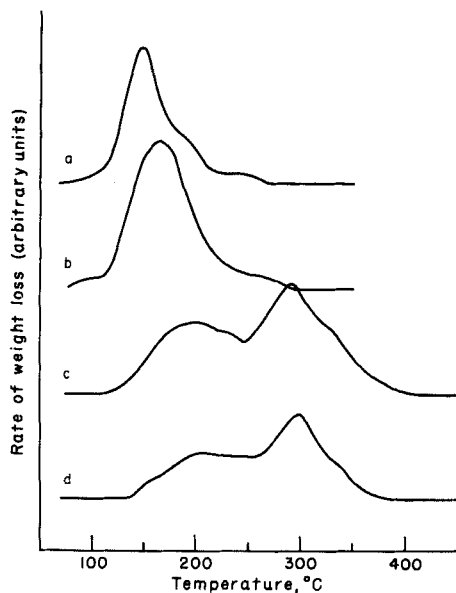


FIG. 7. DTG curves of polychloral after  $\text{CH}_3\text{COCl}$  treatment. (a) LTB: 7.3% mole, refluxed 2 days with  $\text{CH}_3\text{COCl}$ , extracted. (b) LTB: 1.8% mole, refluxed 2 days with  $\text{CH}_3\text{COCl}$ , extracted. (c) LTB: 0.4% mole, refluxed 4 days with  $\text{CH}_3\text{COCl}$ , extracted. (d) LTB: 0.1% mole, refluxed 4 days with  $\text{CH}_3\text{COCl}$ , extracted.

results summarized earlier [13] showed that only incomplete stabilization was achieved and the resulting polymers consisted of two fractions whose DTG curves had maxima at  $210 \pm 15$  and  $300 \pm 15^\circ\text{C}$ .

As a result of the thermal analysis as it is related to the endgroup structure of the polychloral samples, we conclude that the polymer fractions showing the degradation maximum at  $300 \pm 15^\circ\text{C}$  have stable endgroups which were introduced either directly during the polymerization (by the use of chain transfer agents or alkylating counterions) or during the posttreatment procedure. Stabilized polychloral samples prepared by anionic polymerization contain either  $\text{RO}^-$  or  $\text{Cl}^-$  groups from the initiation, and  $\text{RO}^-$  or  $\text{Cl}^-$  or possibly  $\text{RCOO}^-$  terminal groups introduced by the various posttreatment procedures. The following structures of the polychloral chain are possible for the stabilized fraction of the polymer.

For all cases (except 3) the temperature at which the maximum on the DTG curve occurred was observed at  $300 \pm 15^\circ\text{C}$ . In the case of Structure 3 (polymers prepared with  $\text{Ph}_3\text{P}$  as initiator and subjected to posttreatment with a 1 M solution of  $\text{PCl}_5$  in  $\text{CCl}_4$  under reflux), a maximum was often observed at somewhat higher temperatures ( $320\text{--}345^\circ\text{C}$ ). The same high temperature maximum (about



Initiation with  $\text{Cl}^-$  ( $\text{Ph}_3\text{P}$ ,  $\text{R}_3\text{S}^+\text{Cl}^-$ ,  $\text{R}_4\text{N}^+\text{Cl}^-$ ,  $\text{R}_2\text{I}^+\text{Cl}^-$ ,  $\text{C}^+\text{Cl}^-$ ,  $\text{LiCl}$ )

1.  $\text{Cl}-\text{OR}$  (e.g.  $\text{R}_3\text{S}^+$ ,  $\text{R}_2\text{I}^+$ )

2.  $\text{Cl}-\text{OCOR}$  (e.g.  $(\text{RCO})_2\text{O}$ )

3.  $\text{Cl}-\text{Cl}$  (e.g.  $\text{PCl}_5$ )

Initiation with  $\text{RO}^\ominus$  (LTB)

4.  $\text{RO}-\text{OR}$

5.  $\text{RO}-\text{OCOR}$

6.  $\text{RO}-\text{Cl}$

350°C) was observed by us earlier for polymers prepared with  $\text{SbCl}_5$  as initiator. The mechanism of polymerization in this case was not clearly established; however, taking into account the known chlorinating ability of antimony pentachloride, one may speculate that in this case a chloral polymer with chloride endgroups is formed by a cationic polymerization mechanism. Such an assumption would lead to the conclusion that polymer containing chlorine endgroups is more resistant toward thermal degradation than polymer containing tertiary butyl ether or ester endgroups.

When samples of polychloral were analyzed by DTG directly after polymerization without extraction or heat treatment, an additional MTD peak between 90–115°C was also observed. By special extraction techniques and the study of the short wavelength IR spectrum, this was identified to be trapped, nonpolymerized chloral monomer. Since chloral polymerization in bulk proceeds to only about 85% conversion, this result is not surprising. To distinguish between trapped monomer and alkoxide-terminated unstable polychloral fractions by thermal means is not always easy as an equilibrium between trapped monomer and degrading polymer is established which depends on temperature, sample size and shape, and other factors.

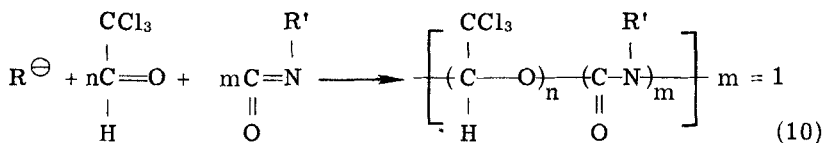
On the basis of all considerations, the assignments of the MDT maxima shown in Table 1 could be made.

TABLE 1.

Maximum at	Endgroup
110 ± 15°C	Trapped, nonpolymerized chloral monomer
170 ± 15°C	$-\text{CH}(\text{CCl}_3)-\text{O}^\ominus$
210 ± 15°C	$-\text{CH}(\text{CCl}_3)-\text{OH}$
300 ± 15°C	$-\text{CH}(\text{CCl}_3)-\text{OR}$ and $-\text{CH}(\text{CCl}_3)-\text{OCOR}$
340 ± 15°C	$-\text{CH}(\text{CCl}_3)-\text{Cl}$

Thermal Stability of Chloral-Isocyanate Copolymers

Instead of introducing a stable endgroup by posttreatment of polychloral with suitable acylating or chlorinating agents or by carrying out polymerization in the presence of suitable chain transfer or terminating agents, it is possible to prepare polychloral with a terminal fragment of the polymer chain which contains a high percentage of urethane linkages. This may be achieved by carrying out the anionic polymerization of chloral in the presence of 5-10 mole % of aromatic or aliphatic isocyanates [3, 4, 14, 21]:



In our previous paper of this series it was shown that chloral and isocyanates have different reactivities in anionic polymerization, and in the first stage of copolymerization of chloral with both aliphatic and aromatic isocyanates a large proportion of chloral is consumed with only a limited consumption of the isocyanate [14, 21]. The conversion of some isocyanates, however, continues to increase at the later stage and, when relative rates with which both comonomers enter the copolymer were examined, the conclusion was reached that an almost alternating copolymer was formed at the latter stage of copolymerization. For such systems the actual nature of endgroups is irrelevant because urethane linkages breaking the sequence of acetal bonds in the terminal fragment of macromolecules effectively stop the depropagation reaction.

Thus copolymerization of chloral with isocyanates provides an alternative route for obtaining stable chloral polymers. This is illustrated by the data shown in Fig. 8 in which DTG curves of unextracted polychloral were compared with those of copolymers of chloral which were prepared from chloral containing 8 mole % of phenyl isocyanate. In the DTG curves of chloral homopolymer two maxima are present; one at 80-90°C which shows the presence of unreacted monomer in the unextracted polychloral sample (bp of chloral is 98°C), and the other broad maximum between 160 and 200°C, indicating the presence of fractions containing both unterminated alkoxide and hydroxyl endgroups. There is also a small peak in the region close to 300°C, showing the presence of a small fraction of stable polychloral formed by a mechanism of unknown character [12]. DTG curves of copolymers (apart from the maximum at 90-100°C caused by unreacted monomer) show only a small maximum in the 210 ± 15°C region with the predominant fraction of polymer decomposing near 300°C.

A number of aliphatic and aromatic isocyanates were copolymerized

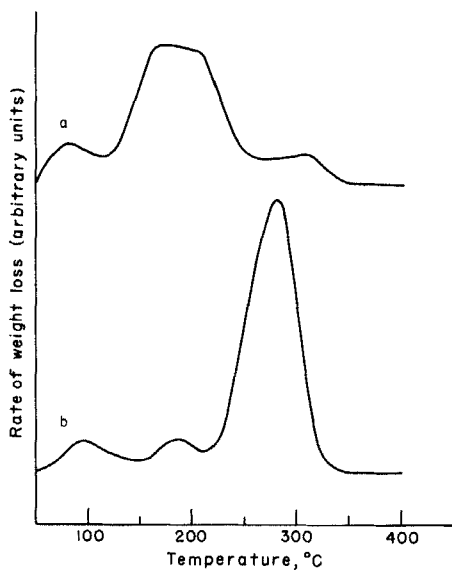


FIG. 8. DTG curves of polychloral and copolymer of chloral with phenyl isocyanate. (a) Chloral homopolymer. LTB: 0.1% mole, unextracted. (b) Chloral-PhNCO (8% mole in feed) copolymer. Ph<sub>3</sub>P: 0.2% mole, unextracted.

with chloral and it was shown that aromatic isocyanates are more reactive in copolymerization than aliphatic isocyanates. Comparison of the thermal degradation properties of the resulting copolymers leads to the conclusion that the general thermal stability behavior of chloral copolymers with different aliphatic and aromatic isocyanates is almost the same (Figs. 9 and 10). This is due to the fact that isocyanates in many cases are mainly incorporated into the terminal fragment of the polychloral chain, and the stable urethane linkages effectively prevent depropagation from terminal endgroups. Because the other endgroup formed in the initiation reaction is the stable RO- or Cl- group, copolymerization with isocyanates leads to the formation of stable chloral polymers.

DTG curves shown in Figs. 9 and 10 were obtained for copolymers prepared from monomer mixtures containing 5 mole % of aromatic or aliphatic isocyanates. For the copolymers prepared with different isocyanates, the actual concentration of isocyanate incorporated into the copolymer was different and usually smaller than the concentration of isocyanate in the feed. Regardless of isocyanate content, however, the solvent-extracted polymers showed only a DTG peak near 300°C, showing that only a very small number of urethane linkages in the copolymer (possibly even only one urethane linkage,

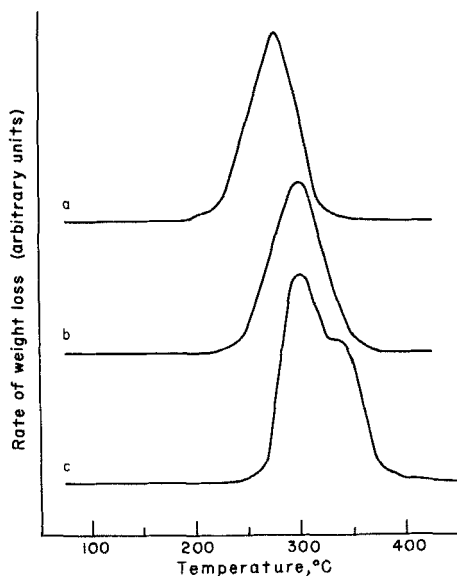


FIG. 9. DTG curves of copolymers of chloral with aliphatic isocyanates. (a) LTB: 0.1% mole. *tert*-BuNCO: 5% mole, extracted. (b) LTB: 0.1% mole. *iso*-PrNCO: 5% mole, extracted. (c) LTB: 0.1% mole. *n*-BuNCO: 5% mole, extracted.

namely the endgroup) are sufficient to give a chloral copolymer with only one DTG peak, the peak at 300°C.

Figure 11 shows DTG curves of chloral/*p*-ClPhNCO copolymers prepared from monomer mixtures containing 1, 3, and 5% mole of isocyanate. It is evident that with increasing concentration of the isocyanate comonomer in feed, the portion of stable fraction with the degradation maximum in the temperature range of 320–340°C increases. For copolymers prepared from a mixture of chloral and 1 mole % of *p*-ClPhNCO, clearly a shoulder near 170°C may be recognized which indicates that under these conditions some alkoxide-terminated chloral polymer is still present which does not have urethane linkages as terminal groups. Increasing the *p*-ClPhNCO concentration in the monomer feed eliminates this maximum, but copolymers were obtained from comonomer feeds containing up to 5 mole % *p*-ClPhNCO although the relative amount of this fraction decreases with increasing concentration of *p*-ClPhNCO. The data in Fig. 11, however, cannot be compared directly with DTG data shown in this paper because the Fig. 11 data were obtained on samples which had been Wiley milled and thereby possibly subjected to some mechanochemical chain cleavage; such cleavage apart from a urethane linkage would introduce an additional amount of apparently "unstabilized" fraction. If such is the case, a decrease in the amount of

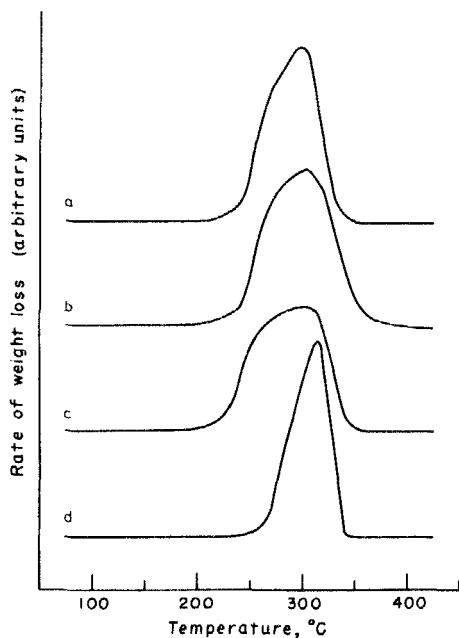


FIG. 10. DTG curves of copolymers of chloral with aromatic isocyanates. (a) LTB: 0.1% mole. *o*-ClPhNCO: 5% mole, extracted. (b) LTB: 0.1% mole. *p*-CH<sub>3</sub>PhNCO: 5% mole, extracted. (c) LTB: 0.1% mole. *p*-CH<sub>3</sub>OPhNCO: 5% mole, extracted. (d) LTB: 0.1% mole. PhNCO: 5% mole, extracted.

"unstabilized" fraction produced by milling with increasing concentration of urethane linkages in the polychloral chain (produced by use of additional isocyanate in the monomer mixture) would be consistent with the observed data.

Comparison of the data shown in Figs. 9 and 10 (LTB-initiated copolymerization) with the data in Fig. 11 (Ph<sub>3</sub>P-initiated copolymerization) indicates that the MDT for the Ph<sub>3</sub>P-initiated samples was somewhat higher (330–340°C). This result is in agreement with the data obtained from DTG studies of homopolymers prepared with LTB and Ph<sub>3</sub>P as initiators and stabilized by a postreaction with PCl<sub>5</sub>. When Ph<sub>3</sub>P was used as the initiator [the real initiator is triphenyl-(dichlorovinyl)oxyphosphonium chloride (CCl<sub>2</sub>=CH-O-P<sup>+</sup>Ph<sub>3</sub>Cl<sup>-</sup>)], for the chloral polymerization and the polymer treated with PCl<sub>5</sub>, polychloral was obtained whose polymer chains were terminated on both ends with chlorine: Cl~Cl. This homopolymer also showed a maximum on the DTG curve at approximately 340°C while PCl<sub>5</sub>-treated polymers prepared with LTB as the initiator (for which the structure RO~Cl was expected) had a maximum at 310 ± 15°C.

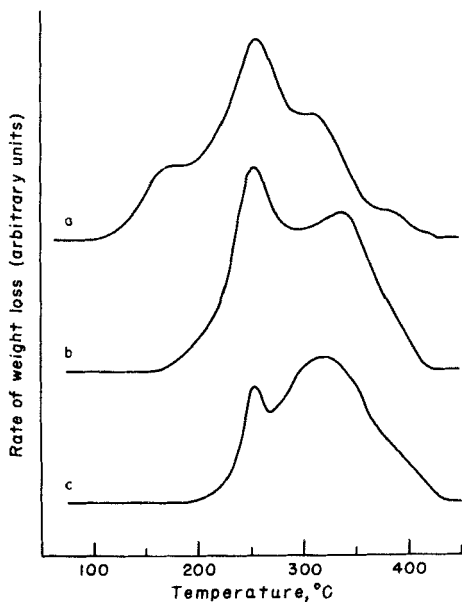


FIG. 11. DTG curves of copolymers of chloral with *o*-ClPhNCO. (a) Ph<sub>3</sub>P: 0.2% mole. *o*-ClPhNCO: 1% mole, extracted. (b) Ph<sub>3</sub>P: 0.2% mole. *o*-ClPhNCO: 3% mole, extracted. (c) Ph<sub>3</sub>P: 0.2% mole. *o*-ClPhNCO: 5% mole, extracted.

Because a similar difference in the positions of maxima on the DTG curves was observed for copolymers prepared with either LTB or Ph<sub>3</sub>P as initiators, containing the same terminal urethane unit, it can be concluded that this difference in thermal stability is due to the different structure of endgroups introduced during the initiation and that the tertiary butoxy endgroup is thermally less stable than chlorine or urethane endgroups in polychloral.

#### The Influence of Heating Rate on DTG Curves

All DTG curves reported in this work were obtained with a constant heating rate of 20°C/min. Thus the results may be used to compare the relative thermal stability of samples of polychloral prepared under different conditions. Because the temperature at which the maximum of DTG curves occurs depends on heating rate, in order to obtain absolute information concerning thermal stability of chloral polymers it was necessary to record DTG spectra at different heating rates and to extrapolate the results to zero heating rate. Figures 12 and 13 show the DTG curves of two polychloral samples obtained at different heating rates: 20°C/min, 10°C/min, 5°C/min,

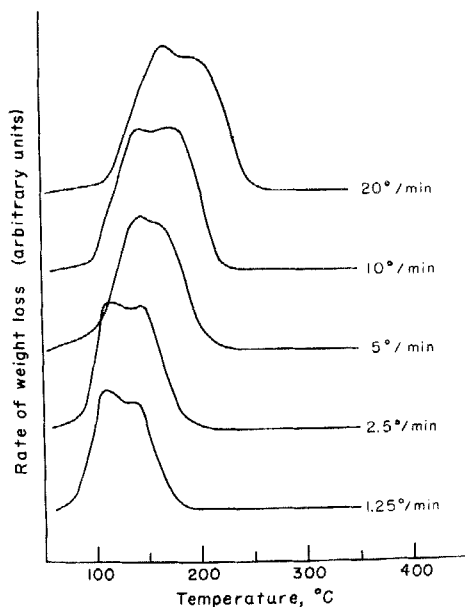


FIG. 12. DTG curves of polychloral sample showing two low temperature maxima obtained with different heating rates.

2.5°C/min, and 1.25°C/min. As expected, decreasing the heating rate leads to a considerable shift of DTG curve maxima toward lower temperatures, while at the same time the degradation peaks become narrower. It should be noted, however, that the shape of the degradation curves did not change with the rate of heating. The bimodal character of the curves shown in Fig. 12 is clearly visible over the whole range of heating rates applied, which proves that the observed shape of the DTG curves is indeed an indication of the presence of fractions of different thermal stability in the polymer sample.

The dependence of the temperature of maximum DTG degradation rate (MDT) on the heating rate is shown in Fig. 14. This dependence is almost linear for low heating rates ( $\leq 5^\circ\text{C}/\text{min}$ ); for higher heating rates deviation from linearity is observed. Extrapolation to zero heating rate leads to the conclusion that the temperature at which the maximum degradation rate would be observed at zero heating rate is 70–80°C lower than the observed MDT for a heating rate of 20°C/min. It may thus be expected that the most stable polychloral samples, for which a maximum was observed at 340°C for a heating rate 20°C/min, would degrade with a maximum rate at a temperature close to 260°C if the heating were carried out at heating rates close to zero, which means under isothermal conditions.

This result corresponds well with the results of isothermal thermal

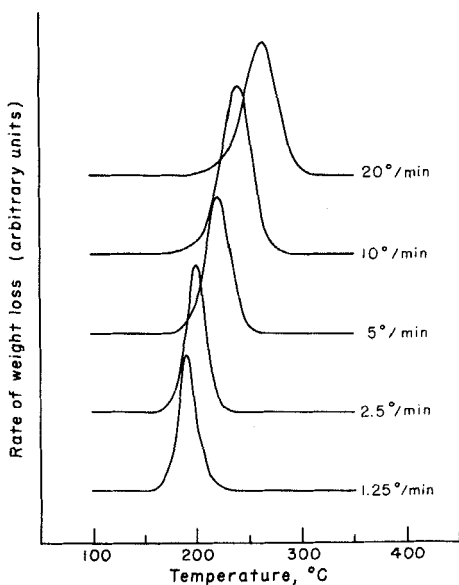


FIG. 13. DTG curves of polychloral sample showing higher temperature maximum obtained with different heating rates.

degradation of cyclic trimers of chloral which may serve as a model for studies of thermal stability of the main chain. It was found that both isomers of the cyclic trimer of chloral began to decompose with a measurable rate in the 200-220°C temperature region, with a decomposition activation energy of 176 kJ/mole (42.0 kcal/mole) for the eea (cis-trans) isomer and 198 kJ/mole (47.3 kcal/mole) for the eee (all cis) isomer. (For a discussion of the stereochemistry of substituted trioxanes, see Ref. 23.) These data indicate that for the best-stabilized polychloral samples (namely those containing two chloride endgroups), the thermal stability of the polymer is limited by the stability of the main polyacetal chain.

The thermal stability of polychloral may be compared with that of polyformaldehyde (unsubstituted polyacetal chain). DTG curves of commercial Delrin samples (fully stabilized) show the maximum at 343°C (heating rate 6°C/min) [22] while under comparable conditions the best stabilized samples of polychloral, namely those terminated on both ends with chlorine, show the maximum at about 300°C (heating rate 5°C/min). This difference should reflect the difference in corresponding activation energies of degradation. For polychloral, the activation energy determined by the method of Freeman and Carroll [24] can be calculated to 134 kJ/mole (32 kcal/mole). This value was determined for samples of polychloral which showed a



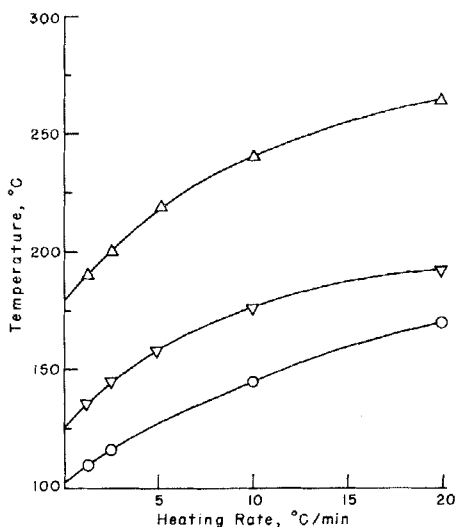


FIG. 14. Dependence of the position of maximum on DTG curve on heating rate. Extrapolation to zero heating rate.

MDT of 300°C (heating rate 20°/min). Consequently, one may expect higher values of activation energy for the best stabilized samples of chloral, namely those for which a MDT of 340°C or even higher was observed (heating rate 20°C/min).

The activation energy of degradation of acetate-capped polyoxymethylene (POM) is, according to Enikolopyan, equal to 134 kJ/mole (32 kcal/mole) [25]. The thermal stability of unstabilized POM prepared under laboratory conditions but without stabilizers is, however, lower than the thermal stability of commercial POM because the maximum of the DTG curve is approximately 20°C lower than that of endcapped and fully stabilized (thermal stabilizer and antioxidants added) [22] POM. Thus the activation energy of POM degradation is between 180 and 200 kJ/mole (43-48 kcal/mole) and is the same for fully stabilized homopolymer or copolymer.

Analysis of the thermal degradation data of chloral leads to the conclusion that the thermal stability of the best stabilized polychloral is nearly the same as that of POM but perhaps slightly lower. This reflects a small difference in the thermodynamic stability of polyacetal chain substituted with relatively bulky  $\text{CCl}_3$  groups.

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