Haloaldehyde Polymers. XIV. Endgroups in Polychloral

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Haloaldehyde Polymers. XIV.*
Endgroups in Polychloral

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ABSTRACT

Chloral polymers prepared by anionic polymerization have
alkoxide endgroups as terminal ends at the end of this polym-
erization. The initiating anion has, as expected, no influence
on the type of terminal group formed. Polychloral with termi-
nal alkoxide ends degrades easily thermally to monomeric
chloral. Alkoxide endgroups in polychloral do not readily react
with alkylating or acylating agents, although partial stabilization
has been observed when alkoxide-terminated polymers were
allowed to stand for periods of time; the endgroups seem to
react either with impurities or with excess chloral in side re-
actions. With protic acids, alkoxide-terminated polychloral is
transformed into hydroxyl-terminated polymer of higher thermal
stability. Studies of the initiation step of the chloral polymeri-
zation revealed that above the ceiling temperature of polymeri-
zation, strong nucleophiles, such as soluble tertiary butoxide,
initiate quantitatively, but polymerization does not proceed until
the mixture is cooled. When chloral is initiated with weaker
nucleophiles such as chloride or carboxylates, the initiation
equilibrium is not on the side of the initiated species, although
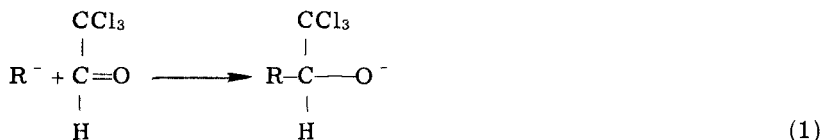it shifts effectively as polymerization proceeds; with carboxylates

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*For Part XIII, see R. W. Campbell and O. Vogl, Monatsh. Chem.,
110, 453 (1979).

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as initiators the ester group has been found incorporated as the initial endgroup in polychloral. With sufficient amounts of lithium tertiary butoxide as anionic initiator, polychloral of low molecular weight was prepared. This polymer does not react with end-capping reagents (other than PCl_5) as does high molecular weight polychloral; in spite of considerable effort it was not possible to prepare low molecular weight soluble polychloral or oligomeric polychloral. Polychloral prepared with cationic initiators is thermally more stable than unstabilized anionically initiated polychloral but is generally crumbly and incoherent. The end-groups of such polymers are usually hydroxyl endgroups. Identification of endgroups of the polymers has been done where possible by IR spectroscopy, for the initiation reaction by NMR spectroscopy, but for high molecular weight insoluble polymers almost exclusively by comparative thermal polymer degradation.
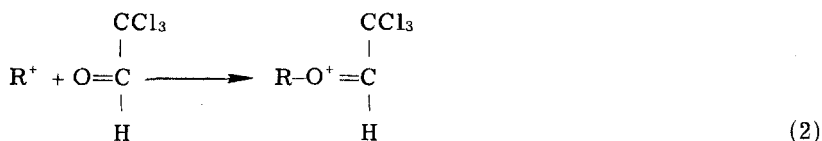
INTRODUCTION

Stability, stabilization, and the nature of the endgroups in haloalde-hyde polymers, particularly in polychloral, have been major subjects of concern and investigation since the earliest studies of these poly-mers. Much of the earlier work was concerned with the polymeriza-tion itself and the identification of effective initiators without much consideration for the mechanism of the polymerization and the stabil-ity of the polymer [1-4]. The last two decades, however, have brought much intensified interest in these polymers as new knowledge in poly-mer chemistry has developed [5-14]. A new concept, cryotachensic polymerization, which allowed the preparation of chloral polymers by direct monomer casting in any desirable shape, recognized the importance of quiescent polymerization conditions and utilized the resultant polymer morphology for the achievement of high conversion in this polymerization [15-17]. The preparation of stable polychloral became of major importance as favorable physical and mechanical properties of these materials, particularly their flame resistance, made their full development greatly desirable.

Chloral can be polymerized with anionic and cationic initiators [Eqs. (1) and (2)] [18]. With anionic initiators, a polymer is obtained by polymerization in a homogeneous gel phase in about 85% yield [15-17]; cationic polymerizations gave erratic yields [4, 10, 19]. Success-ful polymerization depends on the morphology of the polymer as it is deposited during the polymerization as chloral polymers always precipitate or form gels during polymerization. Polychloral pre-pared by different procedures shows great differences in thermal stability and only recently has some characterization of individual polymers and individual polymer fractions taken place [18]. Since chloral polymers are insoluble, characterization techniques for

$$
R^- + \underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}}=O \longrightarrow R-\underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}}-O^- \tag{1}
$$

(A) R = $(CH_3)_3CO$

(B) R = Cl, RCOO

$$
R^+ + O=\underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}} \longrightarrow R-O^+=\underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}} \tag{2}
$$

R = H or Lewis acid or Lewis acid fragment

endgroups in chloral polymers are essentially limited to infrared spectroscopy, but the determination of thermal degradation behavior has also contributed to the understanding of the stability of these polymers [9, 10, 18, 20].

Cationic initiation of chloral with sulfuric acid, trifluoromethane-sulfonic acid, AlCl₃, and SbCl₅ gave polymers in varying yields, but with reasonably good thermal stability. In materials initiated with sulfuric acid, infrared spectra seemed to show the presence of hydroxyl endgroups [4]. As a consequence, a cationic mechanism was proposed for this polymerization in which the proton initiates polymerization by addition to the carbonyl carbon of the chloral monomer; it was suggested that one of the hydroxyl groups in the polymer must be obtained via the initiation step [19]. Polymers obtained with Lewis acids as cationic initiators were much more stable, and it was suggested that some form of chlorination, in the initiating step, the terminating step, or both, gave chlorine-terminated polychloral [19].

Anionically initiated polychloral is in general easier to prepare and only this mechanism provides the gel-type morphology necessary to form coherent pieces of polymer.

In analogy to the work on formaldehyde, it was found that cationi-cally prepared polychloral has accessible hydroxyl endgroups which could apparently be acetylated [10]. Attempts were made to deter-mine molecular weights and endgroups on the basis of C,H analysis of the acetylated polymers; a $\overline{DP}$ of about 50 was suggested for these polymers. There are some doubts about the results of this work, as the polychloral samples do not seem to have been exhaustively ex-tracted prior to the elemental analysis and the possibility exists that other materials (for example, chloral diesters) were present in the

sample and could have increased the percentage of endgroups and con-
sequently have given lower molecular weight for the chloral polymer
samples.

In connection with the study of the rate of polymerization of
chloral, initial work on the initiation step of anionic chloral polymeri-
zation was presented which differentiated between "fast" initiators
and "slow" initiators [21] with additional differentiation within the
group of "slow" initiators. The initiation step, of course, contributes
one of the endgroups to the polymer chain, the "initiating" endgroup.
The second endgroup is contributed by the "terminating agent";
additional "initiating" and "terminating" endgroups could be intro-
duced if chain transfer occurs. Initiating and terminating endgroups
both contribute to the thermal stability; if one of the two endgroups
or both have a thermal stability lower than that of the polymer chain,
polymer degradation will occur from the less stable chain end.

It has been established in other work [22] that depolymerization
of polychloral proceeds entirely to monomer and the ceiling tempera-
ture of chloral polymer is 18°C (1 M solution) and 58°C in bulk.
Unstable bulk-polymerized polychloral generally decomposes at a
measurable rate only at temperatures above 100°C.

It was the objective of this work to determine the endgroups of
"stabilized" and "unstabilized" chloral polymers, especially those
prepared by the cryotachensic method. It was also desired to make
an independent and hopefully unequivocal determination of the nature
of the endgroups in polychloral samples of varying thermal stability
and to correlate thermal stability with the verified presence of specific
endgroups in cryotachensically prepared polychloral.

EXPERIMENTAL

Materials

Chloral (Montrose Chemical Company) was refluxed overnight
over phosphorus pentoxide (about 20 g/liter of chloral) and distilled
from the P_2O_5 into another flask. This flask was transferred to a
distillation apparatus containing a column packed with glass helices
and the chloral was boiled under total reflux for one week. Chloral
was then slowly distilled at a reflux ratio of 10:1. After desired
monomer purity was reached, the required amount was distilled and
used immediately. The impurity level by gas chromatography was
below 0.3% in all experiments and below 0.03% in most [23].

Lithium tertiary butoxide (LTB) (Ventron Alfa Products) was sub-
limed at 135-145°C/0.1 Torr and subsequently transferred within a
dry nitrogen-filled glove bag.

Triphenylphosphine (Ph_3P) (Aldrich Chemical Company) was re-
crystallized from methanol or from acetone/Skelly B. For kinetic
work, it was also sublimed at 100°C/0.3 Torr pressure.

Pyridine (Aldrich Chemical Company) was dried over CaH₂ for 4 days and distilled at atmospheric pressure under nitrogen; bp 114°C. The final two-thirds of the distillate, which showed less than 0.05% impurity by gas chromatography, was used.

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

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

Benzene and cyclohexane (Eastman Kodak Company) were dried for one day over CaH₂, distilled under nitrogen at atmospheric pressure, and stored over liquid NaK alloy. Gas chromatography revealed less than 0.05% impurity.

Purification of Solvents and Reagents

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 done with syringes under continuous nitrogen blanketing.

Because of the sensitivity of the anionic chloral polymerization to water and other compounds containing active hydrogen, a special procedure was used for the preparation of all initiator solutions. Solid initiators, before use in solution preparation, were dried over granular P_2O_5 at 0.05 Torr pressure and room temperature for at least one day. Bottles containing the solid initiators were then placed in a polyethylene glove bag, together with dried flasks, serum stoppers, transfer spatulas, and a small torsion balance. A dish containing anhydrous $CaSO_4$ was then placed in the bag, which was sealed; the gas in the bag was pumped out and the bag was refilled with dry nitrogen several times in succession. The initiator bottles were then opened and the initiators were weighed into the flasks, which were closed with serum stoppers and removed from the dry bag. Solvents were then added with nitrogen blanketed syringes. If the initiator solutions were not used immediately, they were transferred with dry syringes to Schlenk tubes in which they were stored.

Infrared Study of Chloral Initiation with Lithium Tertiary Butoxide above Threshold Polymerization Temperature

An 0.3 M solution of LTB in cyclohexane (2 ml, 0.6 mmole) was injected with a syringe under nitrogen into a dry, nitrogen-purged, serum-stoppered flask. The serum stopper was then punctured with a syringe needle connected to a vacuum line at 20 Torr pressure, and the cyclohexane was allowed to evaporate, finally by gentle heating

with a heat gun until only dry crystals were left in the flask. The flask was then filled with dry nitrogen, and 1 ml of CCl_4 (dried 1 day over 4 Å molecular sieves) was injected into the flask which dissolved the LTB. An infrared spectrum of the LTB solution (0.1 mm NaCl cell with CCl_4 solvent reference) was taken. The spectrum (Fig. 2A) showed absorptions at 2960 cm^{-1}(s), 2865 cm^{-1}(m, C-H stretching), 1473 cm^{-1}(m), 1383 cm^{-1}(m), 1357 cm^{-1}(s), 1040 cm^{-1}(w), 960 cm^{-1}(s), 750 cm^{-1}(w,b), 585 cm^{-1}(s,b), and 510 cm^{-1}(m).

Subsequently, 0.0175 ml (0.026 g, 0.18 mmole) of chloral was dissolved in 0.25 ml of CCl_4 to make a solution of approximately 0.7 M. An infrared spectrum of this solution was taken under the same conditions as above. The spectrum (Fig. 2B) showed absorptions at 3520 cm^{-1}(w) (C-H stretching), 2860 cm^{-1}(m), 1770 cm^{-1}(vs, C=O stretching), 1358 cm^{-1}(m), 1030 cm^{-1}(m), 988 cm^{-1}(s), 855 cm^{-1}(s), 730 cm^{-1}(s), and 620 cm^{-1}(s).

To prepare the LTB-chloral addition compound, 0.25 ml (0.15 mmole) of the LTB solution in CCl_4 was injected into a dry serum-stoppered flask and 0.0175 ml (0.026 g, 0.18 mmole) of chloral was added with a syringe. The mixture was added by syringe to an infrared cell as above and a spectrum was determined. The spectrum showed absorptions at 3460 cm^{-1}(w), 2990 cm^{-1}(s), 2940 cm^{-1}(m), 2860 cm^{-1}-(m), 1770 cm^{-1}(s, excess chloral), 1690 cm^{-1}(m), 1615 cm^{-1}(m), 1475 cm^{-1}(m), 1395 cm^{-1}(m), 1375 cm^{-1}(w), 1330 cm^{-1}(m), 1240 cm^{-1}(s), 1205 cm^{-1}(s), 1170 cm^{-1}(s), 1105 cm^{-1}(w), 1050 cm^{-1}(m), 1030 cm^{-1}-(m), 1000 and 990 cm^{-1}(s), 965 cm^{-1}(m), 917 and 910 cm^{-1}(m), 840 cm^{-1}(s), 655 cm^{-1}(s), 622 cm^{-1}(m), and 505 cm^{-1}(m).

In order to prepare a solution of LTB-chloral addition compound with a slight deficiency of chloral to test for equilibrium, 4 ml of 0.3 M LTB in cyclohexane was injected into a dry serum-stoppered flask and the solvent was removed as before; 2 ml of CCl_4 was added and the flask was shaken, but the solid did not dissolve completely. An infrared spectrum of the solution proved to be identical to the spectrum of the LTB-CCl_4 solution determined earlier.

An 0.25 ml quantity of the LTB solution was injected into a dry serum-stoppered flask, and 0.01 ml (0.015 g, 0.10 mmole) of chloral was added. The mixture was injected into an infrared cell; the infrared spectrum (Fig. 2C) showed absorptions at 3460 cm^{-1}(w), 2990 cm^{-1}(s), 2940 cm^{-1}(m), 2860 cm^{-1}(m), 1730 cm^{-1}(vw), 1695 cm^{-1}(w), 1620 cm^{-1}(m), 1475 cm^{-1}(m), 1445 cm^{-1}(w), 1398 cm^{-1}(m), 1375 cm^{-1}(s), 1330 cm^{-1}(m), 1240 cm^{-1}(s), 1205 cm^{-1}(s), 1130 cm^{-1}(vw), 1045 cm^{-1}(s), 1000 cm^{-1}(s), 970 cm^{-1}(s), 910 cm^{-1}(s), 835 cm^{-1}(s), 660 cm^{-1}(s), and 510 cm^{-1}(m,b). No chloral carbonyl stretching was observed in this infrared spectrum.

Determination of Nature of Stable and Unstable
Endgroups in Polychloral

Preparation and Infrared Studies of Low Molecu-
lar Weight Polychloral Films and Powders.   Six pairs
of 10 in. × 10 in. × 1/8 in. glass plates were washed, rinsed with dis-
tilled water, and dried overnight at 120°C. Each pair of plates was
then clamped together, separated by a 420-den Lycra fiber, in order
to make a film mold. The prepared film molds were then placed in a
70°C oven for 2 hr until needed.
     Six 16 × 150 mm test tubes were washed with distilled water,
flamed out, cooled under dry nitrogen purge, fitted with serum
stoppers, and wired. Chloral (8.0 ml, 12.1 g, 82 mmole) was injected
into each tube followed by placement of the tube into a 70°C oil bath.
The tubes were kept in the oil bath for 10 min and the appropriate
quantity of a 0.3 $\underline{M}$ LTB solution in cyclohexane was injected into the
tube. A portion of the initiated monomer mixture in each tube was
then injected into a film mold with a syringe heated to 70°C. The
film molds and tubes containing the remaining monomer mixture were
then placed into an ice-water bath for 4 hr. Gelation occurred within
a few seconds after the plates and tubes were placed into the ice bath.
The plates were opened and separated and the films were removed
and trimmed.
     Each film was cut into five portions (A through E) which were
respectively treated according to the following procedures: (A) vacuum
drying at room temperature and 20 Torr pressure for 2 hr; (B) ex-
traction in a test tube with three changes (10 ml each) of unacidified
methanol for 4 days; (C) extraction in a test tube with 10 ml of a
mixture of methanol and 10% (v/v) concentrated aqueous HCl for one
day, followed by extraction with two changes (10 ml each) of unacidi-
fied methanol for 3 days; (D) treatment with refluxing acetyl chloride
for 4 days, followed by washing with methanol, extraction for one day
with 10 ml of unacidified methanol, and subsequent washing with meth-
anol again; (E) treatment with a refluxing 1 $\underline{M}$ solution of PCl_5 in CCl_4
for 4 days followed by washing with methanol, extraction for one day
with 10 ml of unacidified methanol, and subsequent washing with
methanol again.
     Each film section was dried for 2 hr at 20 Torr pressure and room
temperature after the respective post-polymerization treatment. The
weights and percent weight retention for each film section were deter-
mined before and after treatment. Infrared and DTG spectra of the
films were determined when sufficient films remained after post-
treatment for such measurements (Table 3).
     A film made with 2.5 mole % of LTB initiator was too brittle to be
removed from the plates. However, the polymer remaining in the
test tube, similarly made with 2.5 mole % LTB initiator, was powdered
by grinding with a spatula and was divided into four unweighed por-
tions treated in the following ways. One sample was placed in

unacidified methanol according to procedure (B) and degraded within
a few minutes, leaving no solid residue. Acidified methanol, as in
procedure (C), did not degrade the polymer powder, and the powder
treated with acidified methanol also did not degrade when subse-
quently placed in unacidified methanol. Treatment with acetyl chlo-
ride according to procedure (D) or with PCl_5 according to procedure
(E) produced polymer powders which did not degrade upon subsequent
exposure to methanol.

Preparation and Infrared Studies of Very Low
Molecular Weight Polychloral Powders. Five dried,
serum-stoppered test tubes were prepared as in the previous experi-
ment. The tubes were injected with appropriate quantities of a 0.3 M
solution of LTB in cyclohexane (Table 4) and placed in a 70°C oil
bath for 10 min. Chloral was injected into another test tube and was
allowed to come to 70°C. The required quantity of warm chloral
was then injected into the LTB solution with a warm syringe. The
tubes were shaken to mix the chloral and LTB solution and then placed
in an ice bath for 48 hr and allowed to stand at room temperature for
72 hr. The polymers were then removed from the tubes with a
spatula. The first two polymers were powders suspended in liquid,
the next two were friable solids, and the last tube (lowest initiator
concentration) contained a solid with some coherence. Each polymer
sample was divided into five parts (A through E), which were respec-
tively treated according to the five procedures A through E of the
previous experiment.

The powdered samples, after being given the appropriate post-
treatments, were used for determination of DTG and infrared spectra.
These latter spectra were determined on CCl_4 mulls of the powdered
polymers. Data from this experiment are tabulated and discussed in
Table 4.

Measurements

Infrared spectra were obtained on a Perkin-Elmer 283 Infrared
Spectrometer (4000-200 cm^{-1}) with a scan time of 12 minutes or on
a Perkin-Elmer 727 Infrared Spectrometer (4000-600 cm^{-1}) at a
"normal" scan rate. Polymer films were used as such; solid low
molecular weight compounds were generally incorporated into KBr
pellets, while the infrared spectra of liquids were usually measured
on neat samples between NaCl plates. Polymer powders were used
as KBr pellets, but better results were generally obtained when poly-
mer powder spectra were measured on mulls of the polymer in CCl_4
between NaCl plates. The polystyrene band at 1601 cm^{-1} was used as
the calibration standard.

Proton nuclear magnetic resonance spectra (^{1}H-NMR) were obtained
on a 60 MHz Hitachi Perkin-Elmer R-24 NMR Spectrometer; when
greater precision was necessary, spectra were obtained on a 90 MHz
Perkin-Elmer R-32 NMR Spectrometer. TMS was used as the internal
standard.

Differential thermogravimetric (DTG) 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 a Varian Associates Model 920 gas chromatograph, with a 2-m column packed with Chromosorb W (100/120 mesh) coated with 36% by weight of diisodecyl phthalate.
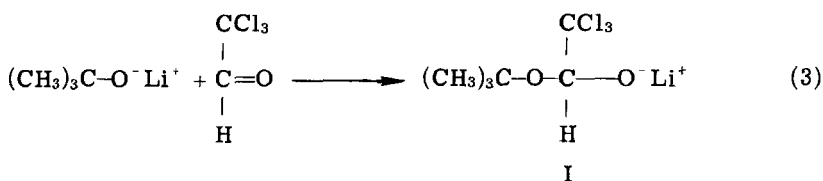
RESULTS AND DISCUSSION

Endgroups in polychloral have been identified by studying initiation steps of the polymerization and by studying low molecular weight and high molecular weight polymers. Spectroscopic techniques and thermal degradation which determined the most unstable of the endgroups in the polymer showed that the alkoxide group is the predominant endgroup of anionically prepared polychloral (with a maximum degradation temperature as low as 120°C). The most common endgroup in cationically prepared polychloral is the OH endgroup with a maximum degradation peak temperature (MDT) near 220°C. The polymer degradation temperature apparently depends somewhat on the morphology of the polymer.

Polychloral samples with endgroups of higher stability were obtained from termination reactions with adventitious impurities, side reactions of the growing polychloral anion with chloral monomer, or reactions of the polymer alkoxide endgroup with some countercations.

Anionic Initiation Mechanisms for Chloral Polymerization

The anionic initiation of chloral polymerization was found by ^{1}H-NMR and IR spectroscopy to proceed by two quite different types of processes dependent on the basicity and nucleophilicity of the initiators used. LTB, a strongly basic initiator, was found by ^{1}H-NMR measurements to add to chloral above the ceiling temperature of chloral polymerization [21]. These results indicated that the reaction between LTB and chloral was fast, almost instantaneous, and that the equilibrium of this reaction was more than 95% on the right side [Eq. (3)].

$$(CH_3)_3C-O^- Li^+ + \begin{matrix} CCl_3 \\ | \\ C=O \\ | \\ H \end{matrix} \longrightarrow (CH_3)_3C-O-\begin{matrix} CCl_3 \\ | \\ C \\ | \\ H \end{matrix}-O^- Li^+ \qquad (3)$$

$$I$$
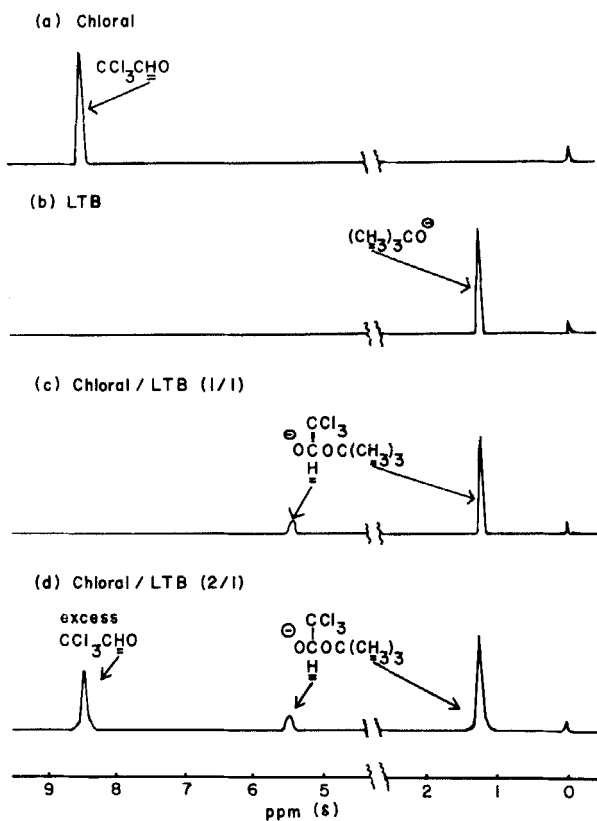
FIG. 1. ^{1}H-NMR study of reaction of LTB with chloral at 35°C (all components 0.6 M in C_6D_6): (a) chloral; (b) LTB; (c) chloral/LTB 1:1; (d) chloral/LTB 2:1.

The reaction of LTB with chloral was followed by ^{1}H-NMR spectroscopy as seen in Fig. 1. When chloral was added to an equimolar amount of LTB in benzene-d_6 at 70°C and the ^{1}H-NMR spectrum of the reaction mixture was measured, it was evident that an essentially quantitative reaction between LTB and chloral had occurred. The aldehyde proton of chloral showed a singlet in the ^{1}H-NMR spectrum with a chemical shift of δ 8.3 (Fig. 1A), but the exact value of the chemical shift depended somewhat on the concentration of chloral and the type of solvent; in CDCl$_3$ or CCl$_4$ solution or without solvent, the chemical shift of the aldehyde proton of chloral was δ 9.2. The tertiary butyl protons of LTB showed a singlet (when observed at 90 MHz) at δ 1.27 (Fig. 1B). For the LTB/chloral mixture (Fig. 1C), a

new signal at δ 5.4 appeared. This has been assigned to the acetal proton of the new alkoxide anion (I) [Eq. (3)] formed by addition of chloral to the tertiary butoxide anion. In addition, the tertiary butyl protons of the new alkoxide at δ 1.30 were shifted downfield by 0.03 ppm from the δ 1.27 of the tertiary butoxide chemical shift. If chloral was in excess, the aldehyde proton absorption could be observed in addition to the alkoxide addition compound (Fig. 1D). However, under normal conditions, no equilibrium between the LTB-chloral mixture and the new alkoxide (I) could be detected in the ^{1}H-NMR spectrum. Similarly, if the chloral monomer was not added rapidly to the NMR tube containing the LTB solution but was instead allowed to flow slowly down the sides of the tube, a side reaction occurred which produced a peak at δ 6.2 immediately after chloral addition (in addition to the acetal proton peak at δ 5.4). In other work, it was found that alkoxide I could not be isolated but could be acetylated with acetic anhydride or methylated with dimethyl sulfate in very high yields [Eq. (4)]. When alkoxide I was heated under reflux in cyclohexane for several hours, tert-butyl 1,2,2,2-tetrachloroethyl ether was obtained as the main reaction product [Eq. (5)].

$$
(CH_3)_3C-O-\underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}}-O^-Li^+
\begin{cases}
\xrightarrow{(CH_3O)_2SO_2} (CH_3)_3C-O-\underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}}-O-CH_3 \\
\xrightarrow{(CH_3CO)_2O} (CH_3)_3C-O-\underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}}-O-CO\cdot CH_3
\end{cases}
$$

$$\text{(4)}$$

$$
(CH_3)_3C-O-\underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}}-O^-Li^+ + n\ \underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}}=O \longrightarrow (CH_3)_3C-O-\underset{\underset{H}{|}}{\overset{\overset{CCl_3}{|}}{C}}-Cl + LiCl \qquad (5)
$$
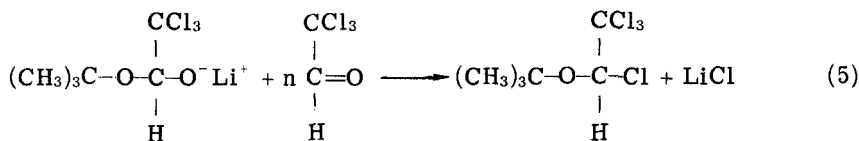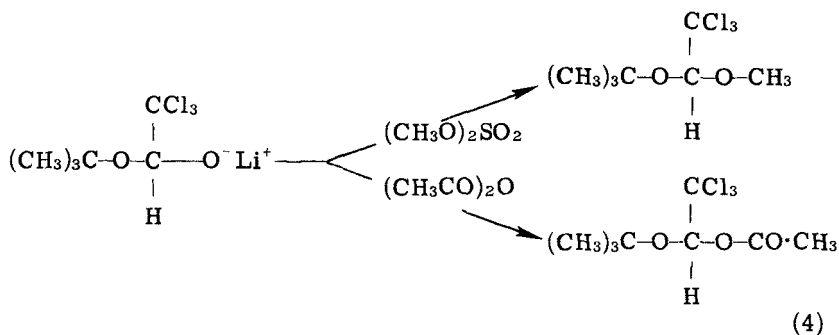
and other products

When the solution of I from the NMR tube was added to a test tube of fresh chloral above its threshold polymerization temperature and the test tube was then placed in an ice bath, immediate polymerization to a hard, tough block of polychloral occurred.

Even stronger support for the essentially quantitative formation of the LTB-chloral addition product was provided by infrared spectroscopy. When a slightly less than equimolar amount of chloral

INFRARED SPECTRUM OF
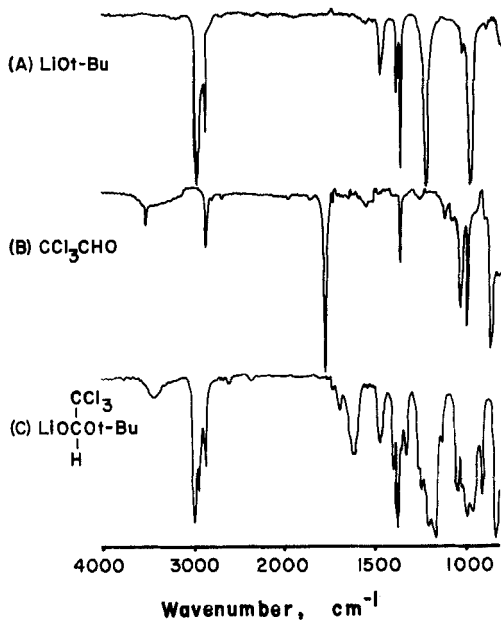## LiOt-Bu–CHLORAL ADDUCT

(0.6 M in CCl$_4$)

FIG. 2. IR study of reaction of LTB with chloral at 25°C (all components 0.6 $\underline{M}$ in CCl₄): (A) LTB; (B) chloral; (C) chloral/LTB (slightly lower than 1:1 ratio).

was added to a 0.6 M solution of LTB in CCl₄, the infrared spectrum of the resultant product has no carbonyl peak (Fig. 2) and resembled neither the spectrum of LTB nor that of chloral nor the sum of these spectra with a number of new peaks appearing in the spectrum of the product. When equimolar quantities of LTB and chloral were mixed in CCl₄ solution with a small amount of excess chloral, a carbonyl peak at 1760 cm^{-1} did appear.

LTB was only the most characteristic and typical anionic initiator of the variety of strong nucleophiles which added essentially quantitatively to the first monomer unit; it was conveniently used because LTB is soluble in hydrocarbons. When NaOCH₃ was used as an initiator for polymerization of neat chloral in which it is not soluble, the side reaction which led to the formation of tert-butyl 1,2,2,2-tetrachloroethyl ether with LTB became the sole reaction. Addition

at 65°C of chloral to NaOCH₃ gave a vigorous and exothermic reaction with methyl 1,2,2,2-tetrachloroethyl ether as the only product.
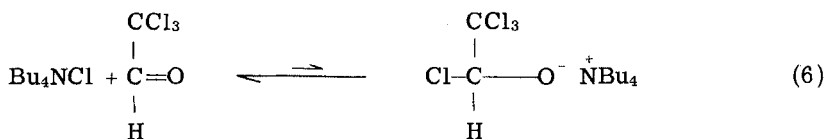
As it became clear that nucleophilicity and basicity were the two important driving forces for the addition of anionic initiators to chloral, a group of alkali or dimethyldistearyl ammonium salts of various anions were prepared and their effectiveness as initiators in chloral polymerization was studied.

Good initiators were salts of acetic acid, stearic acid, benzoic acid, thiophenecarboxylic acid, trifluoroacetic acid and also the halides (chloride and fluoride) and cyanide, cyanate and thiocyanate. Of much lower activity were sulfate, tosylate, nitrate, picrate, bromide, and iodide. Inactive as initiators for chloral polymerization were perchlorate, tetrafluoroborate, hexafluoroantimonate, 2,4,6-trinitrobenzenesulfonate, and hydrogen sulfate.
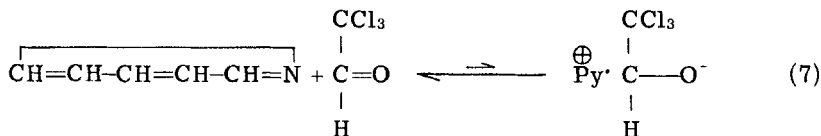
It may be interesting to note that although iodide was a moderately effective initiator for chloral polymerization, no iodine was found in the chloral polymer after proper extraction to remove initiator residues. This result showed that the actual initiator for the polymerization was probably the chloride ion, which must have been obtained by a displacement reaction of iodide with chloral.

Such a displacement reaction has also been found when chloral was initiated with cesium fluoride as most of the cesium fluoride was transformed into cesium chloride (demonstrated by the crystal structure of the recovered salt as determined by x-ray. It is not known whether fluoride or chloride ions were the actual initiators for the successful chloral polymerization with cesium fluoride.

Since it has been established that alkoxide I had a proton resonance of 5.4 ppm, the appearance of a proton signal in this region was considered indicative for the formation of an alkoxide which would have been produced by the addition of any anion to the carbonyl double bond of chloral. As a consequence, additional studies of 1:1 mixtures of chloral with other compounds that were known to initiate the chloral polymerization were undertaken at levels that could be detectable by ¹H-NMR spectroscopy. In order to detect individual initiation equilibria for various initiators, mixtures of Bu₄NCl/chloral [Eq. (6)], pyridine/chloral [Eq. (7)], and 2,4,6-trimethylpyridine/chloral were studied, but none showed any ¹H-NMR signals

$$\text{Bu}_4\text{NCl} + \begin{array}{c} \text{CCl}_3 \\ | \\ \text{C}{=}\text{O} \\ | \\ \text{H} \end{array} \quad \rightleftharpoons \quad \begin{array}{c} \text{CCl}_3 \\ | \\ \text{Cl}{-}\text{C}{-\!-\!-}\text{O}^- \ \overset{+}{\text{N}}\text{Bu}_4 \\ | \\ \text{H} \end{array} \qquad (6)$$

in the δ5 to 5.5 region which would be indicative of an initiation equilibrium where the equilibrium concentration of the alkoxide was sufficient to be detectable by ¹H-NMR spectroscopy (signals of 0.5 mole % concentration could be detected) [21].

$$
\begin{array}{ccc}
& \overset{\displaystyle CCl_3}{\underset{\displaystyle |}{}} & \overset{\displaystyle CCl_3}{\underset{\displaystyle |}{}} \\
\overline{CH=CH-CH=CH-CH=N} + C=O & \rightleftharpoons & \overset{\oplus}{Py} \cdot C--O^- \qquad (7) \\
& \underset{\displaystyle |}{H} & \underset{\displaystyle |}{H}
\end{array}
$$

In all cases polymerization of chloral in the presence of the above mentioned initiators occurred even though the initiators were added in large or even equimolar quantities. (LTB/chloral 1:1 mixtures do not give polymer.) Polychloral samples obtained were tough and of reasonable molecular weight. Good mechanical properties also indicated a high molecular weight of the polychloral samples which demonstrated that the amount of actual initiator produced from the added compound was relatively small; although the initiation reaction was not detectable by ^{1}H-NMR spectroscopy, the initiation still effected chloral polymerization. It is evident that the initiation species in Bu$_4$NCl initiation was the chloride ion [Eq. (6)].
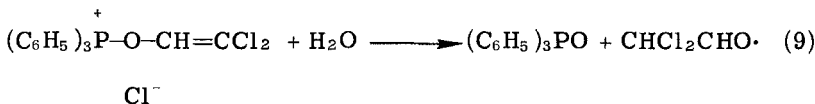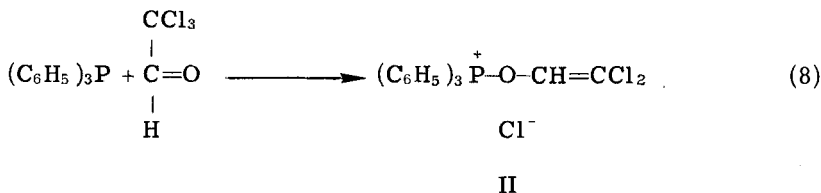
The initiation of chloral with Ph$_3$P proceeded in two steps. When Ph$_3$P was added to excess chloral, it reacted instantaneously with one mole of chloral to form triphenyldichlorovinyloxyphosphonium chloride (II) [Eq. (8)] [24]. The structure of this compound (II) has been well established by infrared [25] and, more recently, x-ray spectroscopy. The progress of this reaction could also be followed by ^{31}P-NMR spectroscopy [21]. The chemical shift of ^{31}P in Ph$_3$P (+ 5.5 ppm) changed to -68 ppm in the phosphonium salt from Ph$_3$P and chloral (II).

The formation of II could also be followed by ^{1}H-NMR spectroscopy [21]. When equimolar amounts of Ph$_3$P and chloral were allowed to react at 70°C in benzene-d$_6$, an oily product separated which was brought into solution by evaporation of the C$_6$D$_6$ and addition of CDCl$_3$. The ^{1}H-NMR spectrum of a solution of II showed that the phenyl protons had shifted 0.7 ppm downfield and a new proton signal at 7.5 ppm had appeared, apparently in agreement with 1 to 15 proton ratio, although integration was difficult because of peak overlap. This solution initiated the chloral polymerization the same way as a solution of Ph$_3$P.

Based on the identification of II as the reaction product of Ph$_3$P with 1 mole of chloral, it became clear that II was the actual initiator for chloral polymerization and, in fact, polymerized chloral at the same rate as if Ph$_3$P was added directly (instead of purified II) to the chloral as the initiator for its polymerization. Initiation with prepurified II or by direct addition of Ph$_3$P gave polychloral of identical mechanical properties.

II reacts readily with water to give dichloroacetaldehyde and triphenylphosphine oxide [Eq. (9)] [24].

Not only does Ph$_3$P react with 1 mole of chloral to give II, but a number of other aromatic tertiary phosphines, aliphatic tertiary phosphines, and aliphatic/aromatic tertiary phosphines also form

$$(C_6H_5)_3P + \overset{\overset{\displaystyle CCl_3}{\displaystyle |}}{\underset{\underset{\displaystyle H}{\displaystyle |}}{C}}=O \longrightarrow (C_6H_5)_3\overset{+}{P}-O-CH=CCl_2 \qquad (8)$$

$$Cl^-$$

$$\textbf{II}$$

$$(C_6H_5)_3\overset{+}{P}-O-CH=CCl_2 + H_2O \longrightarrow (C_6H_5)_3PO + CHCl_2CHO \cdot \quad (9)$$

$$Cl^-$$

II-like compounds. All these compounds are excellent initiators for the chloral polymerization. The chemical shifts of the ^{31}P-NMR resonance of the tertiary phosphines and their 1:1 molar reaction products with chloral are shown in Table 1. It can be seen that aromatic tertiary phosphines have a phosphorus resonance around +5 ppm, a resonance which shifts to about -70 ppm on reaction with 1 mole of chloral. Aliphatic tertiary phosphines have a chemical shift of about +33 ppm which shifts to about -110 ppm on reaction with chloral. Tertiary phosphines which are shielded by steric hindrance (such as triisopropylphosphine) have a chemical shift downfield from that of the unhindered aliphatic tertiary phosphines and the reaction product with chloral is somewhat different. Aliphatic/aromatic tertiary phosphines have chemical shifts somewhere between those of tertiary aromatic phosphines and aliphatic phosphines. Triaryl phosphites, diphenylphosphinous chloride, phenylphosphinous dichloride, and aromatic perfluorinated tertiary phosphines do not seem to react with chloral as seen from the lack of change in the phosphorus chemical shift; these compounds do not initiate polymerization of chloral (Table 1).

When Ph$_3$P was allowed to stand with excess chloral at 60° C, two new single peaks of equal intensity appeared in the ^{1}H-NMR spectrum at 5.5 ppm and 6.3 ppm. Although it was initially believed that the appearance of these peaks was an indication for the establishment of an initiation equilibrium for the chloride ion initiation of chloral, the aged mixture with even larger signals was ineffective as a polymerization initiator. It was later found that the two peaks were characteristic of a single compound, 1,2,2,2-tetrachloroethyl 2,2-dichlorovinyl ether, the product of the reaction of II with 1 mole of chloral at elevated temperature [Eq. (10)].

$$(C_6H_5)_3\overset{+}{P}-O-CH=CCl_2 + \overset{\overset{\displaystyle CCl_3}{\displaystyle |}}{\underset{\underset{\displaystyle H}{\displaystyle |}}{C}}=O \longrightarrow CCl_2=CH-O-CHClCCl_3 + (C_6H_5)_3PO$$

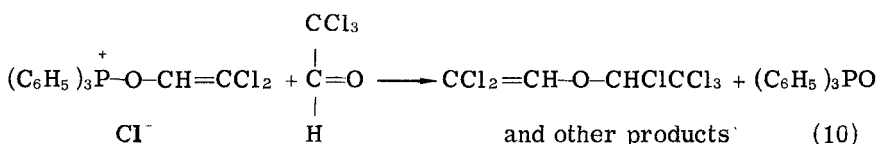$$Cl^- \qquad\qquad\qquad\qquad\qquad \text{and other products} \quad (10)$$

TABLE 1. ^{31}P-NMR Spectra of Tertiary Phosphines, 40.5 MHz at Room Temperature

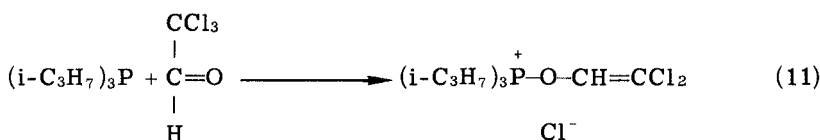| Type of phosphine	^{31}P chemical shift (ppm)[a]	
	Phosphine	1:1 Molar reaction product with chloral
$(n-C_4H_9)_3P$	+32.7	-110.2[b]
$(n-C_8H_{17})_3P$	+32.7	-110.2[b]
$(i-C_3H_7)_3P$	-19.5	-112.2[b]
$(C_6H_{11})_3P$	-11.2[b]	-99.1[b]
$(C_6H_5)_3P$	+5.4[b]	-67.8[b]
$C_2H_5P(C_6H_5)_2$	+12.5	-83.0[b]
$(CH_3C_6H_5)_3P$	+5.3[b]	-68.1[b]
$(C_6H_5O)_3P$	-127.2	-127.5
$(C_6H_5)_2PCl$	-81.9	-82.0
$C_6H_5PCl_2$	-161.1	-161.1

[a]External reference H_3PO_4.
[b]In CDCl$_3$, otherwise no solvent.

This reaction was subsequently further investigated. When the reaction was carried out overnight and the reaction products worked up, 80% of the higher boiling chlorinated products were identified as 1,2,2,2-tetrachloroethyl 2,2-dichlorovinyl ether. Additional careful investigation and identification by mass spectrometry and elemental analysis showed that 5% of the reaction product was 1,2,2,2,1',2',2',2',-octachlorodiethyl ether, 4% was 2,2-dichlorovinyl trichloromethyl ketone and 2% was 1,2,2,2-tetrachloroethyl 1',2',2'-trichloroethyl ether. In addition, 95% of the phosphorus of Ph$_3$P was isolated as tri-phenylphosphine oxide. Additional study of II by ^{36}Cl radioactive label-ing of the chloral showed that much of the radioactivity was in the octachlorodiethyl ether and high activity was left in the residue from the distillation of triphenylphosphine oxide indicating some phosphorus containing salt with high ^{36}Cl activity did not react to form triphenyl-phosphine oxide.

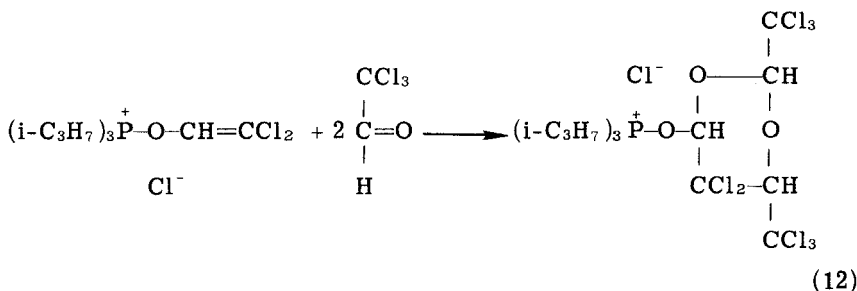It is also interesting to note that only one isomer of the octa-chlorodiethyl ether was obtained, the structure of which has not been identified but may be the meso compound. In principle, a meso and racemic form of this compound could be expected from the reaction of II with excess chloral. When octachlorodiethyl ether was synthe-sized by chlorination of 1,2,2,2-tetrachloroethyl 2,2-dichlorovinyl

ether, two stereoisomeric compounds were obtained which could be separated by GC.

When the salt formed from triisopropylphosphine and chloral [Eq. (11)] was allowed to react with a large excess of chloral, the reaction took a different course than that of II with excess chloral. A single reaction product, having a ratio of 1 mole of triisopropyl-phosphine and 3 moles of chloral, was obtained. Careful analysis
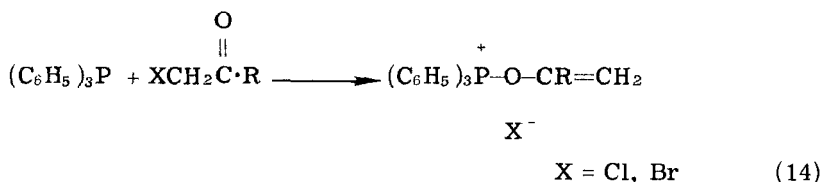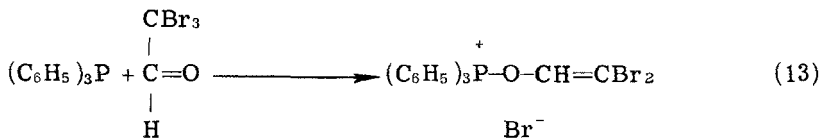
$$
(i\text{-}C_3H_7)_3P + \overset{\overset{\displaystyle CCl_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{=}O \longrightarrow (i\text{-}C_3H_7)_3\overset{+}{P}\text{-}O\text{-}CH{=}CCl_2 \qquad (11)
$$
$$
Cl^-
$$

by ^{13}C-NMR spectroscopy showed this compound to be cyclic, as indicated in the structure in Eq. (12).

$$
(i\text{-}C_3H_7)_3\overset{+}{P}\text{-}O\text{-}CH{=}CCl_2 + 2\; \overset{\overset{\displaystyle CCl_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{=}O \longrightarrow (i\text{-}C_3H_7)_3\overset{+}{P}\text{-}O\text{-}CH
$$

$$
Cl^-
$$

$$
\begin{array}{c}
CCl_3 \\
| \\
Cl^- \quad O\!\!-\!\!-\!\!-CH \\
| \quad | \\
(i\text{-}C_3H_7)_3\overset{+}{P}\text{-}O\text{-}CH \quad O \\
| \quad | \\
CCl_2\text{-}CH \\
| \\
CCl_3
\end{array}
$$

$$
(12)
$$

Initiators such as LTB, Ph$_3$P, and aliphatic tertiary phosphines behave differently in their long range activity as initiators for the polymerization of chloral. When the LTB-chloral reaction product is allowed to stand in the presence of an excess of chloral for some time at 60°C, the initiation capacity of LTB decreases rapidly indi-cating that side reactions cause LTB to be used up. This is probably caused by the formation of the reaction product indicated in Eq. (5). Salt II [Eq. (8)], from Ph$_3$P degrades relatively rapidly [Eq. (10)], and after 1 or 2 hr at 60°C (II) has lost all its effectiveness as an initiator for chloral polymerization. On the other hand, the cyclic 1/3 salt of triisopropylphosphine with chloral [Eq. (12)] remains active even when stored overnight at 60°C indicating that the cyclic salt does not undergo any further reaction which would then render it ineffective.

The phosphonium salts, II and the 1:1 and 1:3 salt from triiso-propylphosphine, were analyzed for molecular weight. Cryoscopic measurements in DMSO gave M/2 while VPO measurements in CHCl$_3$ gave the molecular weight itself.
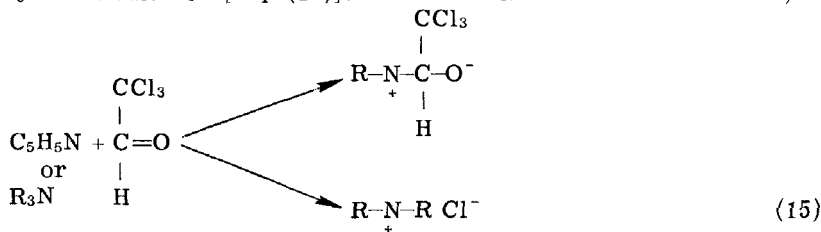
Ph₃P also reacted with bromal to give a 1:1 salt of triphenyl(di-bromovinyloxy)phosphonium bromide [Eq. (13)] in analogy to the re-action of Ph₃P with chloral [25-29]. Ph₃P also reacted with chloro-and bromomethyl ketones to give analogous salts [Eq. (14)]. These materials have been identified by analysis and ^{31}P-NMR spectroscopy.

$$
(C_6H_5)_3P + \underset{H}{\overset{CBr_3}{\underset{|}{\overset{|}{C}}}}\!\!=\!\!O \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-O-CH}\!\!=\!\!CBr_2 \qquad (13)
$$
$$
Br^-
$$

$$
(C_6H_5)_3P + XCH_2\overset{O}{\overset{\|}{C}}\!\cdot R \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-O-CR}\!\!=\!\!CH_2
$$
$$
X^-
$$
$$
X = Cl, Br \qquad (14)
$$

It was therefore concluded that the so-called initiation of chloral polymerization with Ph₃P was actually initiation by the chloride ion of II, similar to the initiation of chloral with Bu₄NCl or triphenyl-methylphosphonium chloride, all of which gave similar rates of chloral polymerization.

The initiating species in chloral initiation with pyridine and 2,4,6-trimethylpyridine is still unknown. One possibility is that the amines react with chloral in a manner similar to that of Ph₃P to give quater-nary ammonium salts containing chloride ions which function as the actual initiating species. However, such reactions would be expected to proceed more rapidly at higher temperatures, and in the ¹H-NMR experiments no new peaks could be detected in amine/chloral mix-tures even after standing for two days, while these amines cause polymerization of chloral to 30-70% conversion within 10 min of cooling to 0°C.

Hence, it would seem more likely that the actual initiating species in amine initiation of chloral may be a zwitterionic species caused by reaction of one molecule of chloral with one molecule of pyridine C_5H_5N or amine R_3N [Eq. (15)]. In the formation of this zwitterion,

$$
\begin{array}{c}
\underset{R_3N}{\underset{or}{C_5H_5N}} + \underset{H}{\overset{CCl_3}{\underset{|}{\overset{|}{C}}}}\!\!=\!\!O
\end{array}
\begin{array}{c}
\nearrow \quad R\text{-}\overset{+}{N}\text{-}\underset{\underset{H}{|}}{\overset{CCl_3}{\overset{|}{C}}}\text{-}O^- \\
\\
\searrow \quad R\text{-}\overset{+}{N}\text{-}R \; Cl^-
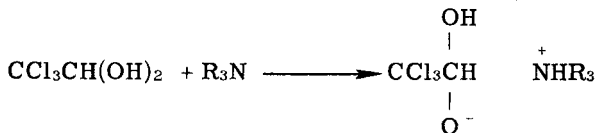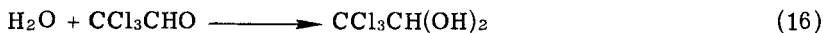\end{array}
\qquad (15)
$$

charge separation would occur which would perhaps make this initiation pathway seem likely. However, similar claims of zwitterionic species are made for the reaction of Ph₃P with β-propiolactone [30] in anionic polymerization of β-propiolactone and also in the reactions of pyridine and other amines with β-propiolactone, propane sultone, or acrylic acid [31].

If such zwitterions were present in amine-chloral mixtures, they would be in concentrations too small to be detected by ^{1}H-NMR. As long as the mixture remains above the threshold polymerization temperature of chloral polymerization, the position of the equilibrium remains far to the left. When the mixture is cooled below the chloral threshold temperature, however, the zwitterion is removed from the equilibrium by rapid propagation with formation of polychloral as a gel phase.
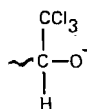
Support for the "unstable zwitterion" hypothesis for initiation of chloral polymerization by tertiary amines is also found in the polymerization of bromal (tribromoacetaldehyde) [29], dibromochloroacetaldehyde [32], and bromodichloroacetaldehyde [33]. Pyridine and other tertiary amines effectively polymerize these aldehydes, whereas compounds such as alkali bromides or Ph₃P (which reacts with these aldehydes to yield salts with bromide anions) do not cause polymerization. Preformed II (from Ph₃P and chloral) which is a chloride salt, does, however, polymerize these brominated aldehydes.

If pyridine and other tertiary amines were to initiate trihaloacetaldehyde polymerization by reacting first with the aldehyde to give a quaternary halide, as does Ph₃P, the halide salts from the brominated aldehydes would be expected to be bromides, but bromide ion is not an effective initiator for polymerization of these aldehydes. Initiation by tertiary amines must be by another mechanism, with the zwitterionic mechanism being a possibility.
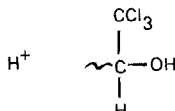
It must also be mentioned that McCain and Sanders [34] proposed that initiation of chloral with tertiary amines required water or another protic coinitiator and proceeded as in Eqs. (16) and (17). The latter anionic species could then add chloral units, initiating a

$$H_2O + CCl_3CHO \longrightarrow CCl_3CH(OH)_2 \tag{16}$$

$$CCl_3CH(OH)_2 + R_3N \longrightarrow CCl_3\overset{\displaystyle OH}{\underset{\displaystyle O^-}{C}}H \quad \overset{+}{N}HR_3$$

polymer chain. This mechanism cannot be excluded, but sufficient evidence is not available to differentiate between the two mechanisms as small amounts of protic impurities are always present and cannot effectively be excluded.
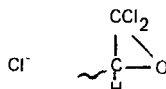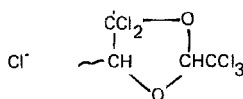
$$\begin{array}{c} CCl_3 \\ | \\ \sim\!\!C\!-\!O^- \\ | \\ H \end{array}$$

III

$$H^+ \quad \begin{array}{c} CCl_3 \\ | \\ \sim\!\!C\!-\!OH \\ | \\ H \end{array}$$

IV

$$H^+ \quad \begin{array}{c} CCl_3 \\ | \\ \sim\!\!C\!=\!O \end{array}$$

V

$$Cl^- \quad \begin{array}{c} CCl_2 \\ | \quad \diagdown \\ \sim\!\!C\!-\!O \\ | \\ H \end{array}$$

VI

or termination with
initiator fragment

$$Cl^- \quad \begin{array}{c} \dot{C}Cl_2\!-\!\!-\!O \\ | \qquad\qquad | \\ \sim\!\!CH \qquad CHCCl_3 \\ \diagdown\!\!\diagup \\ O \end{array}$$

VII

Thin films of pyridine-initiated polychloral do not show evidence of pyridine residues in the infrared spectrum after extraction with acetone or methanol. It must be mentioned that polychloral initiated with amines tends to adhere very tenaciously to glass; it is often very difficult to separate the two glass plates of a mold containing an amine-initiated polychloral film. Such suggests that the polychloral may be chemically bonded to the glass; the amine may deprotonate surface hydroxyl groups of the glass to form R_3SiO^- anionic sites which could initiate polychloral chains bound to the glass surface.

Polychloral Yields and Yield Determinations

When chloral was polymerized in the bulk with sufficient amounts of effective initiators, polymer was obtained in approximately 85% yield. When an inert diluent was used, polymer was obtained from monomer in as high as 97% yield. The end of polymerization is apparently reached when the monomer can no longer reach the polymerization site because the chloral monomer becomes immobile in the polymer matrix and/or the growing polymer sites become occluded and inaccessible for further monomer addition. In bulk polymerization of chloral, this is achieved at conversions of about 85%.

When chloral polymerization was completed, the mixture consisted of unreacted monomer, unstable polymer and stable polymer in amounts depending on type and amount of initiator, fortuitous or added terminating agent and reaction conditions such as time and temperature

which determine the morphology of the polymer obtained. The poly-
chloral was usually obtained as a translucent or somewhat opaque
material which was a solid or had the structure of a sponge with very
small porous channels. In more porous materials, internal surfaces
as high as 10 m^2/g have been measured.

The determination of the yield of polymer was not very easy as
equilibria are always being established between the unstable fraction
and unreacted monomer. Yield in chloral polymerizations has been
determined in various ways. The carbonyl absorption at 1770 cm^{-1}
can be used for the determination of trace amounts of chloral in
thin films of polychloral. For large amounts of remaining chloral
(up to 80% conversion to polymer), ^{1}H-NMR spectroscopy has been
used for determining the disappearance of the aldehyde proton of
chloral monomer at δ 9.3. At higher concentrations and in thicker
samples, such as 3 mm sheet, and for yield determinations between
80% and 90% polymer (5-20% of residual chloral monomer), the dis-
appearance of the overtone of the aldehyde hydrogen in the infrared
(5400 cm^{-1}) or even the second overtone of the carbonyl at 6135 cm^{-1}
has been used for these purposes.

More practical ways to determine yields of polychloral in shaped
samples are solvent extraction and air oven aging; both methods are
effective but suffer deficiencies. In air aging at 100-110°C for 1 hr,
8-10% of the monomer (60% of the total monomer left) can be removed.
The remaining chloral is tightly bound to the polymer and remains in
the polymer matrix. More drastic methods of heat treatment at
higher temperatures not only remove monomer but also causes
degradation of some of the less stable polymer. Extended heatings
also cause slow degradation of the less stable fraction of polychloral;
while weight losses are observed, the amount of monomer in the
polymer (6-8%) remains approximately constant. The amounts
described here are based on results on sheets about 3 mm thick.
Monomer is more efficiently removed in thinner sections but remains
more tightly bound in thicker plugs.

Extraction of the monomer can be carried out with a number of
solvents. Most efficient are the solvents that react with chloral, for
example, methanol (which immediately forms the hemiacetal) but
also acetone and methylenechloride. Continuous extraction in a
Soxhlet apparatus with any of these solvents not only removes all
chloral but also degrades some of the less stable fraction of polymer.
It is the only way to remove completely chloral monomer from the
polymer but the polymer yield values after extraction are usually
much lower than after heat treatment. It is believed that in general
the "unstable" fraction is completely removed but some stabilization
can be obtained during this reaction as the solvent may react with the
initiator residue and/or remove it from the reaction mixture.

Extraction is also effective in thicker sections but, in general,
penetration of the solvent into thick sections is adequate to remove
all chloral but inadequate to degrade all the unstable portion.

The number-average molecular weight of polychloral produced by

LTB initiation is essentially inversely related to the amount of initiator used as LTB initiates essentially quantitatively. When LTB is used in concentration greater than 1 mole %, the polychloral produced is without mechanical strength and crumbles easily. On the other hand, initiation with halide ion or halide ion precursors such as Ph₃P causes very little initiator to be formed above the threshold temperature of polymerization as the equilibrium for formation of the initiating species (tetrachloroethoxide ion) is far to the side of the reactants (chloral and chloride ion); effective initiation can occur because the tetrachloroethoxide ion is removed from the equilibrium by polymerization when the initiated chloral is cooled below the chloral polymerization temperature. This indicates again that only a small amount of the initiator is effective for the polymerization initiation. Because only a small concentration of the initiating species exists at any time, high molecular weight polychoral is formed. Polychoral plugs obtained with high Ph₃P initiator concentration (3.2 mole % of initiator) were hard and tough, with no substantial decrease of molecular weight as compared with plugs prepared with lower Ph₃P concentrations; a $\overline{DP}$ of about 1000 is estimated for these polymers. Below 0.05 mole % initiator concentration, the yield of polymer was very low. The practical minimum initiator concentration of Ph₃P is 0.2 mole %, and in the range of 0.8 mole % the polymer yield (as determined by methanol or acetone extraction) is about 75%.

Elucidation of Nature of Endgroups in "Stable" and "Unstable" Polychloral

One of the problems in past attempts to stabilize polychloral against thermal degradation has been that the nature of the actual endgroups of polychloral, especially of polychloral prepared by anionic initiation, was not known.

Rosen and co-workers [10] prepared polychloral by initiation with Brönsted and Lewis acid initiators such as H_2SO_4, $AlCl_3$, and $AlBr_3$, anionic initiators such as tributylamine and methyltributylammonium iodide, and organometallic initiators such as diethylzinc. In all cases, the initiators were added to chloral monomer (with or without solvent) below its threshold polymerization temperature; the polymer therefore formed as a powder instead of a coherent block or film. The polymer was then treated with carboxylic acid chlorides or anhydrides at 125-180°C. The stability to treatment with DMF at 130°C for 30 min was substantially increased by this endcapping procedure. An attempt was made to determine molecular weight of the polychloral by treating the polymer with lauroyl chloride at 180°C and analyzing the treated polymer for carbon, with the assumption that each polymer chain had originally two hydroxyl endgroups which were fully acylated by the treatment. By this procedure, the degree of polymerization of all cationically initiated polychloral samples tested was determined to be below 200, while the best anionically initiated samples were estimated as having $\overline{DP}$ values near 600.

TABLE 2. Comparison of Infrared Absorptions of Anionically Initi-
ated Polychloral Films and Cationically Initiated Polychloral Powder
of Novak and Whalley [4]

Wave number (cm^{-1})		Peak assignments
Films	Powder [4]	(Novak and Whalley [4])
3980 (vw)		
3810 (vw)		
3640 (vw)		
	3500 (vw)	OH stretching (end groups)
	3360 (vw)	
2955 (m)	2945 (m)	CH stretching
	2910 (w)	? CH stretching (non-crystalline)
	2845 (vw)	CH stretching or combination
2705 (vw)		
	2680 (vw)	1360 + 1325
2620 (w)		
2350 (w)		
2190 (w)	2180 (vw)	2 × 1085
2150 (w)	2150 (vw)	1085 + 1070
1385 (w)	1386 (w)	803 + 582
1360 (s)	1360 (m)	CH bending
1325 (s)	1325 (s)	CH bending
1260 (w, irreproducible)		
1230 (vw)	1230 (vw)	
1125 (vs)	1122 (vs)	
1085 (s)	1085 (vs)	C–O stretching
1070 (vs)	1070 (vs)	
1030 (m)	1028 (m)	CH bending (?)
970 (vs)	975 (vs)	C–O stretching
847 (s)	842 (vs)	
830 (s)	840 (vs)	C–C and C–Cl stretching
805 (vs)	803 (vs)	

(continued)

TABLE 2 (continued)

Wave number (cm^{-1})		Peak assignments
Films	Powder [4]	(Novak and Whalley [4])
682 (s)	681 (s)	C–Cl stretching
678 (s)	675 (s)	
	630 (w, sh)	skeletal, non-crystalline
585 (s)	582 (s)	C–Cl stretching
492 (m)	496 (m)	C–Cl stretching or skeletal bending
	463 (w)	
	448 (w)	
	422 (vw)	skeletal bending
	402 (vw)	
	388 (vw)	
	376 (sh)	
365 (m)	366 (m)	? C–Cl bending
	345 (vw)	
	330 (vw)	
	306 (w)	
272 (w)		
265 (w)		

However, the precision of this method was very low for $\overline{DP}$ values above 300, and the presence of two hydroxyl endgroups on all poly-chloral chains could not be verified.

In polychloral determined as being of "low" molecular weight by the above procedure, infrared absorptions which had been attributed by Novak and Whalley [4] to hydroxyl groups were seen, which disappeared after treatment with the acid halides and were replaced by a peak in the carbonyl region (1753 cm^{-1}) attributed to ester endgroups. In polychloral whose DP was estimated at 550, neither type of peak could be seen (Table 2).

No change in the infrared spectrum of a polychloral film prepared cryotachensically by anionic initiation was detected after refluxing with acetyl chloride [20].

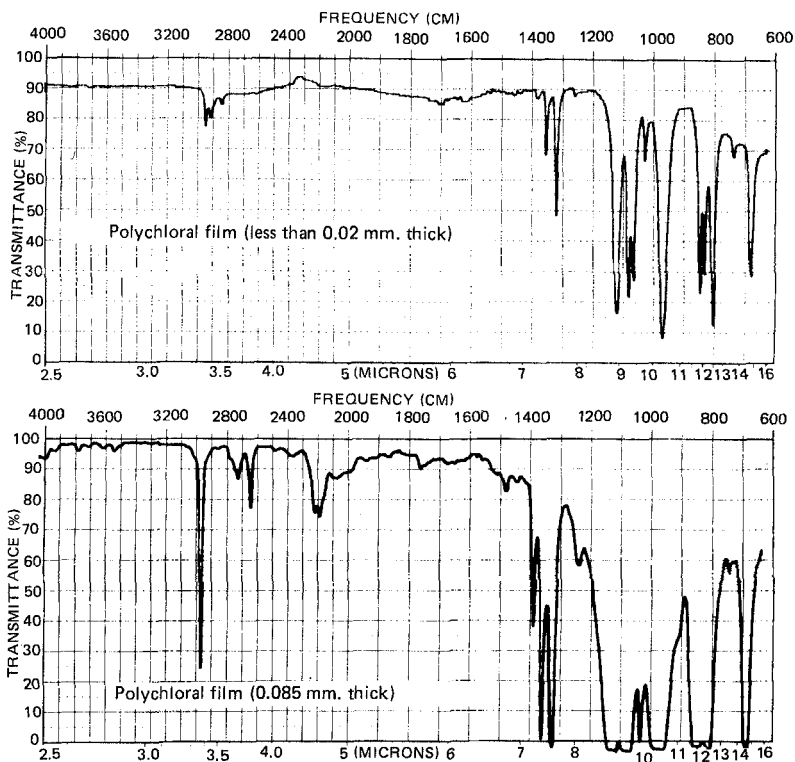However, it was known from previous preliminary work that

FIG. 3. IR spectra of polychloral films: (a) 0.02 mm thick; (b) 0.085 mm thick.

polychoral prepared with different initiators had different degrees of thermal stability, with polychloral prepared anionically by cryota-chensic methods often less stable than cationically prepared poly-chloral. This suggested a difference in endgroups. The following work was undertaken in an attempt to determine, by infrared spec-troscopy, extraction stability and DTG analysis, the endgroups in polychloral prepared by different initiators and given different post-treatments; the possible terminal endgroups of polychloral (without consideration of initiator fragments) are shown as III-VII.

Attempted Endgroup Determinations on High Molecular Weight Polychloral Films. A number of polychloral films were prepared with low concentrations of LTB, pyridine and Ph₃P initiators, to determine the stabilizing effect and infrared spectral changes caused by post-treatment with a refluxing 0.85 $\underline{M}$ solution of PCl_5 in CCl_4, a procedure found to increase the thermal stability of chloral homopolymer.

Infrared spectra on all thin films were similar (Fig. 3); they are listed in Table 1 and are compared with the infrared spectrum obtained by Novak and Whalley [4] for polychloral produced by cationic initiation with sulfuric acid. All of the major peaks are the same in the two spectra, but there are differences with respect to some of the weaker absorptions. Most significantly, no film prepared by initiation with pyridine or Ph_3P showed broad absorptions in the region near 3300–3500 cm^{-1} characteristic of hydroxyl endgroups. By contrast, polychloral powders initiated with H_2SO_4 and $SbCl_5$, when examined as CCl_4 mulls between NaCl plates, showed a very strong, broad peak at 3400 cm^{-1}, indicative of hydroxyl endgroups. Hence hydroxyl groups could not be detected in the anionically prepared films of thickness 0.02–0.06 mm.

Preparation and Infrared Study of Low Molecular Weight Polychloral. It was felt that a possible reason for the absence of observable hydroxyl absorption in the infrared spectra of polychloral films of high molecular weight was that the molecular weight of the polychloral was too high for endgroup absorptions to be observed reliably. Hence it was decided to prepare polychloral of lower molecular weight. To accomplish this, increased concentrations of a "rapid" initiator, LTB (for which initiation was instantaneous relative to propagation) were used. "Slow" initiators, such as Ph_3P, are ineffective in producing low molecular weight polychloral even when used at high concentration.

Two experiments were performed in an attempt to prepare (and characterize) low molecular weight polychloral by cryotachensic techniques. In the first experiment, plugs and films of polychloral were prepared from polymerization mixtures containing from 0.1 to 2.5 mole % LTB with respect to chloral. The resultant polymers were treated by one of five different procedures and the stability of the polymers after these treatments was determined; infrared and sometimes DTG spectra were taken on the samples after treatment. The results are shown in Table 3.

Several points are obvious from Table 3. First, polychloral initiated with LTB is very unstable to extraction with methanol, with stability decreasing generally with increasing amount of LTB initiator used. The sample prepared with 2.5 mole % LTB (for which the film was not coherent and the friable polymer plug was used) depolymerized completely upon treatment with methanol. Preliminary treatment for one day with methanol containing 10% (v/v) of concentrated aqueous HCl produced over 80% stabilization to methanol extraction in the polychloral films prepared with less than 0.4 mole % LTB and over 70% stabilization in the lower molecular weight polymer. Treatment with acetyl chloride or phosphorus pentachloride caused stabilization to methanol extraction approximately 10% in excess of that obtained by pretreatment with acidified methanol alone. Simple vacuum drying at 20 Torr pressure with no prior extraction caused no weight loss; volatile chloral monomer had apparently evaporated before the films were placed into the vacuum chamber.

TABLE 3. Stability and DTG Determinations for Low Molecular
Weight Polychloral Films Subjected to Various Post-treatments

LTB concn for chloral initiation (%)	Treatment[a]	Stability (%)	DTG	
			Peaks (°C)	Area (% of total)
0.1	A	100	224	100
	B	4		
	C	87	217	100
	D	98	205	36
			300	64
	E	98	300	100
0.2	A	100		
	B	11	240	100
	C	89		
	D	96		
	E	96		
0.4	A	100		
	B	4		
	C	86		
	D	89	200	40
			290	60
0.8	A	100		
	B	1		
	C	77		
	D	86		
	E	87		
1.6	A	100		
	B	0		
	C	75		
	D	81		
	E	86		

(continued)

TABLE 3 (continued)

LTB concn for chloral initiation (%)	Treatment[a]	DTG		
		Stability (%)	Peaks (°C)	Area (% of total)
2.5	A		225	100
	B			
	C			
	D		165	78
			274	22
	E		290	100

[a]Treatments: (A) vacuum drying at room temperature/20 Torr pressure for 2 hr; (B) methanol extraction for 3-4 days at room temperature, followed by (A); (C) methanol/10% HCl treatment for one day, followed by (B); (D) treatment with refluxing acetyl chloride for 4 days, followed by (B); (C) treatment with 1 M PCl₅/CCl₄ for 4 days at 60°C, followed by (B).

DTG spectra of samples unextracted, extracted with methanol, or pretreated with acidified methanol followed by extraction with methanol were all similar, with peaks between 215 and 240°C. The samples treated with acetyl chloride showed considerably increased stabilization; their DTG spectra were bimodal, showing one peak near or below 200°C and another in the range of 270-300°C. This bimodality suggests the presence of two different types of polymer fractions based on polymer molecules with two different endgroups. It was thought that the first peak might represent hydroxyl-ended polymer and the second acetylated polymer, but no carbonyl peaks could be seen in the spectra of the polymer treated with acetyl chloride even in a sample in which the 300°C peak included 64% of the total area under the DTG curve. The extent of stabilization with acetyl chloride treatment decreased with increasing amount of LTB initiator used to prepare the polymer, with the higher temperature DTG peak accounting for only 22% of the total area for the powdery sample initiated with 2.5 mole % LTB.

Treatment with PCl_5 in CCl_4 at 60°C, in contrast to acetyl chloride treatment, eliminated the lower DTG peak both in samples prepared with small (0.1 mole %) and large (2.5 mole %) amounts of LTB initiator. The onset of decomposition in PCl_5-treated samples did not occur until near 200°C, indicating the elimination of polymer fractions of low stability which decomposed below this temperature.

No characteristic broad hydroxyl peak in the 3300-3500 cm^{-1} range

could be observed for any of the polymers prepared, except for the
polymer powder prepared with 2.5 mole % LTB, when observed in a
pellet of KBr and one of the unextracted polymer films containing
significant amounts of monomer. It was, however, noticed that a
number of the films showed a carbonyl peak at 1170 cm^{-1} character-
istic of chloral monomer. All unextracted samples and even samples
treated with acidified methanol showed this peak.

Because it was difficult to detect hydroxyl peaks in the spectra
of the films prepared in the two previous experiments, it was decided
to use still higher initiator concentrations—from 1.8 to 29 mole % of
LTB with respect to chloral. Polychloral films prepared at these
initiator concentrations were incoherent; infrared spectra therefore
had to be determined on polymer powders ground in a mortar. KBr
pellets could not be used because of the possibility of introducing
-OH groups because the KBr is hygroscopic. Nujol mulls and films
pressed from the polymer powder gave poor spectra. The technique
which was found to give the best results, and which was used there-
after, was to place the polymer powder between NaCl plates and then
to add a drop or two of CCl$_4$, which filled the spaces between the
particles and decreased infrared scattering. All infrared spectra
were determined on these powders wet with CCl$_4$.

In the infrared spectra, broad hydroxyl absorptions centered at
3400 cm^{-1} were seen for most samples, in contrast to the results
of previous experiments. Three peaks on each spectrum were
measured: the broad hydroxyl absorption centered at 3400 cm^{-1},
the sharp C–H stretching absorption at 2955 cm^{-1} (used as a stand-
ard), and the residual monomer peak near 1770 cm^{-1}. For each
peak, the ratio A of transmittance T at the peak to baseline trans-
mittance T_0 was determined. Since the C–H stretching peak at
2955 cm^{-1} would be unaffected by post-treatments intended to sta-
bilize the polychloral by endcapping, this absorption was used as a
reference standard for estimating changes in the concentrations of
other species caused by posttreatments. These ratios are tabulated
in Table 4 for hydroxyl and carbonyl peaks in each sample, together
with DTG data.

As can be seen from Table 4, there is a general increase in the
absorbance ratio of OH to CH and CO to C H with increase in initiator
concentration for a given posttreatment technique, and, at constant
initiator concentration, a general decrease as posttreatment tech-
nique changes from CH$_3$OH/HCl soaking to CH$_3$COCl reflux to PCl$_5$/
CCl$_4$ reflux. The stabilization of the polymer samples as shown by
the change in the DTG peak temperatures parallels particularly the
decrease of the relative absorbance of the OH group. The much
greater suppression of the hydroxyl peak relative to the CH stretch-
ing peak standard by the effective stabilizing agent PCl$_5$ than by the
much less effective stabilizing agent acetyl chloride can be readily
seen.

The infrared data for polymers prepared with 15 and 29 mole %
LTB gave erratic results; the polymers obtained were probably

TABLE 4. Polychloral Endgroups: OH/CH and C=O/CH Peak Absorbance Ratios and DTG Maximum Degradation Rate Temperatures for Low Molecular Weight Polychloral after Various Post-treatments

	LTB initiator concn (mole % relative to chloral)	Peak absorbance ratios[a]		DTG (°C)[b]	
Post-treatment		OH/CH	CO/CH	Initial decomp.	Peak (s)
CH₃OH/HCl	1.8	0.32	0	110	166 (57%)
(1 day, room					222 (43%)
temperature)	3.7	0.65	0.79	120	154
					195 (sh)
	7.3	1.32	0.64		
CH₃COCl	1.8	0.18	0	80	152
(2 days, reflux)					260 (sh)
	3.7	0.13	0.09	50	102 (sh)
					166
	7.3	0.82	0.33	50	91 (16%)
					173 (84%)
PCl₅/CCl₄	1.8	0	0	190	274
(2 days, 60°C)	3.7	0.02	0	190	275
	7.3	0.37	0.10	150	265

[a]IR Spectra determined on powders in CCl_4 mull; OH absorbance at 3300-3500 cm⁻¹; CH at 2955 cm⁻¹; CO at 1770 cm⁻¹.
[b]Heating rate 20°C/min.

higher molecular weight fractions of mixtures in which the fractions of lower molecular weight had been removed. Unextracted materials and those extracted by unacidified methanol are omitted from Table 4 because the unextracted samples rapidly degraded to chloral monomer. All samples degraded completely when placed into unacidified methanol unless treated with acid first; samples taken from the test tubes were stable when placed into acidified (in contrast to unacidified) methanol.

No characteristic absorption frequencies of the tertiary butyl group at 1355 and 1380 cm⁻¹ could be seen in the polymers, even those of lowest molecular weight, because they were overlain by polychloral bands. (In the infrared spectrum of the addition compound

of LTB with one mole of chloral (Fig. 2), the 1355-1360 cm^{-1} peak is very weak although the peak at 1380 cm^{-1} is strong.)

In comparison with the values observed in Table 4 for low molecular weight anionically initiated polychloral, a sample prepared cationically by initiation with 1.2 mole % of H_2SO_4 had OH/CH and CO/CH absorbance ratios of 1.68 and 0.41, respectively, and a DTG peak at 230°C. A sample prepared by initiation with 2.0 mole % of SbCl$_5$ had OH/CH and CO/CH absorbance ratios of 1.40 and 0.72 and a similar DTG peak. As one can see from these data, the concentration of hydroxyl endgroups is apparently higher in these cationically polymerized samples than even in the anionically polymerized samples initiated with 7.3 mole % of LTB. Hence the samples produced cationically are apparently very low in molecular weight, which accounts for the difficulty in obtaining coherent polymers by cationic mechanisms.

Caution must also be used in the interpretation of the 3440 cm^{-1} peak as completely due to hydroxyl groups, because a similar peak appears in the infrared spectrum of the LTB-chloral addition compound (Fig. 2). However, it is felt that the peak in the polymers is due to hydroxyl groups because these spectra were determined on polymers pretreated with acidified methanol and hence stable (unlike the raw alkoxide-terminated polymers) to further extraction with unacidified methanol. Pretreatment with acidified methanol dramatically improves the stability of LTB-initiated polychloral apparently by transforming the labile alkoxide groups into more stable hydroxyl groups.

From the above endgroup studies, we can draw the following conclusions.

(1) Polychloral, at least when initiated with LTB, is terminated with living alkoxide groups which are degraded when the polymer samples are extracted with methanol. Extraction with methanol degrades lower molecular weight polychloral completely and leaves less than 10% residue when higher molecular weight polychoral is expected.

There remains, however, a possibility that adventitious (or internally generated) protic impurities may convert a portion of the alkoxide endgroups to hydroxyl endgroups. As an example, a plug of unextracted polychloral initiated with 0.1% LTB showed peaks in the DTG spectrum at 100°C possibly due to alkoxide-terminated polychloral (48%) and a peak at 211°C falling within the hydroxylic region typical of cationic polychloral and acid-treated polychloral films (52%) (Fig. 4), with only the latter peak evident after methanolic HCl treatment. DTG spectra of unextracted LTB-initiated films, in contrast to plugs, showed only the hydroxyl peak (Table 3) because of the much more rapid diffusion of atmospheric moisture and CO_2 into the thin films upon removal from the molds.

(2) Pretreatment of LTB-initiated polychloral with acidified methanol dramatically increases its stability to subsequent extraction with unacidified methanol. This stabilization apparently occurs by
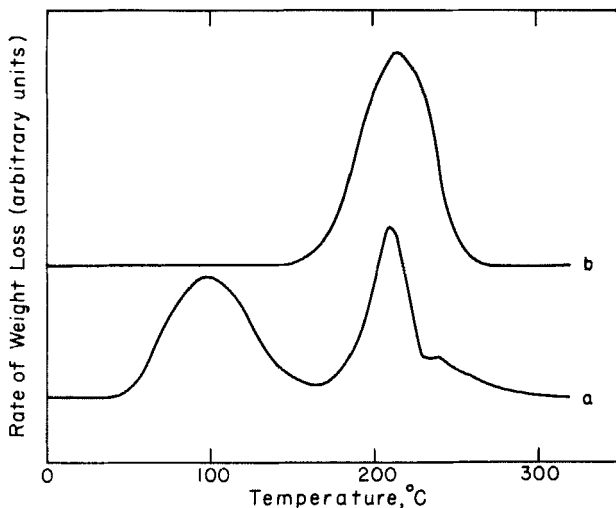
FIG. 4. DTG traces of polychloral initiated with 0.1 mole % LTB: (a) before treatment; (b) after treatment with CH_3OH/HCl.

protonation of alkoxide endgroups, neutralization of alkoxide residues in the polymer by the acid, and possible removal of lithium salts from the polymer. The resultant hydroxyl groups can be detected in the infrared spectra of polychloral prepared with 1.5-2 mole % or more of LTB, but not of higher molecular weight polychloral. Cationically initiated polychloral has very strong hydroxyl absorptions in the infrared. Hydroxyl-terminated polychloral will have a DTG degradation rate peak in the 200-220°C range if of reasonably high molecular weight, with the peak sometimes lower in very low molecular weight polychloral.

(3) Post-treatment with refluxing acetyl chloride or PCl_5 will stabilize LTB-initiated polychloral to subsequent methanol extraction. It will also produce a DTG peak near or above 300°C, partially for acetyl chloride treatment and quantitatively for PCl_5 treatment.

ACKNOWLEDGMENTS

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