

The Depolymerization of Low Molecular Weight Poly(chloroacetaldehydes)

G. H. McCAIN and J. M. SANDERS, *Diamond Shamrock Corporation,
Painesville, Ohio 44077*

Synopsis

Stability of low molecular weight ($\overline{D.P.} < 300$) polychloral has been found to be a function of the amine used as the polymerization initiator. The polymer produced with diethylamine unzips much more rapidly than that made with triethylamine. This investigation also showed that ester endcaps provide little protection from amine-induced depolymerization. The amine-initiated copolymer of chloral and dichloroacetaldehyde behaves anomalously in that it is unstable in the presence of normally inert organic solvents. Mechanisms are proposed to account for these observations.

INTRODUCTION

Previous reports from this laboratory¹⁻⁴ have described the preparation and properties of high molecular weight poly(chloroacetaldehydes). These polymers, in contrast to their low molecular weight analogs, are fairly stable at moderate temperatures even when not endcapped. That polychloral should be thermodynamically unstable at room temperature is not surprising in view of the low ceiling temperature, variously reported as 11°C⁵ and 12.5°C.⁶ Mita et al.⁵ found that in an equilibrium polymerization initiated with sodium naphthalene at -78°C, polychloral rapidly depolymerized on warming to room temperature, providing the degree of polymerization $\overline{D.P.}$ was ≤ 150 . We can infer that the reduced bulk depolymerization rate they noted at high $\overline{D.P.}$ was caused by occlusion of the "living" ends in precipitated polymer. On the other hand, in the work reported here, the polymerizations were initiated with amines and are not believed to be of the "living" type. Since unzipping of "nonliving" polymer must be initiated by some event occurring at an endgroup, it is reasonable to expect a higher probability of such a thing happening when the concentration of nonoccluded ends is great. This is the situation which exists when the $\overline{D.P.}$ is low. The factors affecting the rapid depolymerization of low $\overline{D.P.}$ amine-initiated polychloral and chloral/dichloroacetaldehyde copolymers were the subject of this investigation.

EXPERIMENTAL

Monomers and Solvents

Chloral was purified by distillation under dry nitrogen through a short, packed column, with only the middle fraction being retained. The chloral/

dichloroacetaldehyde mixture was supplied by an internal (Diamond Shamrock Corporation) source and was treated in a manner identical to chloral. Its composition was determined to be 67% chloral and 33% dichloroacetaldehyde by vapor-phase chromatography. All monomers were stored under nitrogen in the dark.

The other reactants and solvents were the purest available commercial grades and were used as received.

Polymerization

Two techniques were used to prepare the polymers: solution polymerization in diethyl ether and bulk polymerization.

Solution polymerizations were carried out on a 0.2 gram-mole scale in a small, thoroughly dried, round-bottom flask containing a magnetic stirring bar and sealed by a rubber septum pierced by a 20-gauge hypodermic needle. The flask was well flushed with dry nitrogen prior to sealing, and the inert atmosphere was maintained by connecting the needle to a low-pressure nitrogen source. Equal volumes of diethyl ether and chloral (or chloral/dichloroacetaldehyde mixture) were injected through the septum with hypodermic syringes and the reactor was immersed in a bath at -25°C . A period of about 30 min with vigorous agitation was allowed for temperature equilibration.

For polymerization of chloral with triethylamine (TEA), a 7% solution of TEA in diethyl ether was prepared and cooled to -25°C . The cold solution (5.5 ml) was rapidly injected through the rubber septum. Polymerization was almost instantaneous. With diethylamine (DEA) as the initiator, no dilution of the amine was required, and solidification generally required about 15 min. Chloral/dichloroacetaldehyde copolymerizations were carried out with initiation by undiluted TEA, and about 15 min were required for solidification. In each case, the reaction mixture was kept at -25°C for 1 hr and overnight at 20°C . Most of the ether was stripped off by distillation at ca. 20 mm Hg. Purification was completed by lowering the pressure to 0.1 mm Hg for 6 hr with the flask cooled to 0°C . Occasionally, it was necessary to pulverize the polymer in a Waring Blender prior to the final drying procedure. Conversions varied between 90% and 98%. The dried polymers were stored at -20°C .

Bulk polymerizations, used only for chloral homopolymerization, were carried out very simply. Chloral was injected with a hypodermic syringe into a test tube through which dry nitrogen was slowly flowing. The tube was placed in a bath at 21°C , and ca. 1% (based on chloral) of DEA or TEA was injected with a hypodermic syringe just under the aldehyde surface. The mixture was stirred briefly with a glass rod and allowed to stand for 3 hr. The hard product was dispersed in 2% aqueous HCl with a Waring Blender and washed with water and petroleum ether. Finally, the powder was dried for 2 hr at $0^{\circ}/1$ mm Hg and stored at -20°C .

The inherent instability of the polymers made exhaustive extraction to remove carbonyl impurities impractical. It is not believed that such im-

purities can cause any serious error since this study is based on the increase in carbonyl content, not the absolute quantity. It must be noted, however, that zero times, zero decompositions shown on the several curves represent extrapolations from first measurements and are not experimentally determined points.

Capping

Polymers were endcapped with the respective acid chlorides as described previously.¹ However, when trifluoroacetyl chloride was used as the capping agent, the reactions were carried out in sealed tubes at 45°.

Molecular Weight Determination

Number-average molecular weights were determined by endgroup analysis, a variation of the method of Rosen et al.¹ In this instance, polymers were capped with trifluoroacetate groups and degrees of polymerization calculated from elemental analysis for fluorine. Molecular weights determined in this way cannot be considered highly accurate, but are useful as reasonable estimates. Typical results are listed in Table I.

The degrees of polymerization of polychlorals prepared in bulk with either TEA or DEA initiation are not significantly different. The considerable increase in the $\overline{D.P.}$ of polychloral made in solution using TEA initiation over that of bulk polymerized polymer made with the same catalyst is clearly due to the lower solution reaction temperature (−25°C vs. 21°C). The change of $\overline{D.P.}$ in the reverse direction when DEA is the initiator is more difficult to understand. A possible explanation is that unzipping has occurred during capping. Such a reaction would very quickly reduce the molecular weight. As will be discussed later, DEA-initiated polychloral is less stable than that made with TEA and is thus more likely to depolymerize under capping conditions. The apparent failure of similar unzipping to occur in bulk-polymerized polychloral is not understood and may just be due to a fortuitous combination of conditions.

TABLE I
Degrees of Polymerization of Various Chloral Polymers as Determined by
Endgroup Analysis

| Polymerization initiator | Polymerization system | Fluorine, % ^a | $\overline{D.P.}$ |
|--------------------------|-----------------------|--------------------------|-------------------|
| TEA ^b | Bulk | 0.50 | 150 |
| DEA ^c | Bulk | 0.40 | 190 |
| TEA | Solution | 0.20 | 390 |
| DEA | Solution | 1.9 | 39 |
| TEA ^d | Solution | 0.28 | 300 |

^a An average of at least two determinations.

^b Triethylamine.

^c Diethylamine.

^d Chloral/dichloroacetaldehyde copolymer.

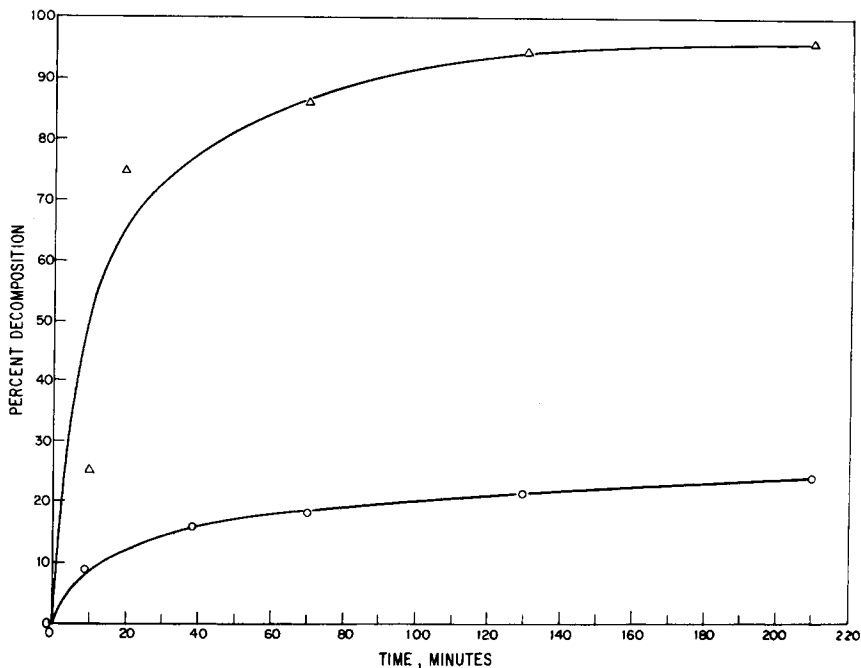


Fig. 1. Decomposition of polychloral: (O) triethylamine-initiated polymer; (Δ) diethylamine-initiated polymer.

Depolymerization Measurements

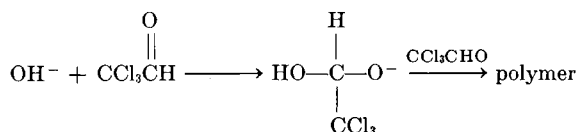
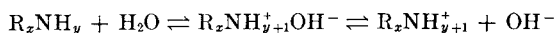
Infrared spectrophotometry was the chief technique used to study the depolymerization rate. A suspension of 0.4 g (weighed to ± 0.1 mg) of polymer was prepared in 500 ml CCl_4 . Aliquot fractions of this slurry were removed periodically with a hypodermic syringe fitted with a Millipore filter. Absorbances of the filtrates were determined with a Perkin-Elmer Model 521 infrared spectrophotometer and the concentration of free monomer calculated by reference to calibration curves prepared with pure chloral or chloral/dichloroacetaldehyde solutions. The peak at 1725 cm^{-1} was used for chloral, and the absorptions at 1745 and 1725 cm^{-1} were employed for chloral/dichloroacetaldehyde. All measurements were made at room temperature, ca. 20°C . Aldehyde concentrations as low as $0.006\text{ g}/10\text{ ml CCl}_4$ could be measured by this method.

An alternative thermogravimetric analysis (TGA) method was employed in a few instances. A Stanton thermobalance Model HT-M was employed at room temperature. Powdered polymer (~ 360 mg) was placed in the instrument under a slow nitrogen sweep and the weight loss with respect to time automatically recorded. This technique suffers from the disadvantage of superimposing a volatilization rate on the depolymerization rate so that the results are not numerically the same as are found with the infrared method.

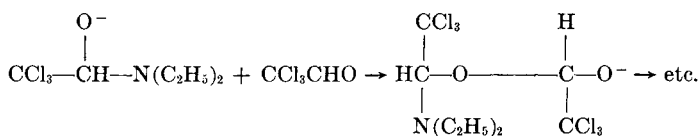
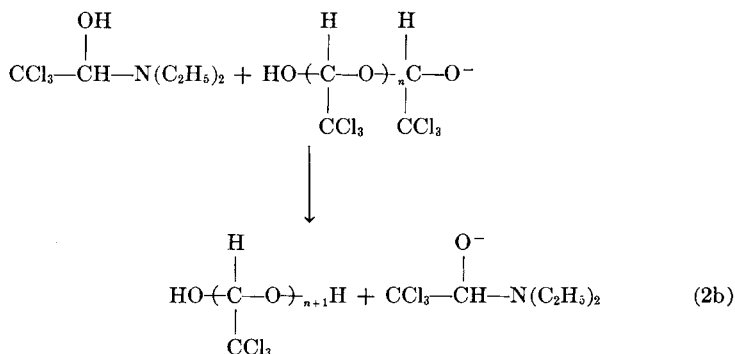
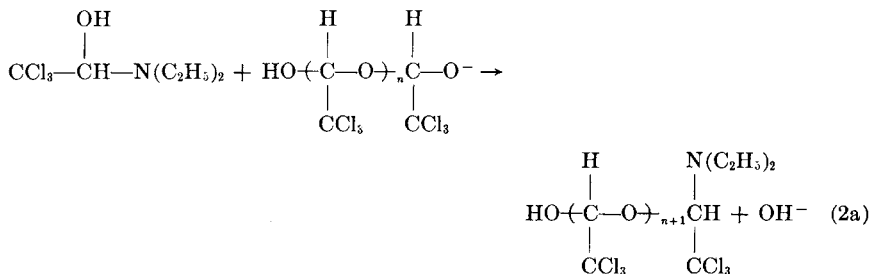
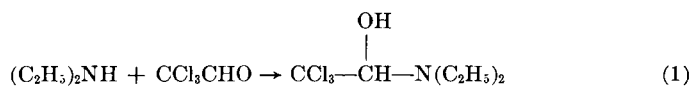
RESULTS AND DISCUSSION

Polychloral

Shapes of the decomposition curves (Fig. 1) are generally very similar to those found for polyacetaldehyde by Graessley et al.⁷ The strong dependence of stability on initiator is, however, unexpected. Amine-induced chloral polymerization requires a trace of water as a cocatalyst and would be expected to take place as follows:



We hypothesize that when the initiator is a secondary amine, as diethylamine, an addition reaction (1) with monomeric chloral can take place in competition with polymerization initiation. The product of this reaction would make possible routes (2a) and (2b):



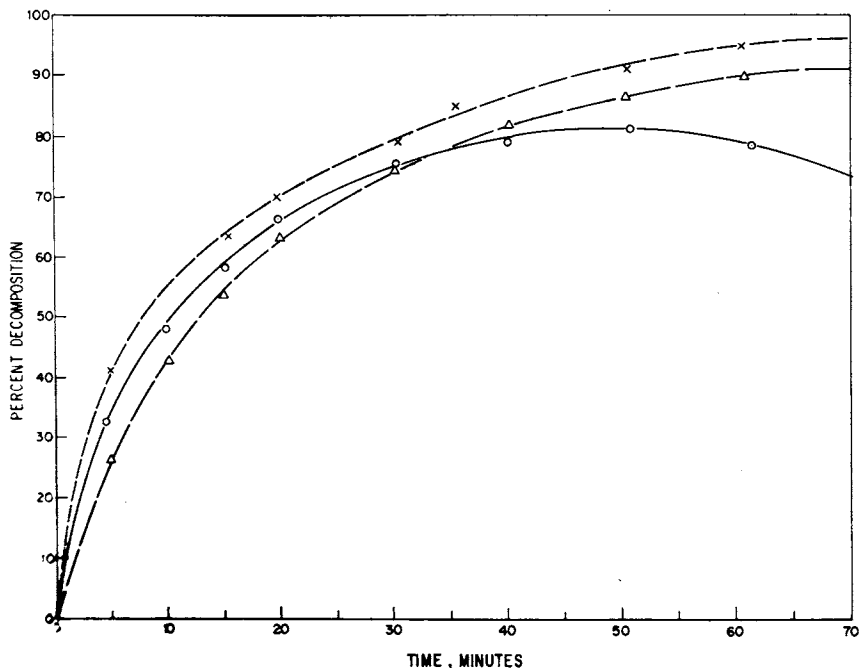


Fig. 2. Diethylamine-induced decomposition of polychloral: (Δ) 0.002 ml diethylamine/50 ml CCl_4 ; (\times) 0.02 ml diethylamine/50 ml CCl_4 ; (\circ) 0.06 ml diethylamine/50 ml CCl_4 .

Either (2a) or (2b) would give an amine containing endgroup which should be inherently unstable. It is not known if step 1 can occur, but the analogous reaction with ammonia has been reported.⁸ This type of interaction cannot take place between a tertiary amine such as triethylamine and chloral so that a somewhat more stable, OH-terminated polymer should result in that instance.

An alternative explanation for differences in polychloral stabilities lies in the possible presence of unremoved initiator traces. Figures 2 and 3 show the effect on depolymerization of deliberately introducing small amounts of di- and triethylamine into slurries of polychloral prepared by triethylamine catalysis. Both amines greatly enhance the rate of unzipping, but diethylamine is only slightly more effective than its tertiary analog. There being no reason to expect one initiator to remain behind in significantly greater concentration than the other, it is unlikely that the observed stability differences can be caused by residual amines. It thus is reasonable to attribute variations in stability to moieties contributed by the initiator and incorporated into the polymer structure.

An interesting by-product of the study was the discovery that converting the hydroxyl endgroups to esters provided no protection against attack by amines. Thus, polymers capped with either acetate or trichloroacetate groups decomposed to the extent of at least 80% in 1 hr when suspended in CCl_4 and treated with 0.02 ml of either di- or triethylamine. These same dispersions were free of aldehyde carbonyl absorptions during the 5 hr pre-

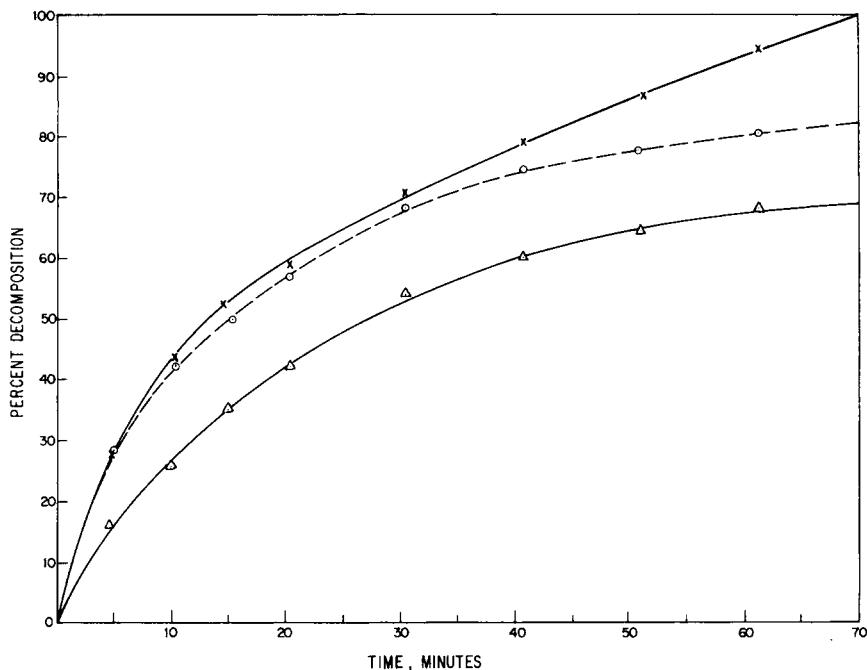
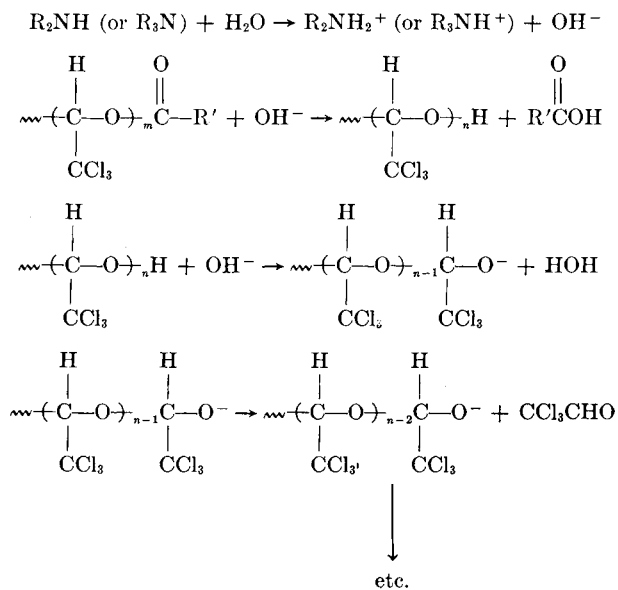


Fig. 3. Triethylamine-induced decomposition of polychloral: (Δ) 0.002 ml triethylamine/50 ml CCl_4 ; (\times) 0.02 ml triethylamine/50 ml CCl_4 ; (\circ) 0.06 ml triethylamine/50 ml CCl_4 .

ceding exposure to amine. This is taken as evidence for attack by an amine at the ester endgroup, assisted by traces of water. These endgroups are made vulnerable to such a reaction by the inductive effect of the trichloromethyl group, i.e.,



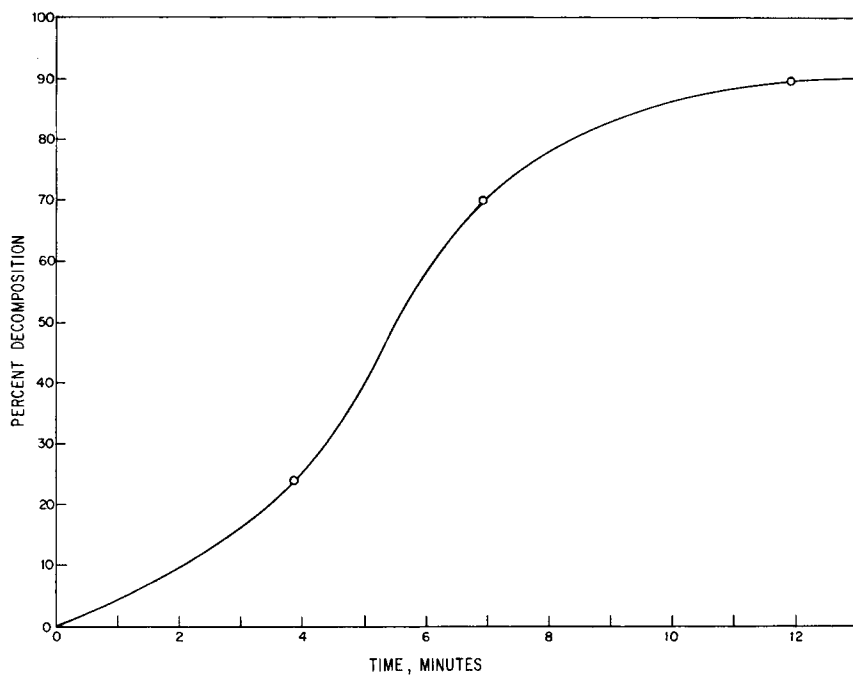


Fig. 4. Decomposition of chloral/dichloroacetaldehyde copolymer in CCl₄ slurry.

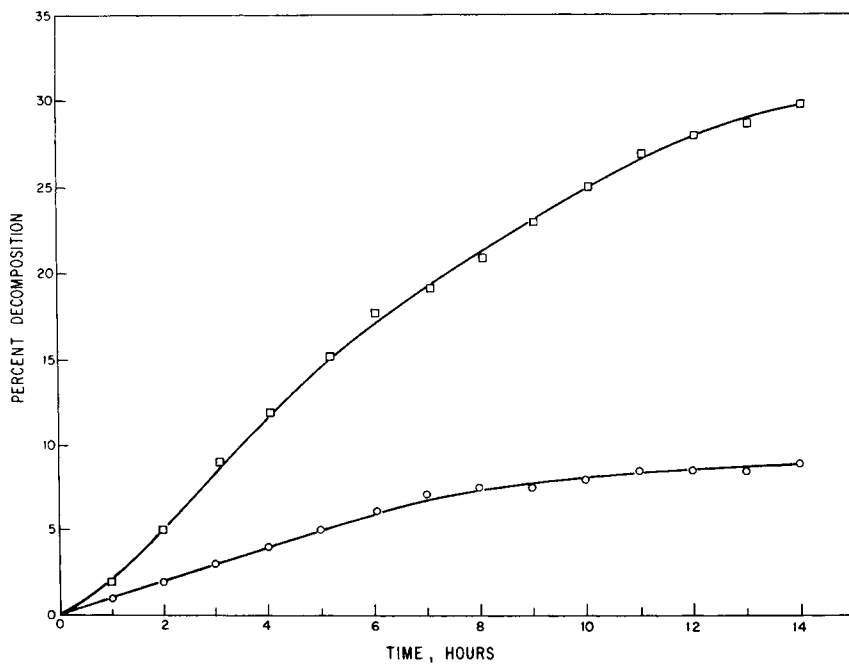
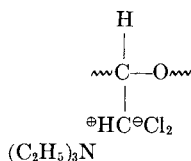


Fig. 5. Decomposition of chloral/dichloroacetaldehyde copolymer in TGA apparatus: (O) nitrogen stream alone, (□) nitrogen containing CCl₄.

Chloral/Dichloroacetaldehyde Copolymer

The effect of amines on the depolymerization of a chloral/dichloroacetaldehyde copolymer has already been discussed in considerable detail by Novak and Poziomek.⁹ In general, under such conditions the pattern of unzipping is much like that of polychloral. However, in contrast to homopolymer, the decomposition rate of the 67/33 (weight) chloral/dichloroacetaldehyde copolymer is peculiarly dependent upon environment even when amines are apparently absent. Uncapped copolymer is relatively stable under nitrogen at room temperature, undergoing only a 10–15% weight loss in 20 hr in the TGA apparatus. When slurried in CCl_4 , however, 90% of the copolymer reverted to monomer in about 12 min (Fig. 4). Similar behavior occurred in hexane, showing that some specific interaction with CCl_4 was not involved. Further evidence of the unusual effect of organic solvents on copolymer stability is illustrated by Figure 5. Here, it can be readily seen that even when the nitrogen used in TGA contains CCl_4 vapor, the unzipping rate of the copolymer is accelerated.

We speculate that instability of the chloral/dichloroacetaldehyde copolymer in solvents can be attributed to traces of triethylamine initiator held in the polymer by interaction with the weakly acidic α -hydrogens of dichloroacetaldehyde:



Under the necessarily mild conditions used to purify the polymer, some of the amine could remain bound to the chain and available for participation in the depolymerization reaction. It can be anticipated that the copolymer would then exist in equilibrium with the monomers and that, when solvents were present, the aldehydes would be able to diffuse away from the polymer. The dilution would decrease the probability of recombination so that the net effect is one of depolymerization. The TGA results fit the same explanation, for CCl_4 vapor should improve the chloral and dichloroacetaldehyde-removing efficiency of the gas stream sufficiently to displace the equilibrium in the observed direction.

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