Degradation of Poly(vinyl Chloride)*

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Synopsis

The decomposition of poly(vinyl chloride) below 155°C has been examined by thermogravimetric analysis. Degradation is enhanced by irradiation with 1 MeV electrons. Later stages of isothermal weight loss for thermal and radiolytic decomposition follow 3/2-order kinetics and a similar reaction scheme is inferred. A free radical mechanism for dehydrochlorination involving allyl and polyenyl radicals is postulated.

INTRODUCTION

Thermal degradation of poly(vinyl chloride) yields conjugated unsaturation or polyenes. Below 300°C, the gaseous decomposition product is largely hydrogen chloride.[1,2] The rate of degradation was observed to be 3/2-order in monomer and a free radical chain mechanism with termination by the combination of chlorine atoms postulated.[1] On the other hand, below 200°C, the evolution of hydrogen chloride was found to be zero order.[2] The dehydrochlorination may be initiated by rupture of labile carbon–chlorine bonds associated with unsaturated chain ends and tertiary chlorides.[3] An increasing body of evidence is consistent with a free radical mechanism for poly(vinyl chloride) degradation in vacuum.[1,2,4,5,6] Electron spin resonance experiments confirm that the formation of free radicals is associated with dehydrochlorination.[7]

Information on thermal degradation is particularly relevant to the design of stabilizer systems.[8,9] Stabilizers can react with poly(vinyl chloride) to replace certain labile chlorines and thereby stabilize potentially weak links.[10-12] On exposure of poly(vinyl chloride) to ionizing radiation, it is likely that a free radical chain dehydrochlorination is initiated by radiation-induced carbon–chlorine bond scission.[13] Subsequent reactions are similar to those accompanying thermal degradation[14] and thermal and radiolytic decay may be closely related.

The decomposition of poly(vinyl chloride) has been examined by thermogravimetric analysis at temperatures below 155°C. The results should be relevant to the stability of poly(vinyl chloride) during processing and use. In addition, isothermal weight loss following low temperature irradiation

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with 1 MeV electrons was studied.   Comparison with thermal decay may enhance our understanding of poly(vinyl chloride) stability.

EXPERIMENTAL

Poly(vinyl chloride) was Opalon 660 powder (Monsanto Chemical Co.) molded at 120°C to yield colorless, transparent films, 12 mils thick.   For thermogravimetric analysis, poly(vinyl chloride) film was placed in Pyrex tubes, outgassed at 10^{-5} mm for 6 hr, and sealed.   Subsequent to treatment the tubes were opened, the sample was placed on the pan of an electrobalance (Cahn R. G.), the system was purged with nitrogen and heated at 320°C/min to a desired temperature, and thermogravimetric analysis was pursued in nitrogen at a flow rate of 30 cc/min (Perkin-Elmer TGS-1). Alternately, poly(vinyl chloride) samples ($\sim$7 mg) were placed in aluminum dishes and sealed in a nitrogen atmosphere in a glove bag (Instruments for Research and Industry).   The aluminum containers were placed in Pyrex tubes, outgassed at 10^{-5} mm for 6 hr, and sealed prior to treatment and thermogravimetry.

The Perkin-Elmer TGS-1 thermogravimetric analyzer combines a microfurnace with a Cahn R. G. automatic electrobalance inside a vacuum jacket.   The small furnace permits heating rates up to 320°C/min over a temperature range of 25°–1000°C.   For samples weighing about 7 mg, weight losses in excess of 0.3 μg are reproducibly detected.

The temperature of the furnace was calibrated at the Curie points of three ferromagnetic standards: Monel (65°C), Alumel (163°C), and nickel (359°C).   Intermediate temperatures were interpolated.   For calibration, standards are positioned within the furnace at the same location as measured samples.   A magnetic field surrounds the standard.   The transition is observed as an apparent weight loss as the furnace is heated at a constant rate.   Curie points were determined at five heating rates between 80° and 0.31°C/min and extrapolated to zero heating rate for isothermal weight loss studies.

Tubes were irradiated in liquid nitrogen (-196°C) with 1 MeV electrons from a van de Graaff generator at a dose rate approximating 4 Mrads/ min.[15]   Samples were exposed in 1-min intervals and the level of liquid nitrogen was adjusted between pulses.   Subsequent to irradiation, tubes were stored in a Dewar of liquid nitrogen.   Before analysis, tubes were removed from liquid nitrogen, warmed to 25°C, opened, and either poly(vinyl chloride) film or a previously sealed aluminum dish containing film was removed.   For thermogravimetric analysis, aluminum dishes were punctured to permit evolution of gaseous decomposition products.   The alternative procedures gave identical results.

RESULTS AND DISCUSSION

Thermogravimetric analysis of poly(vinyl chloride) film in dry nitrogen at a heating rate of 20°C/min is shown in Figure 1.   In the vicinity of

300°C, a continuous loss of weight attaining about 60% of the initial weight is noted, corresponding to the hydrogen chloride content in poly(vinyl chloride). Above 400°C, decomposition is more extensive and probably involves the polymer backbone. From this observation,[16] as well as from analyses of gaseous decomposition products,[1,2] it is inferred that the lower temperature weight loss is entirely due to dehydrochlorination.

Isothermal weight loss studies were pursued at 78°, 126°, and 155°C on poly(vinyl chloride) films before and after irradiation with energetic electrons. These results are illustrated in Figures 2, 3, and 4. In these studies, observed weight losses are ordinarily less than 1%. Resultant polymers
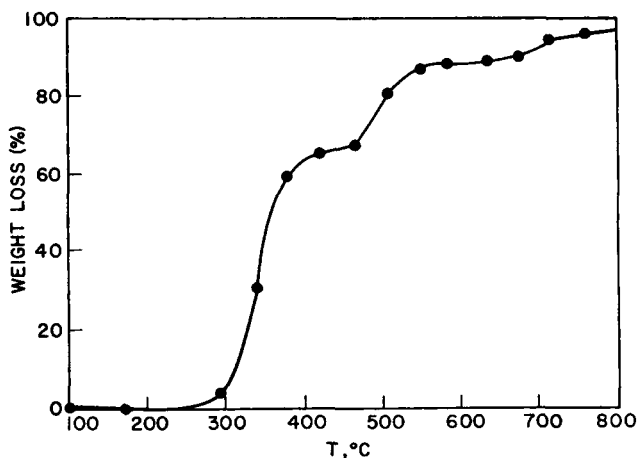

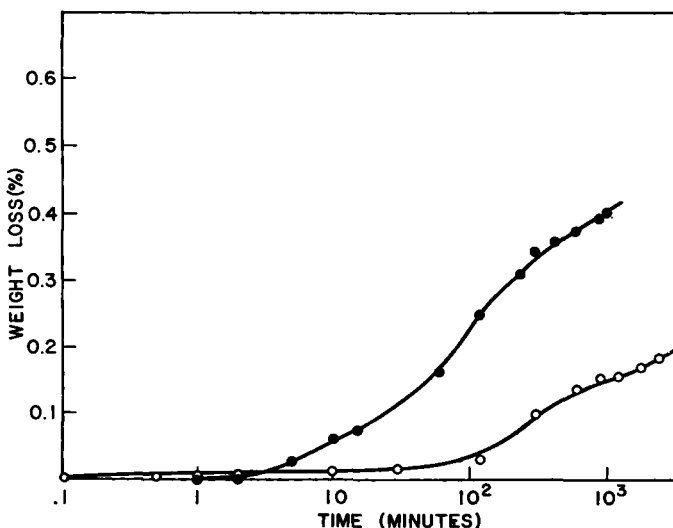Fig. 1. Volatilization of poly(vinyl chloride) at 20°C/min in nitrogen.

Fig. 2. Volatilization of poly(vinyl chloride) at 78°C: (O) 0 Mrad; (●) 25 Mrad.
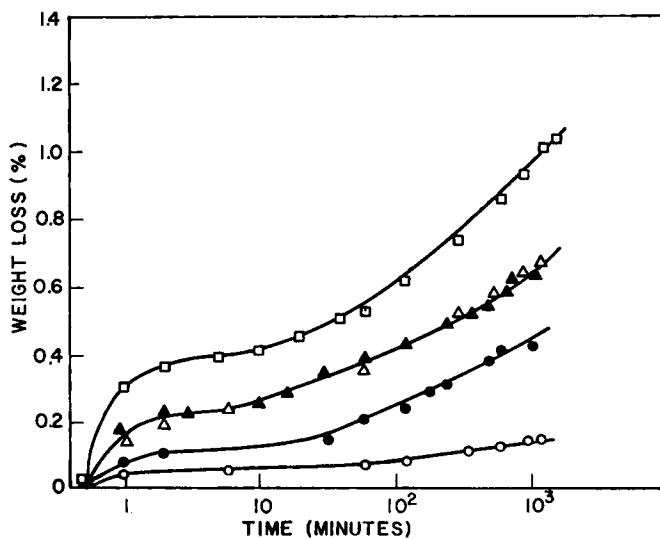
Fig. 3. Volatilization of poly(vinyl chloride) at 126°C: (O) 0 Mrad; (●) 4.4 Mrad; (△) 12.5 Mrad; (▲) 12.7 Mrad; (□) 25 Mrad.
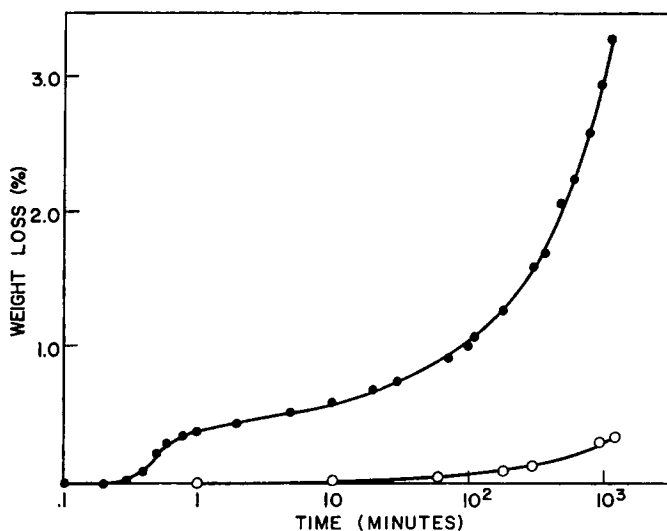

Fig. 4. Volatilization of poly(vinyl chloride) at 155°C: (O) 0 Mrad; (●) 25 Mrad.

are highly colored.   The weight loss is not a linear function of time; therefore, dehydrochlorination was not a simple zero-order reaction as previously reported for the thermal degradation of poly(vinyl chloride) at temperatures below 200°C.[2]   It was found that, after an initial period, weight losses for unirradiated and irradiated poly(vinyl chloride) could, however, be fitted to a 3/2-order reaction and $C^{-1/2}$ was linear with time (Figs. 5–7). The C value is the fraction of undegraded monomer units, expressed as a

ratio of the mass of hydrogen chloride in the sample at any given time to the mass of hydrogen chloride in the original sample. For thermal decomposition of unirradiated poly(vinyl chloride), 3/2-order kinetics were derived for a free radical chain dehydrochlorination.[1] It was postulated that the reaction is initiated by carbon–chlorine bond scission and propagated by hydrogen abstraction by the chlorine atom to produce hydrogen chloride. Termination involved the combination of chlorine atoms. Since molecular chlorine was not observed as a gaseous decomposition product it was suggested that molecular chlorine adds to unsaturation in degraded poly(vinyl chloride).[1] Since 3/2-order kinetics obtained for
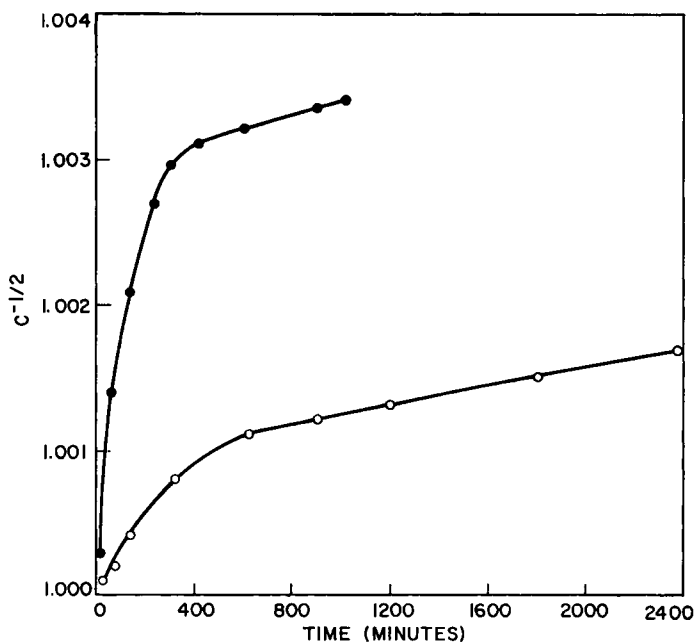

Fig. 5. $C^{-1/2}$ versus time at 78°C: (O) 0 Mrad; (●) 25 Mrad. (C is the concentration of undegraded monomer units.)

unirradiated poly(vinyl chloride), the suggested kinetic scheme[1] may be applicable to low temperatures and conversions. Within experimental error, weight losses at 78° and 126°C were indistinguishable, implying that the process is not activated. It should be noted that the glass transition temperature of poly(vinyl chloride) was observed in the calorimeter at a heating rate of 20°C/min at 83°C. (It is possible that the zero activation energy is due to the fact that one goes through the glass transition temperature in this kinetic range.) The rate of weight loss increases at 155°C. Comparison of rate constants at 126° and 155°C (Table I) indicates an activation energy of about 27 kcal/mole. This compares with a value of about 30 kcal/mole previously reported.[1]

TABLE I
Rate Constants for 3/2-Order Thermal Decomposition

Temperature, °C	Rate constant, $\times 10^{-7}$/min	
	0 Mrad	25 Mrad
78	5.32	10.6
126	5.32	34.6
155	54.6	358.

The rate constants for thermal decomposition of poly(vinyl chloride) films, unirradiated and irradiated to 25 Mrads, as derived from appropriate slopes of linear portions in Figures 5–7, are collected in Table I. The rate constants are considerably lower than those reported for elevated temperatures and conversions.[1]

Following irradiation in liquid nitrogen, thermal decomposition is enhanced (Figs. 2–4). After a rapid initial weight loss, the reaction was 3/2-order in monomer (Figs. 5–7). For decomposition at 126°C, the initial weight loss depended on dose (Fig. 6). This loss in weight may be due to molecular dehydrochlorination during irradiation. However, the initial weight loss depends on temperature as well, and the thermal decomposition of particularly unstable structures generated by irradiation is inferred. The temperature dependence of the initial weight loss is influenced by the rate of diffusion of hydrogen chloride out of the film and the rate of decomposition. The evolution of trapped hydrogen chloride perceived as the initial weight loss requires 35 sec at 120°C and 9 sec at 150°C. This ap-
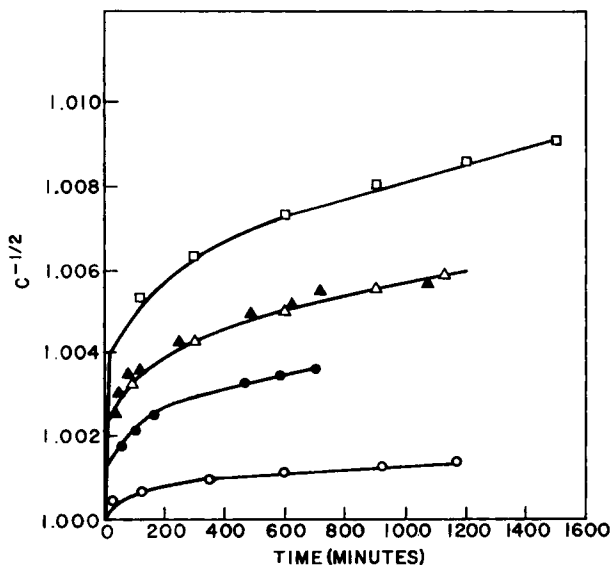

Fig. 6. $C^{-1/2}$ versus time at 126°C: (O) 0 Mrad; (●) 4.4 Mrad; (△) 12.5 Mrad; (▲) 12.7 Mrad; (□) 25 Mrad.

proximated a calculated diffusion time for methane through 3 mil poly-
(vinyl chloride) film at 120°C.[17]

In unirradiated poly(vinyl chloride), carbon–chlorine bond scission initi-
ating subsequent dehydrochlorination is believed to occur at labile sites,
such as allylic chloride or tertiary chlorine atoms at branch points.[12] Irra-
diation enhancement of dehydrochlorination may be due to the formation
of additional labile structures on irradiation. For example, radiation-in-
duced molecular dehydrochlorination generates allylic chloride. Another
reactive site would be the allyl radical, tentatively identified in irradiated
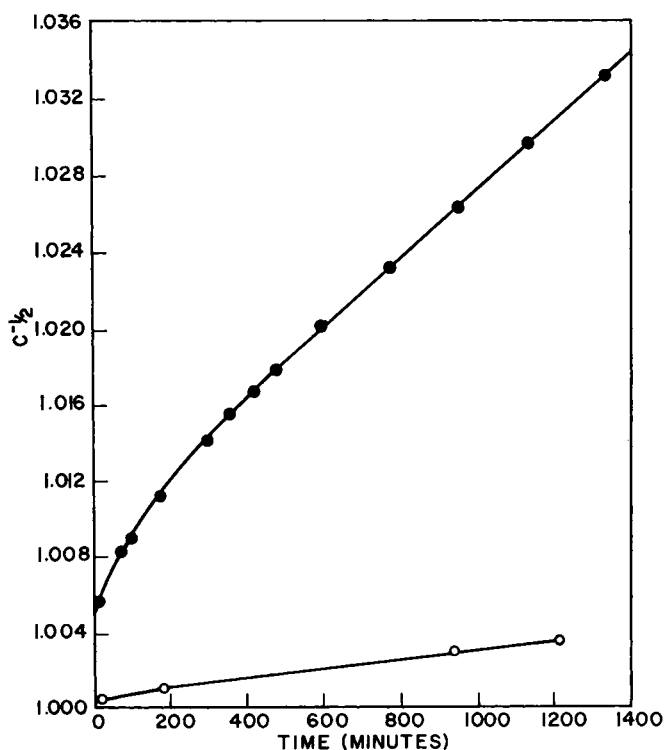
Fig. 7. $C^{-1/2}$ versus time at 155°C: (O) 0 Mrad; (●) 25 Mrad.

poly(vinyl chloride).[18]   Aside from the generation of additional initiating
sites and, therefore, the observation of larger rate constants (Table I),
thermal decomposition of irradiated poly(vinyl chloride) proceeds with a
similar rate law to unirradiated poly(vinyl chloride) (Figs. 5–7).   Indeed,
the temperature coefficient of the rate constant for 126°C and 155°C yields
an activation energy of 27 kcal/mole, just as for unirradiated poly(vinyl
chloride).

In view of the similarity in decomposition kinetics between irradiated
and unirradiated poly(vinyl chloride), irradiation may facilitate accelerated
testing of the polymer and the evaluation of stabilizers.   The ability of

additives to stabilize labile structures can be measured by thermogravimetry.

The mechanism suggested for 3/2-order dehydrochlorination[1] may be oversimplified. Chain transfer reactions, the presence of allyl and polyenyl free radicals,[18] and the formation of long sequences of conjugated unsaturation[19] may imply a more complex mechanism. The elimination of molecular hydrogen chloride by allyl and polyenyl free radicals with frequent transfer of the reactive site to other poly(vinyl chloride) chains may be a likely alternative to a chain reaction propagated by chlorine atoms. A possible reaction scheme is suggested:

1. Initiation

$$
\begin{array}{ccccc}
H & H & H & H \\
-C-C-C-C- \\
H & Cl & H & Cl
\end{array}
\xrightarrow{k_i}
\begin{array}{cccc}
H & H & H & H \\
-C-C-C-C- & + \cdot Cl \\
H & \cdot & H & Cl
\end{array}
$$

2. Propagation

$$
\begin{array}{cccc}
H & H & H & H \\
-C-C-C-C- \\
H & \cdot & H & Cl
\end{array}
\xrightarrow{k_p}
\begin{array}{cccc}
H & H & H & H \\
-C-C-C=C- & + HCl \\
H & \cdot
\end{array}
$$

allyl

$$
\begin{array}{ccccc}
H & H & H & H & H \\
-C-C-C-C=C- \\
Cl & H & \cdot
\end{array}
\xrightarrow{k'_p}
\begin{array}{c}
H \\
-C \\
\cdot
\end{array}
\left(
\begin{array}{cc}
H & H \\
C=C \\
\end{array}
\right)_2 + HCl
$$

$$
\begin{array}{ccc}
H & H & H \\
-C-C-C \\
Cl & H & \cdot
\end{array}
\left(
\begin{array}{cc}
H & H \\
C=C \\
\end{array}
\right)_n
\xrightarrow{k''_p}
\begin{array}{c}
H \\
-C \\
\cdot
\end{array}
\left(
\begin{array}{cc}
H & H \\
C=C \\
\end{array}
\right)_{n+1} + HCl
$$

polyenyl

3. Transfer

$$
\begin{array}{c}
H \\
-C \\
\cdot
\end{array}
\left(
\begin{array}{cc}
H & H \\
C=C \\
\end{array}
\right)_n
+
\begin{array}{cccc}
H & H & H & H \\
-C-C-C-C- \\
H & Cl & H & Cl
\end{array}
\xrightarrow{k_{tr}}
$$

$$
\begin{array}{c}
H \\
-C \\
Cl
\end{array}
\left(
\begin{array}{cc}
H & H \\
C=C \\
\end{array}
\right)_n
+
\begin{array}{cccc}
H & H & H & H \\
--C-C-C-C- \\
H & \cdot & H & Cl
\end{array}
$$

In vacuum, there is no evidence of radical decay for a prolonged period[14] so that termination occurs by the formation of very long, unreactive polyenyl free radicals. In air, radicals react with oxygen forming peroxides and other oxidation products.

CONCLUSIONS

The dehydrochlorination of poly(vinyl chloride) at temperatures below 155°C may be sensitively measured by thermogravimetric analysis. The rate of evolution of hydrogen chloride is increased by preirradiation with energetic electrons. Isothermal weight loss for unirradiated and irradiated poly(vinyl chloride), after an initial weight loss, followed 3/2-order kinetics, implying that thermal and radiation-initiated decay are similar. In analogy to a thermal reaction initiated by carbon–chlorine bond rupture at labile chlorine, ionizing radiation induces carbon–chlorine bond scission and the generation of labile structures. A free radical mechanism for the dehydrochlorination involving allyl and polyenyl radicals is postulated.

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