

Thermal Analysis of Irradiated Poly(vinyl Chloride)

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Synopsis

The thermal decomposition and resultant disposal of waste poly(vinyl chloride) (PVC) is facilitated by preliminary exposure to ionizing radiation, such as energetic electrons, in an oxygen atmosphere. The results of isothermal and temperature-programmed thermogravimetry, differential thermal analysis, and effluent gas analysis in nitrogen and in oxygen indicate that the major effect of irradiation is to render PVC increasingly susceptible to oxidation. The presence of oxygen during heating enhances the decomposition. Crystalline order in PVC is destroyed by irradiation.

INTRODUCTION

The accumulation of waste polymeric materials is a major component of environmental pollution.¹ About 1 million tons of PVC are discarded annually. It is suggested that the thermal decomposition of poly(vinyl chloride) (PVC) following exposure to ionizing radiation in an oxygen atmosphere would facilitate disposal. Radiation-induced oxidation initiates free radical chain dehydrochlorination and the quantitative evolution of hydrogen chloride.² The resultant unsaturated polymer can be used directly, perhaps as a filler, or yield simple hydrocarbons on pyrolysis. The feasibility of this approach is examined by thermal analysis of irradiated PVC.

Irradiation of PVC in vacuo produces free radicals,^{3,4} polyenes,^{3,5} and crosslinks⁶ and is accompanied by the evolution of hydrogen chloride.² Irradiation in air yields, additionally, chain scission and carbonyl groups.⁷ Thermal degradation of PVC produces similar products and has been reviewed.^{8,9,10}

EXPERIMENTAL

The PVC used in these experiments was an unstabilized commercial material prepared by bulk polymerization (Rucon B-20, Hooker Chemical Corp.). The number- and weight-average molecular weights are 19,000 and 49,000, respectively, as determined by gel permeation chromatography.⁷ The PVC powder ($\sim 100 \mu$ resin beads) was placed in thin (1 mm) layers on the bottom of vials open to air on a conveyor belt set to traverse an electron beam. The polymer was irradiated to a series of doses in a beam of 1.5 MeV electrons from a Van de Graaff generator (State University of

New York at Buffalo) equipped with a 14-in. scanner. Samples were exposed to 5.8, 11.6, 17.4, 29.0, and 52.2 Mrad by repeated traversal of the beam. Each pass under the beam took 0.53 min, and the dose rate was 1.16 Mrad/pass. A fan was used during irradiation to minimize the accumulation of ozone. The dose rate was determined by the bleaching rate of blue cellophane calibrated with the Fricke dosimeter, which is the radiation-induced oxidation of ferrous ions.¹¹

Molecular weight changes in the irradiated PVC were measured by gel permeation chromatography.⁷ From the reduction in average molecular weights at low doses and the formation of increasing amounts of gel at high doses of irradiation, it was inferred that both main chain scission and cross-linking occurred during irradiation in air.

Thermogravimetry (TG) was performed in a vertical tubular oven (~ 9 mm I.D.) in atmospheres of oxygen or nitrogen which were renewed 5 times/min flowing past the samples. The samples, 10 mg each, were contained in shallow platinum dishes (~ 6 mm in diameter) and the sample weight monitored with an electrobalance (Cahn RG) and continuously recorded. Thermogravimetry was either isothermal (150°C) or at a heating rate of 10°C/min. For isothermal thermogravimetry, the furnace with the sample in place was heated from room temperature in about 6 min.

Differential thermal analyses (DTA) were conducted at 10°C/min on 300-mg samples contained in the 1.2- to 1.4-mm annular space formed when a capillary tube containing a thermocouple is located along the axis of a 4-mm-I.D. Pyrex glass tube. The sample containing length of this concentric tube arrangement was located symmetrically in a cylindrical metal block furnace. A glass microbead reference in matching configuration was used throughout. The height of the sample can be varied from 10 to >35 mm without changing the thermal cross section of sample sensed by the thermocouple. This configuration assures a relatively small thermal gradient in the sample and consequently good resolution of adjacent thermal effects even with unusually large samples. This larger sample is an asset when analysis of the effluent gas or residue is desired. Sensitivity to dehydrochlorination, however, is much greater in TGA than in DTA. Oxygen or nitrogen gas flowed through the sample so that the atmosphere surrounding the particles was renewed every few seconds.

Effluent offgases from DTA were led through thin Teflon tubing into a stirred aqueous scrubber and titrated with 0.1052*N* sodium hydroxide using phenolphthalein indicator.

X-Ray diffraction scans of PVC samples were generated between 2θ values of 13° and 34° using an x-ray diffractometer (Norelco) with a copper target x-ray tube ($\lambda = 1.54 \text{ \AA}$).

RESULTS AND DISCUSSION

Isothermal thermogravimetry (TG) at 150°C in flowing oxygen atmosphere is summarized in Figure 1 for control and irradiated samples. Data

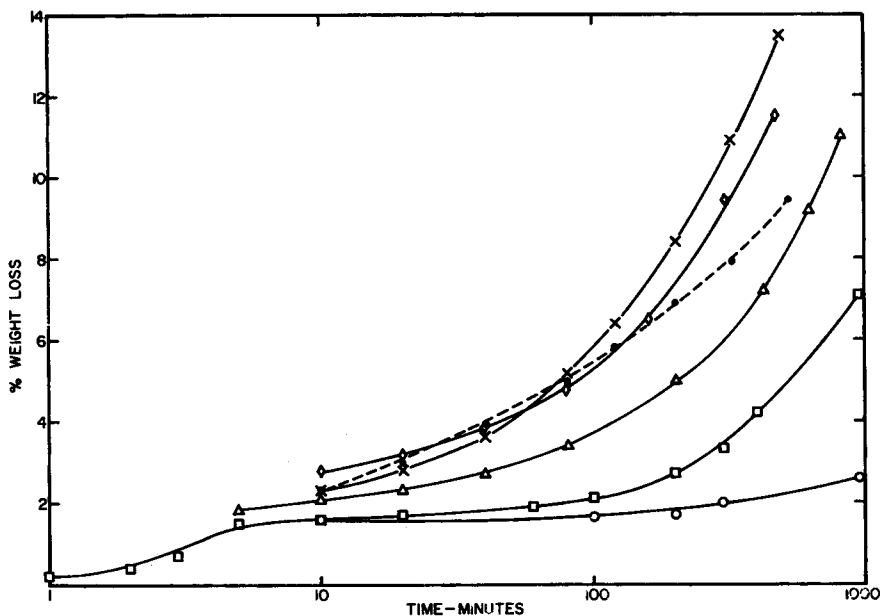


Fig. 1. Isothermal thermogravimetry of irradiated PVC-150°C, oxygen atmosphere: (O) control (□) 5.8 Mrad; (Δ) 17.4 Mrad; (◇) 29.0 Mrad; (×) 52.2 Mrad; (—●—) 52.2 Mrad, in nitrogen.

in a flowing nitrogen atmosphere for the PVC sample irradiated to 52 Mrad are included for comparison. The time marked on the abscissa includes warm-up from 25°C. Any initial weight loss which occurs during the heating of the sample up to 150°C, preceding isothermal TG, is recorded in Figure 1.

PVC undergoes continual weight loss by the evolution of HCl.^{12,13} Initial heating to 150°C produces a weight loss in excess of 1.5%, largely independent of irradiation. Both 0- and 5.8-Mrad samples gave identical results. This may correspond to the volatilization of trapped low molecular weight impurities from synthesis. There is a trend toward an increase in initial weight loss with increasing radiation dose. We infer that the amount of trapped radiolytic HCl is increased. Less initial volatiles were noted at the highest dose (52 Mrad). Perhaps a larger fraction of radiolytic HCl escapes during the irradiation as one prolongs the period of local heating in the radiation field, at the highest dose, leaving less HCl to evolve on initial heating to 150°C. The initial weight loss is independent of atmosphere at 52 Mrad as the initial portion of the weight loss curves coincide in oxygen and nitrogen.

The overall rate of weight loss increases markedly with irradiation dose. This corresponds to a free-radical chain dehydrochlorination enhanced by the radiation-induced generation of at least two types of labile chlorine.¹³ Crosslinking by irradiation produces tertiary chloride at branch points, and radiolytic dehydrochlorination produces allyl chloride. Both struc-

tures are labile and are readily susceptible to subsequent thermal decomposition.

In an inert atmosphere, the total weight loss is reduced compared to that in oxygen. Peroxides and hydroperoxides formed by the reaction of oxygen with radical fragments from irradiation^{7,14} decompose thermally and induce additional chain dehydrochlorination. The presence of oxygen during TG facilitates decomposition as continual scavenging of transient radicals by oxygen yields labile peroxides. Radical termination by combination and disproportionation reactions are favored in the absence of oxygen, and the observed weight loss is reduced in nitrogen atmosphere.

Thermogravimetry (TG) of PVC programmed at a heating rate of 10°C/min in an oxygen atmosphere is illustrated in Figure 2. On heating to temperatures in excess of 100°C a first stage of weight loss of about 1% to 2% is observed. Major loss ensues above 150°C corresponding to the evolution of HCl. (The theoretical content of HCl is 58% by weight of the PVC molecule and is marked by arrows on the ordinate.)

The temperature dependence of weight loss decreases on further heating until a second stage of decomposition is attained over 400°C. A more complex decomposition pattern is then presented corresponding to main chain fragmentation.¹²

The incipient temperature for rapid weight loss decreases from 200° to ~160°C on irradiation. The temperature at the onset of rapid decomposition above 70% weight loss is also reduced, for example, from 429° to 413°C by irradiation to 5.8 Mrad. The rate of weight loss in this stage of decomposition (70% to 90%) is enhanced by irradiation. The temperature for the onset of final carbonization is reduced on irradiation (0–52 Mrad) from 476° to 425°C. The process is complete at ~600°C. Increasing the irradiation dose from 29 to 52 Mrad had only minor effect on thermogravimetry.

Differential thermal analysis (DTA) of the same samples of irradiated PVC was pursued in an atmosphere of flowing nitrogen and at a heating rate of 10°C/min in order to elucidate decomposition patterns. Resultant curves are shown in Figure 3 as a composite plot of the temperature difference (ΔT) between reference and standard as the ordinate with ΔT displaced for clarity. An endothermic displacement between 70° and 80°C corresponds to the glass transition and is observed in all samples. Any possible change in glass transition temperature on irradiation is very small. Thermal activity is next detected about 200°C and may correspond to the final melting of PVC crystallites. This feature is absent following irradiation at doses ≥ 17.4 Mrad. It is possible that endothermic dehydrochlorination obscures the melting endotherm. Since DTA would be less sensitive to the initial loss of hydrogen chloride than TGA, it is likely that DTA results indicate that crystalline order is destroyed by irradiation. X-Ray determinations were performed on duplicate PVC samples, and low levels of crystallinity are estimated.^{15,16} Control and PVC samples irradiated to 5.8 Mrad have well defined crystalline diffraction peaks at 2θ values of

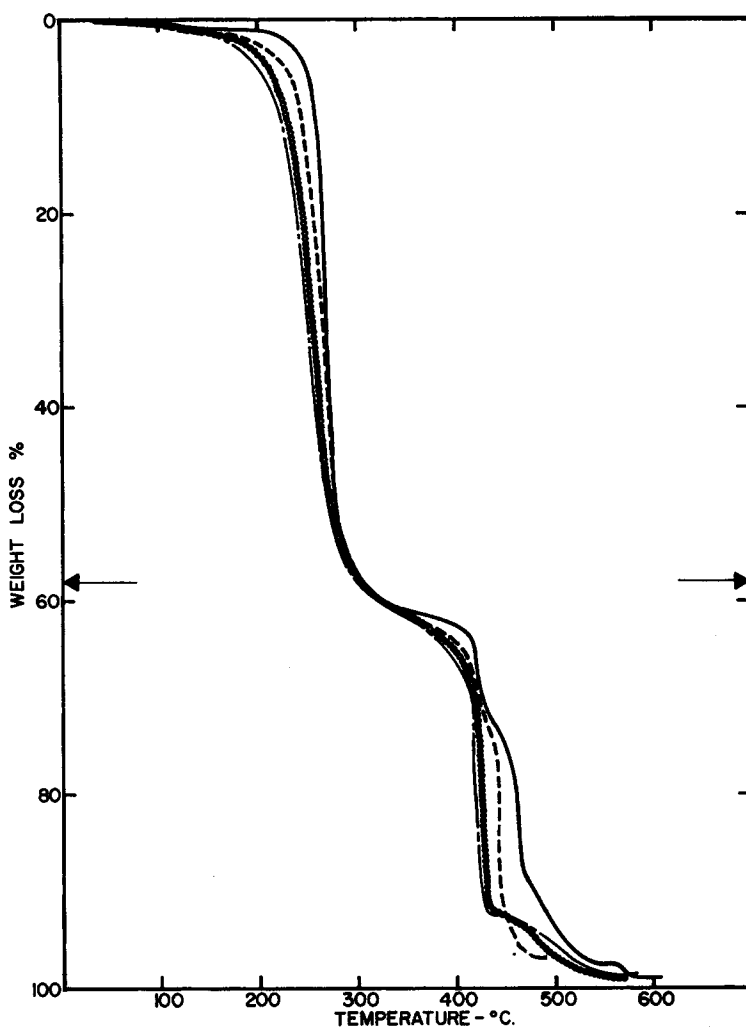


Fig. 2. Thermogravimetry of irradiated PVC—heating rate, $10^{\circ}/\text{min}$, oxygen atmosphere: (—) control; (---) 5.8 Mrad; (OOOOOOOO) 29.0 Mrad; (-·-·-) 52.2 Mrad.

17° , 19° , and 25° (corresponding to d spacings of 5.15, 4.67, and 3.65 Å), indicating crystallinities of 20% and 15%, respectively. Following 52-Mrad irradiation, no crystalline diffraction peaks are discernible.

Simultaneous effluent gas analysis (EGA) in nitrogen atmosphere is reported in Figure 4. These data are consistent with DTA of PVC in nitrogen in which the major feature is a large endotherm between 250° and 300°C assigned to dehydrochlorination. Increasing irradiation dose facilitates the evolution of HCl at low temperatures. Consequently, residual HCl is more tenaciously bound. This is consistent with a previous suggestion

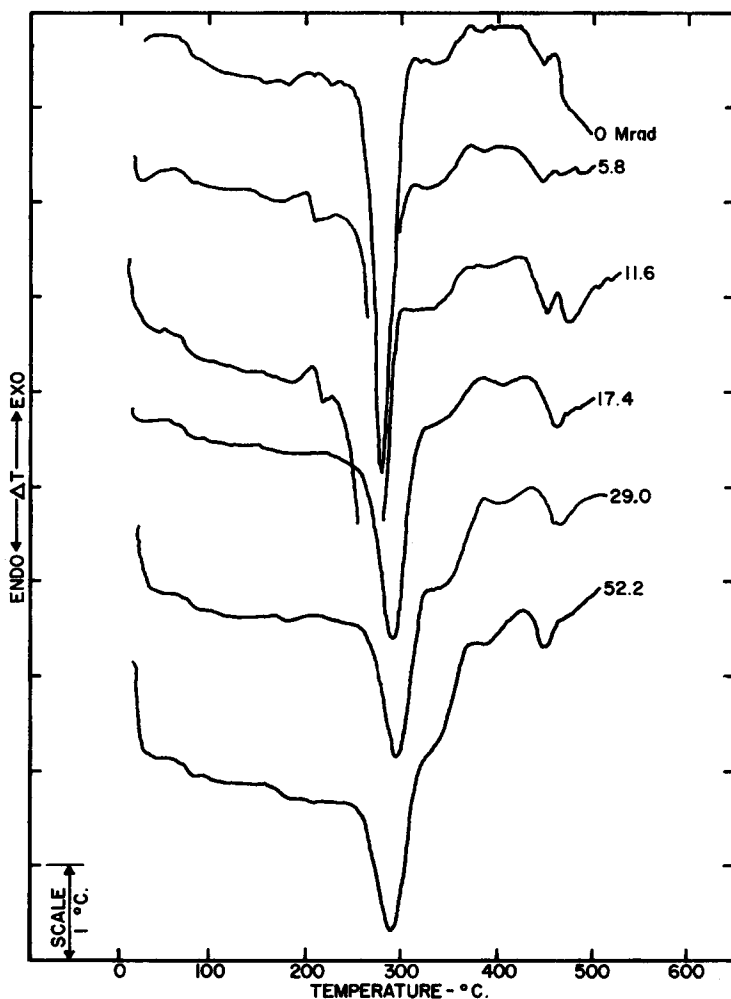


Fig. 3. Differential thermal analysis of irradiated PVC: heating rate, $10^{\circ}\text{C}/\text{min}$; nitrogen atmosphere.

that increasing irradiation dose facilitates the evolution of HCl during irradiation.

Analogous to Figure 3, a composite plot of DTA in flowing oxygen is shown in Figure 5. Again, the curves are displaced for clarity. Thermometric patterns are considerably affected by the presence of oxygen during heating. An endothermic displacement associated with the glass transition at $\sim 75^{\circ}\text{C}$ in unirradiated PVC becomes less prominent with increasing dose. This appears to be a real effect and will be subsequently studied. Further heating reveals a peak at 200°C associated with crystalline melting. This is not observed at doses in excess of 17.4 Mrad. Crystalline melting is observed in the 17.4-Mrad sample heated in oxygen but not in nitrogen.

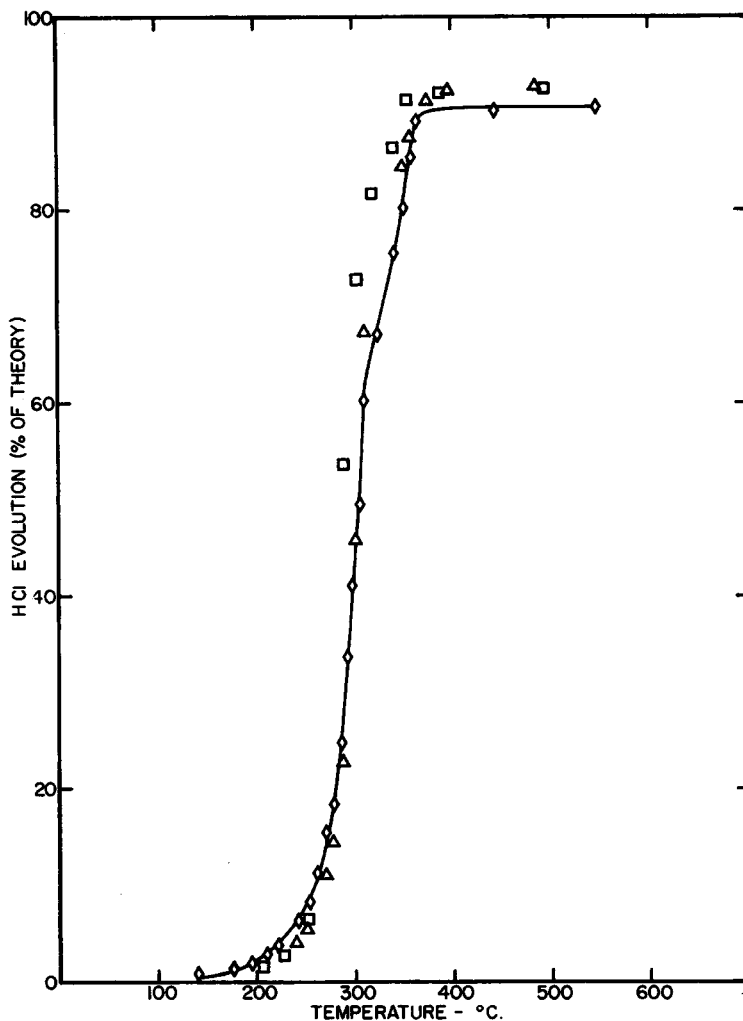


Fig. 4. Effluent gas analysis of irradiated PVC: heating rate, $10^{\circ}/\text{min}$; nitrogen atmosphere; (\square) 5.8 Mrad; (\triangle) 17.4 Mrad; ($-\diamond-$) 29.0 Mrad.

This may be due to greater chain scission occurring on heating in oxygen. The scission induced crystallization of high molecular weight poly(tetrafluoroethylene) has been reported.¹⁷

A huge exotherm is observed in Figure 5 between 200° and 300°C and is absent in Figure 3. This occurs at lower temperatures with increased dose. This is associated with oxidation and may indicate the decomposition of peroxides formed on irradiation and on heating in oxygen. It is likely that at all irradiation doses endothermic dehydrochlorination is superposed on oxidation. At doses in excess of 17.4 Mrad, this endotherm is largely obscured. We suggest that the effect of irradiation is to render PVC increasingly susceptible to oxidation.

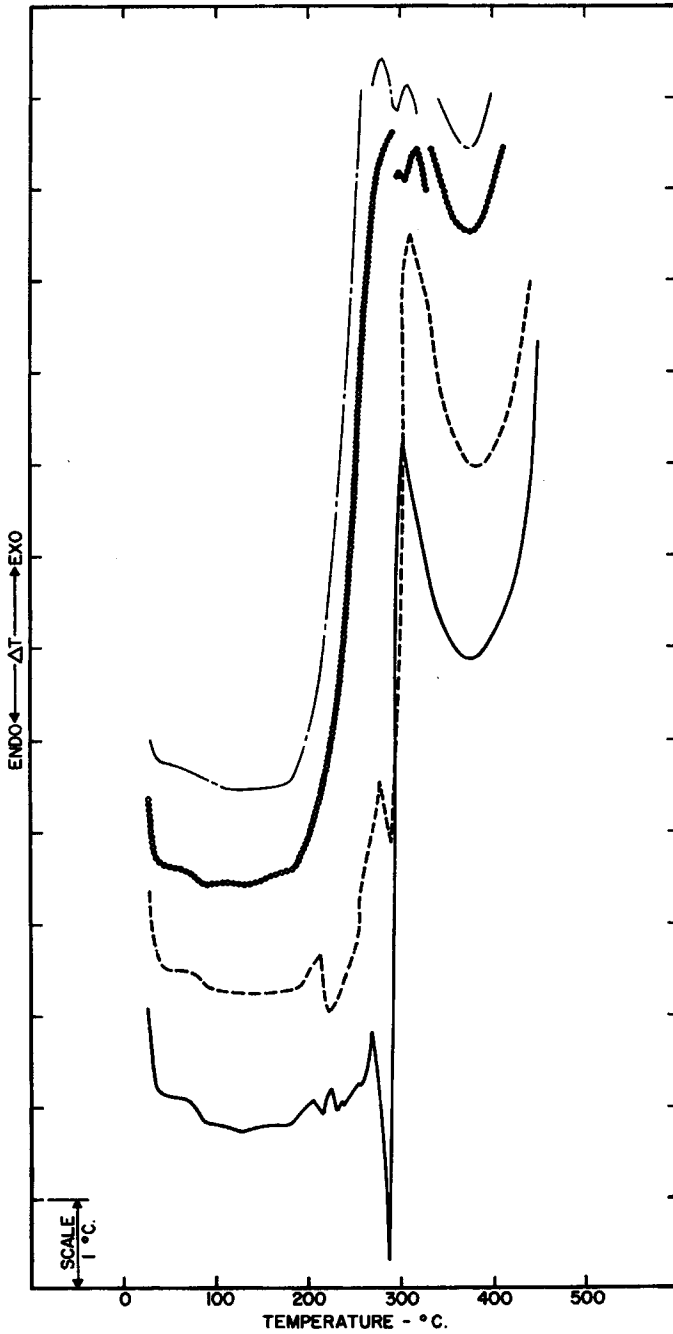


Fig. 5. Differential thermal analysis of irradiated PVC: heating rate, $10^\circ/\text{min}$; oxygen atmosphere; (—) control; (---) 5.8 Mrad; (OOOOOOOO) 29.0 Mrad; (- - - -) 52.2 Mrad.

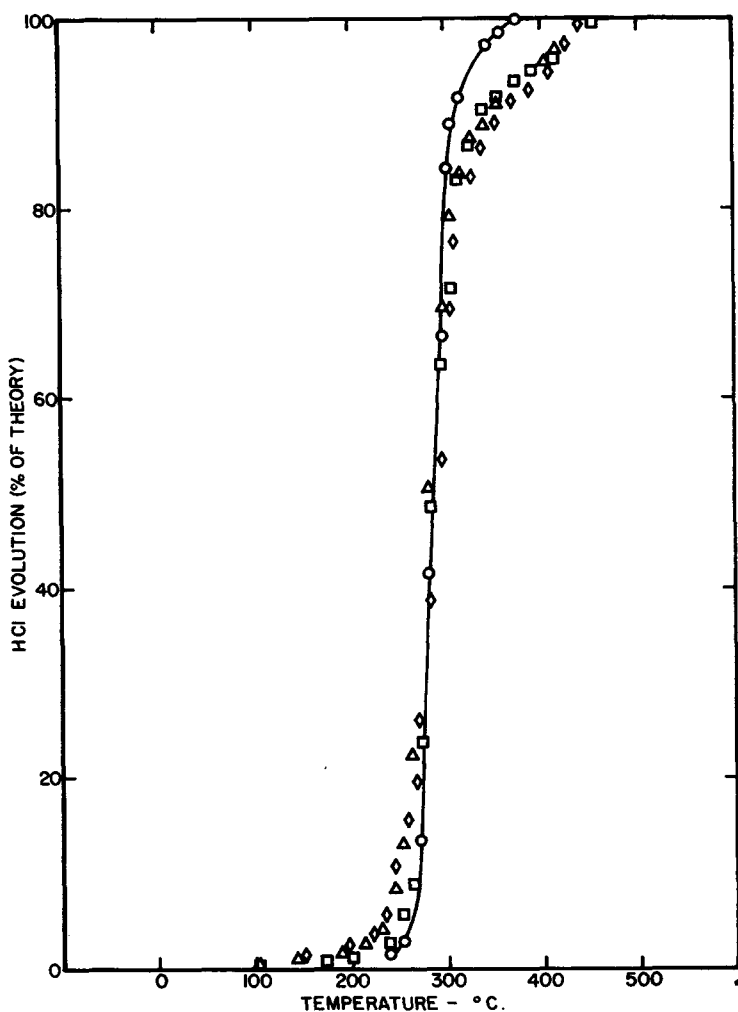


Fig. 6. Effluent gas analysis of irradiated PVC: heating rate, $10^{\circ}/\text{min}$; oxygen atmosphere; (—○—) control; (□) 5.8 Mrad; (Δ) 17.4 Mrad; (\diamond) 29.0 Mrad.

EGA of PVC in flowing oxygen is shown in Figure 6. Again dehydrochlorination observed between 250° and 300°C coincides with a calorimetric endotherm. A comparison of EGA in oxygen and nitrogen atmospheres indicates that the evolution of HCl follows a similar temperature pattern, with dehydrochlorination occurring about 15°C lower in oxygen.

CONCLUSIONS

The isothermal rate of decomposition of preirradiated PVC on heating at 150°C increases with irradiation dose and is enhanced in oxygen atmosphere. The increased thermal instability is consistent with the radiation-induced generation of labile chlorides and, in oxygen, labile peroxides.

The two major stages of thermal decay observed on programmed heating of irradiated PVC occur at reduced temperatures after irradiation. From x-ray and DTA results, it is inferred that crystalline order in PVC is lost on irradiation. Dehydrochlorination of PVC is endothermic. In oxygen atmosphere, DTA of preirradiated PVC is dominated by oxidation. The major effect of irradiation is to render PVC increasingly susceptible to oxidation.

The radiation damage appears to be nonlinear, with maximal effect at lower doses. Low-temperature fine structure in DTA of irradiated PVC will be elaborated further.

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