Thermal Analysis of Poly (vinyl Chloride) Fractions

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Synopsis

The thermal stability of commercial poly(vinyl chloride) and its four fractions having different intrinsic viscosities (1.152–0.397 dl/g) has been investigated thermogravimetrically in the presence of atmospheric oxygen, up to a temperature of 400°C, by using the nonisothermal technique. The results indicate that the thermal stability of the polymer is inversely proportional to its intrinsic viscosity. The kinetic parameters have been evaluated for the early stages of decomposition (2% to 20%). The results have been explained on the basis of different structures of the polymer chain in fractions of high and low intrinsic viscosity.

INTRODUCTION

Studies with model compounds have indicated that the poly(vinyl chloride) (PVC) backbone is intrinsically stable.[1] It has been suggested[2] that the dehydrochlorination of poly(vinyl chloride) is initiated from some weak sites in the polymer chain. The weak sites may be the tertiary chlorine or allyl-type chlorine or the catalyst fragments present at the chain ends. The terminal double bonds in PVC are introduced as a result of chain transfer reactions.[3] Investigations with different molecular weight samples of PVC can help in elucidating the role of chain ends in the initiation of dehydrochlorination.

The reports in the literature regarding the thermal stability of PVC as a function of molecular weight are rather contradictory. An inverse relationship between the rate of dehydrochlorination and molecular weight has been reported.[4,5] That the rate of dehydrochlorination is independent of the molecular weight of the PVC has been suggested by other workers.[6] In the experiments mentioned above, different molecular weight samples of PVC were prepared under different reaction conditions. However, working with the fractions of commercial PVC in solution and in nitrogen atmosphere, it was found that there is no systematic dependence of dehydrochlorination on molecular weight.[7] Sato and Asahina[8] have reported that lower and higher fractions of PVC degrade faster than the middle fractions.

In this work, we have investigated the thermal degradation of PVC fractions in the presence of atmospheric oxygen by using a Stanton thermogravimetric analyzer, which is a useful device for investigating the thermal stability of polymeric materials. The sample was heated at a constant

heating rate of 6°C/min, and the weight of the test sample was auto-
matically recorded against temperature.

EXPERIMENTAL

The sample of PVC was the commercially available material (CSI make)
prepared by Calico Co. Ltd. This was fractionated by using a tetra-
hydrofuran (THF) and water system. An approximately 1% solution of
PVC in peroxide-free THF was prepared and placed in a three-necked flask
fitted with a stirrer. The temperature was maintained at 25°C by placing
the flask in a thermostat. Nitrogen was passed for some time, and then
water was added from the side inlet. The appearance of a permanent
turbidity marked the separation of the first fraction. The flask was then
transferred to a bath maintained at 40°C for $1/2$ hr. It was again flushed
with N_2 and transferred back to the bath at 25°C. The precipitated
polymer was separated after 24 hr, and the above procedure was repeated
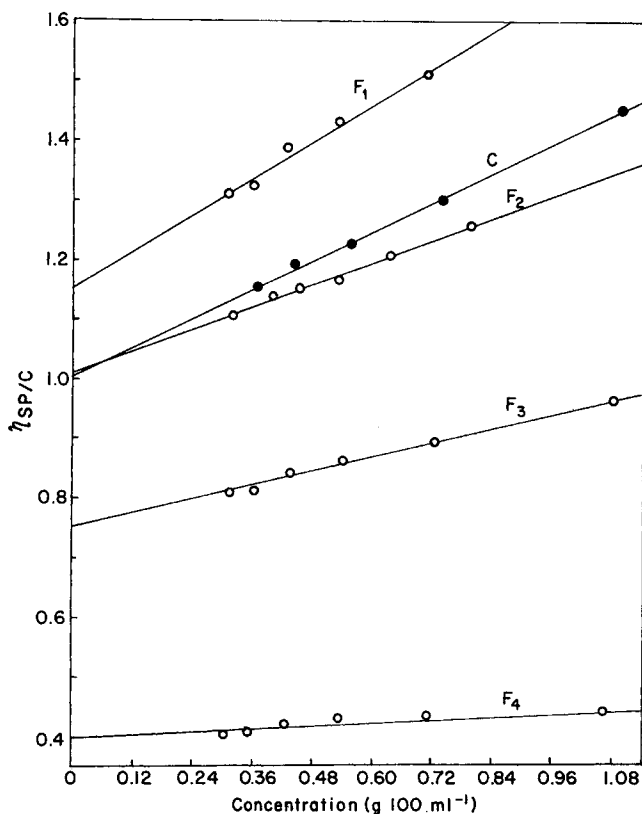with the remaining solution. In this way, seven fractions were collected.

Fig. 1. Intrinsic viscosity determination of PVC fractions (F_1, F_2, F_3, F_4) and com-
mercial precipitated polymer (C) at 30°C in cyclohexanone.

The precipitated fractions were dissolved in THF and reprecipitated using methanol.

The intrinsic viscosity of the fractions at 30°C in cyclohexanone was determined using a Ubbelohde suspension-level viscometer. After characterization, only four fractions were left in sufficient quantities for further studies (F_1, F_2, F_3, F_4). Figure 1 shows the intrinsic viscosity determination of these fractions as well as of commercial PVC (C) which had been purified by total precipitation using methanol and THF. The degradation of the samples was done using a Stanton Model HT-D thermogravimetric balance, and 27 ± 0.6 mg of the polymer sample was used.

RESULTS AND DISCUSSION

The thermograms obtained by plotting percentage residual weight versus temperature for the various fractions of PVC are shown in Figure 2. The degradations were carried out in the presence of atmospheric oxygen. Decomposition was observed to begin in almost all the fractions above
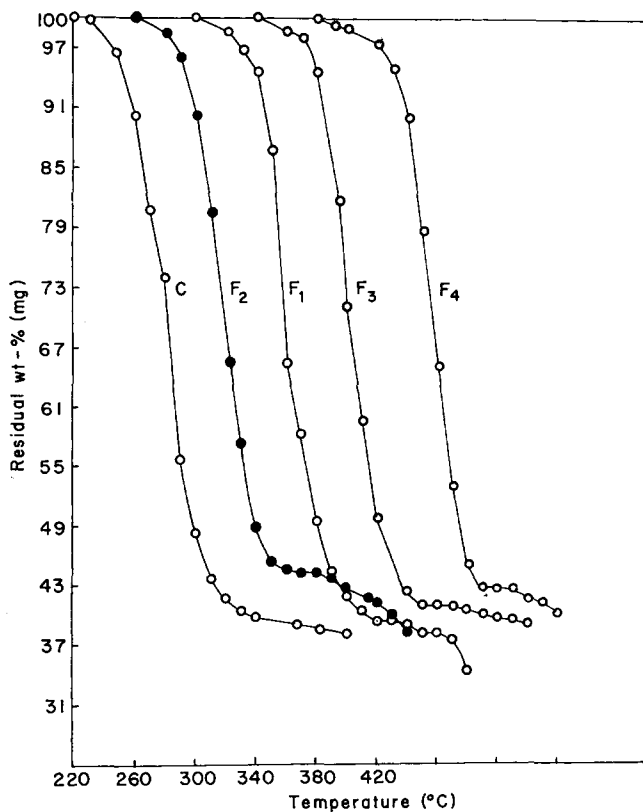

Fig. 2. Thermogravimetric curves for the degradation of various PVC fractions. Sample weight 27 ± 0.6 mg; heating rate 6°C/min. Axis has been shifted along x-axis to avoid superimposition of points.
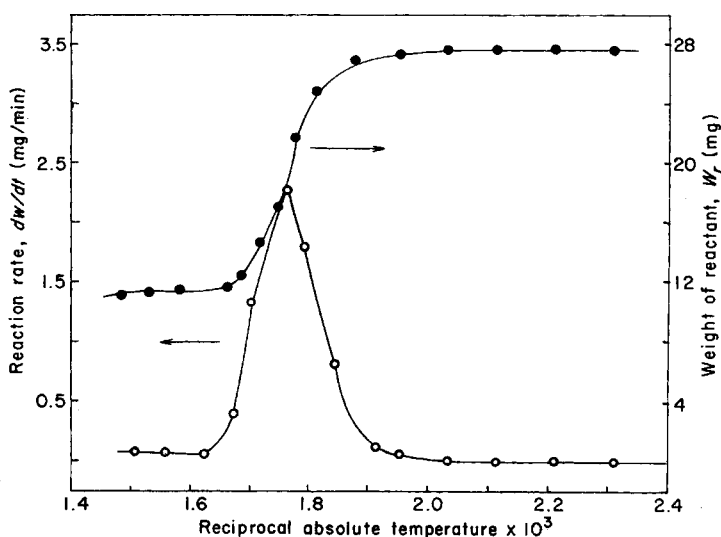
Fig. 3. Graph of reaction rate, dw/dt, and weight of reactant, W_r, as a function of reciprocal absolute temperature for degradation of PVC fraction F_4 in the presence of atmospheric oxygen.

200°C and became very rapid above 250°C. The reaction was carried up to 400°C in all the cases, and this resulted in an approximately 64% loss in weight. One should expect a 57.5% loss in weight for complete dehydrochlorination of PVC. It may be possible that oxidative scission of the polyene chain took place and that small fragments of polymer backbone were eliminated along with HCl. In the degradation of PVC under vacuum, Stromberg and co-workers[9] have reported the formation of benzene and toluene along with HCl, due to cyclization of polyene chains and subsequent scission. Thus, weight loss will be greater than that theoretically expected for dehydrochlorination. The polymer attained some stability above 300–380°C when the weight loss was very small. In some PVC fractions degradation was carried up to 550°C, when ≈ 97% loss in weight was recorded. Since above 60% conversion the decomposition would amount to decomposition of hydrocarbon chains, these results are therefore not included in the present discussion.

Figure 3 shows a typical plot of the rate of weight loss, dw/dt, in mg/min, and weight of the reactant, W_r, as functions of reciprocal absolute temperature. Similar graphs were drawn for all the PVC fractions and also for commercial PVC (C).

The relative thermal stability of various PVC fractions was evaluated with the help of these graphs by finding the temperatures at which 10%, 30%, and 50% decomposition (DT) had occurred. The temperature at which maximum rates of decomposition were observed has also been recorded. These data are given in Table I. A similar method has been used by Jeffreys[10] for finding the stability of phenolic resins.

TABLE I
Evaluation of Relative Thermal Stability of PVC Fractions

PVC sample	Intrinsic viscosity, dl/gm	10% DT, °C	30% DT, °C	50% DT, °C	Max. rate DT, °C
C[a]	1.002	260	279	297	284
F₁	1.152	261	279	291	284
F₂	1.012	260	277	298	276
F₃	0.752	268	279	300	278
F₄	0.397	277	293	313	295

[a] Commercial PVC.

Analysis of this table shows that the decomposition temperatures are inversely proportional to the intrinsic viscosity of the fractions. On this basis, sample F_4, which has the lowest intrinsic viscosity, appears to be more stable than F_1 or commercial PVC. The greater thermal stability of low molecular weight fractions of PVC can be explained by a difference in the structure of high molecular weight and low molecular weight polymers.
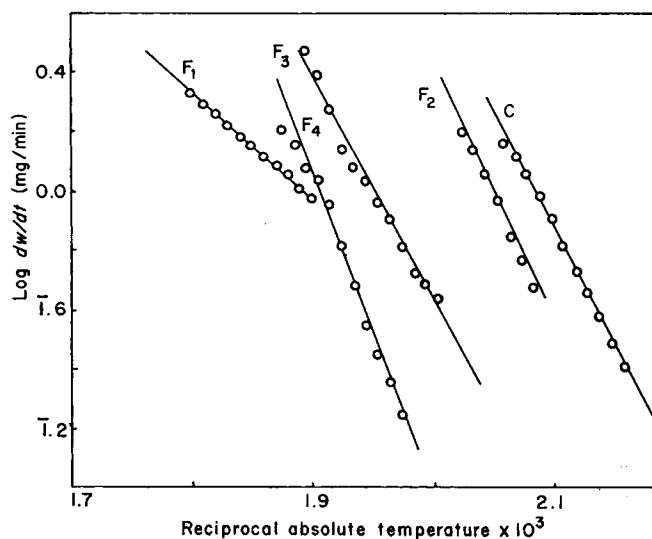

Fig. 4. Temperature dependency plot of the thermal degradation of PVC fractions for the early stages of reactions. Conversion for C, F_2, and F_3, $\approx$ 2–16%; for F_1, 5–20%; and for F_4, 2–12%. Axis has been shifted along the temperature axis to avoid superimposition of points.

A high molecular weight material may have more branches due to chain transfer reaction with the polymer during polymerization, and thus the proportion of tertiary chlorine and allylic chlorine will be greater in this case.[7] A low molecular weight material may consist of a linear polymer chain. Thus, it can be said that the thermal stability of PVC does not
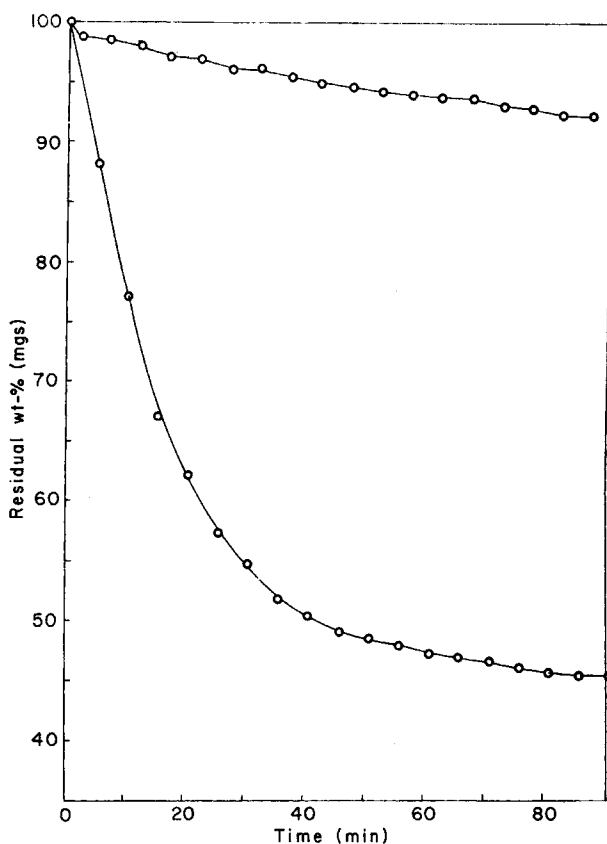
Fig. 5. Thermogravimetric curves for the degradation of PVC fraction F_4 at 210°C and 250°C.

necessarily depend on the molecular weight, but is dependent on the structure of the polymer chain.

An attempt was made to calculate activation energy by the method of Anderson and Freeman[11] between 2% and 20% conversion by plotting $\Delta\log dw/dt$ values as a function of $\Delta\log W_r$ at equally spaced intervals of $1/T$. Because there was considerable scatter in the plot, accurate evaluation of kinetic parameters was not possible.

The temperature dependency plot for the low-stage decomposition of PVC fractions, shown in Figure 4, indicates zero-order kinetics. The activation energy was calculated from the slope of the lines and is reported in Table II. The activation energy for sample F_4 was also determined by isothermal method, i.e., by carrying the degradation of 26 mg of sample at two different temperatures (Fig. 5) and following the weight loss with the thermogravimetric balance. A value of 46 kcal/mole was obtained by this isothermal procedure. The value is very similar to the value obtained by nonisothermal technique.

TABLE II
Energy of Activation for the Decomposition of PVC Fractions[a]

Sample	Activation energy, kcal/mole
C	35
F_1	17
F_2	40
F_3	35
F_4	48

[a] Conversions 2% to 20%; C = commercial PVC.

The values of the activation energy thus obtained, with the exception of F_1 and F_3, are higher than those reported earlier in the literature.[5,9,12] The decomposition carried out by those workers was done either under vacuum or in inert atmosphere. In our experiments, the atmospheric oxygen may have played a role in the oxidation of the olefinic chain. This reaction may have a higher energy, and so the value measured by our method will have contributions of both dehydrochlorination as well as oxidative chain scission reactions and will therefore be higher. However, more work on the decomposition of PVC in inert atmosphere is necessary to elucidate this point. There is also a variation in the values of the activation energy among the various PVC fractions which is a bit difficult to explain. It may be possible that oxidative chain scission reactions which may be responsible for high activation energy are more frequent in cases of low molecular weight fractions than in the high molecular weight material.

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