

Investigations on Thermal Dehydrochlorination of Poly(vinyl Chloride)

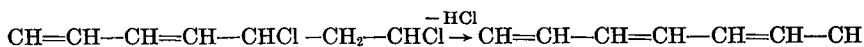
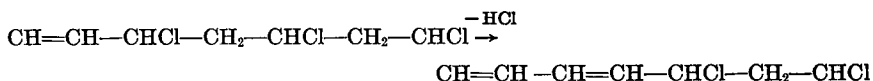
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Synopsis

The thermal dehydrochlorination of PVC has been examined on some samples prepared by fractionation of a commercial PVC, and some other samples obtained by polymerization at different temperatures. The results disagree with the concept of a continuous dehydrochlorination from one side to the other of the chain, that necessitates initiating structural anomalies in the macromolecule itself.

INTRODUCTION

In a widely accepted theory of decomposition of poly(vinyl chloride), the main sources of instability are envisaged in the terminal double bonds and in the tertiary chlorides arising during the polymerization from the reactions of termination by disproportionation and of chain transfer to monomer and polymer.¹⁻³ Starting from these weak points the dehydrochlorination reaction proceeds, zipperlike, along the polymer chain as follows:



the loss of every HCl molecule leaving a new double bond next to a chlorine atom (allylic chlorine) and thus restoring a configuration analogous to the previous one, i.e., with a weak point.

Poly(vinyl chloride) samples of different number-average molecular weight, such as those obtained by fractionation of the polymers prepared at the usual temperatures, have to be considered as carrying different amounts of terminal double bonds.⁴

The polymerization of vinyl chloride at different temperatures was found to produce polymers with different degrees of branching, the latter almost disappearing at very low temperatures.⁵ Since formation of the branches implies formation of tertiary chlorides, the amount of this type of weak point should vary accordingly. Naturally also the number

of chain ends and the fraction of these chain ends carrying a double bond vary in these polymers, because of the dependence on temperature of the molecular weight and of the chain transfer reaction.

Morover, as the temperature is lowered well below room temperature modification in stereoregularity takes place⁶ which also may affect the thermal stability of the poly(vinyl chloride).

In this work, the dehydrochlorination kinetics of fractions of different number-average molecular weight and of polymers prepared at different temperatures were determined for the purpose of testing the validity of the above views.

EXPERIMENTAL

Preparation of Samples

Commercial poly(vinyl chloride) was fractionated into eleven fractions by means of the usual fractional precipitation procedure with the tetrahydrofuran-water system. Eight fractions were retained and employed in the dehydrochlorination experiments without further purification.

Alternatively, vinyl chloride was polymerized in bulk at the following temperatures: +25, 0, -20, -40, -60, and -78°C. with the system $B(n-C_4H_9)_3(0.5\%)/O_2(0.07\%)$ as initiator. All the polymers were purified by dissolution in cyclohexanone and precipitation with methanol. Some of the polymers, specifically those prepared at not too low temperature for which such a procedure was possible, were further purified by dissolution in tetrahydrofuran and precipitation with water. Finally all the polymers were dried under vacuum at 60°C.

Determination of Molecular Weight

In all the determinations, viscosity measurements were made. For the unfractionated polymers the number-average molecular weight was determined by using the equation of Danusso et al.:⁷

$$[\eta] = 2.4 \times 10^{-5} \bar{M}_n^{0.77}$$

which holds at 25°C. with cyclohexanone as solvent. With the fractions we adopted the equation

$$[\eta] = 0.89 \times 10^{-5} \bar{M}^{0.89}$$

which we calculated by means of the least square method from the data reported by Krasovec,⁸ Batzer,⁹ and Staudinger¹⁰ at 25°C. in tetrahydrofuran solution.

Determination of Stereoregularity

The stereoregularity of some of the polymers prepared at low temperatures was measured as suggested by Fordham⁶ by determining the ratio between the absorbencies of the infrared bands at 635 and 692 cm^{-1} ,

which refer to the syndiotactic and isotactic structures of the polymer chain, respectively. For the measurements, films obtained by dissolving the polymers in cyclohexanone and evaporating the solvent were employed.

Dehydrochlorination

The dehydrochlorination runs were carried out *in vacuo* in the temperature range 193–233°C. a glass apparatus and a metal mass thermostat, regulated to $\pm 1^\circ\text{C}$. being used. The evolution of gaseous products from the samples in the solid state was followed by measuring at constant volume and temperature the pressure increase by means of a mercury pressure gauge. Since the gaseous products can be safely assumed to be only hydrogen chloride, the pressure data could be converted readily into fractions of degraded monomeric units.

To allow the reaction to occur constantly *in vacuo*, the hydrogen chloride as evolved was collected into a liquid nitrogen trap connected to the heated cell through a vacuum tap. The readings were made at intervals, after the vacuum tap had been closed and the trap had been brought up to the room temperature. In all of the runs, the system was continuously evacuated by means of a diffusion pump for several hours before the introduction of the sample cell into the thermostat and for 10 min. after, to ensure the removal of gases and volatile substances. In this way the initially split off hydrogen chloride was lost and accordingly all the dehydrochlorination curves begin at a value of 10 min. instead of at the origin of the graph.

RESULTS

The dehydrochlorination runs with the eight fractions of poly(vinylchloride) were made at 220°C. The results are shown in Figure 1, in which the dehydrochlorination reaction extent is plotted against time. Most of the curves almost coincide, except those corresponding to the low molecular weight samples, which gradually depart from the others and exhibit an increasing upward curvature as the molecular weight lowers. The dehydrochlorination rates could be calculated, in every case, by the initial slopes, and are reported in Table I, together with the intrinsic viscosity and the molecular weight calculated by the latter.

The dehydrochlorinations of the polymers prepared at different temperatures were carried out at 193, 213, and 233°C. The results are shown in Figures 2, 3, and 4, respectively, in which the reaction extent-time curves are shifted an equal distance along the y -axis, for the sake of clarity, since they were nearly equal in all cases. Except for the initial portion, all the curves are straight lines and thus the dehydrochlorination rates could be readily determined. All these rate values are summarized in Table II, where the molecular weight and absorbency ratio between the 635 and 692 cm^{-1} bands are also recorded; the latter however are not determined for all the polymers.

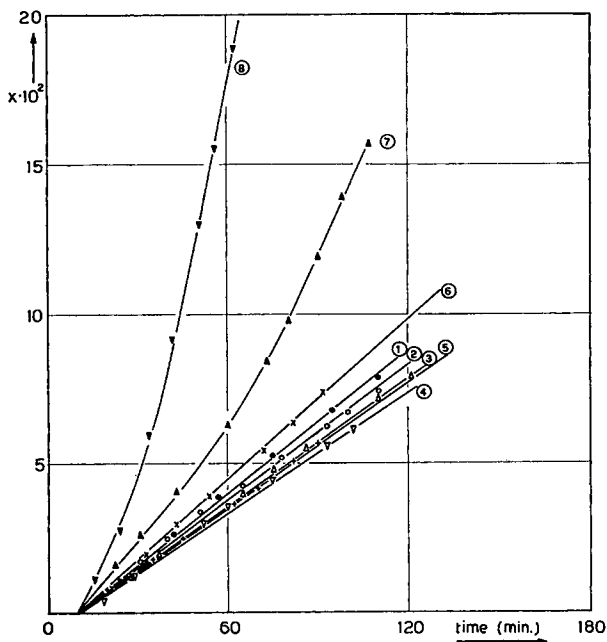


Fig. 1. Curves of extent of hydrochlorination vs. time under vacuum at 220°C. for the eight poly(vinyl chloride) fractions of Table I.

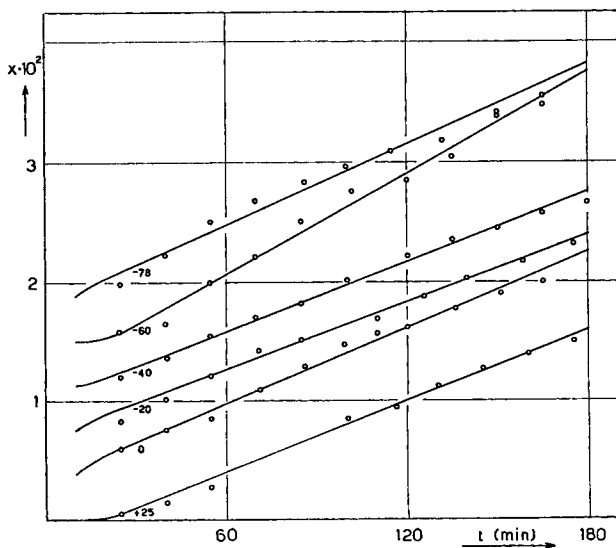


Fig. 2. Curves of extent of dehydrochlorination vs. time under vacuum at 193°C. for the polymers of Table II.

The measurement of the dehydrochlorination rates, performed in heterogeneous phase, is not to be considered very accurate, and in this case the difficulty of the purification must be added, since the polymers prepared at very low temperatures require prolonged heating for the

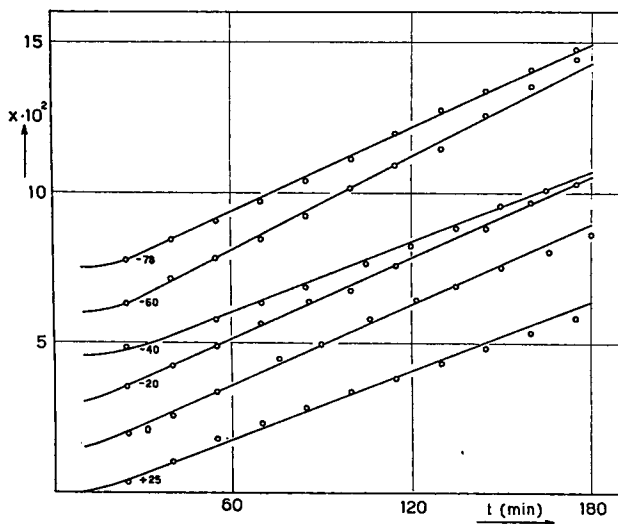


Fig. 3. Curves of extent of dehydrochlorination vs. time under vacuum at 213°C. for the polymers of Table II.

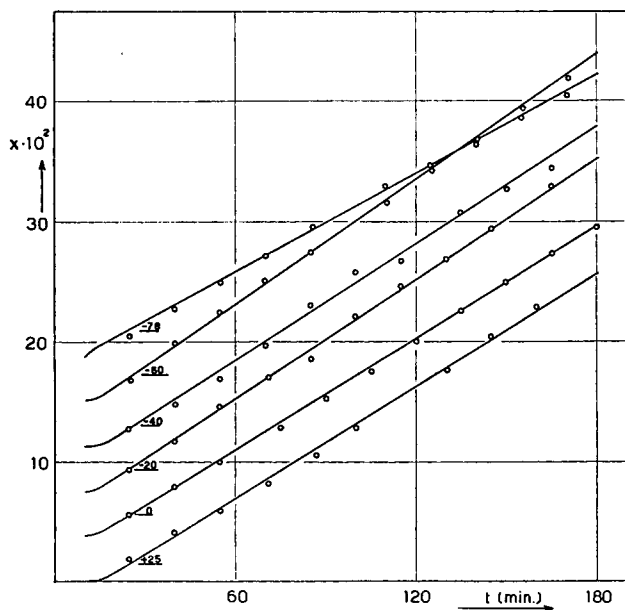


Fig. 4. Curves of extent of dehydrochlorination vs. time under vacuum at 233°C. for polymers of Table II.

TABLE I
Intrinsic Viscosity, Molecular Weight, and Dehydrochlorination Rates at 220°C. of the Poly(Vinyl Chloride) Fractions

Fractions	$[\eta]$, l./g.	Molecular weight	$\Delta X/\Delta t \times 10^6$, sec. ⁻¹
1	0.132	90,000	12.8
2	0.122	82,000	12.2
3	0.107	70,000	11.6
4	0.095	61,000	10.5
5	0.083	52,000	11.4
6	0.075	46,000	15.0
7	0.057	33,500	20.0
8	0.038	21,000	33.3

TABLE II
Number-Average Molecular Weights, Absorbency Ratios of the 635 and 692 cm.⁻¹ Bands and Dehydrochlorination Rates of the Polymers Prepared at Various Temperatures

Polymerization temperature of the samples, °C.	\bar{M}_n	A_{635}/A_{692}	Dehydrochlorination rates $\Delta X/\Delta t \times 10^6$, sec. ⁻¹		
			193°C.	213°C.	233°C.
+25	55,000	1.79	1.66	6.42	26.2
0	95,000		1.78	7.40	26.0
-20	142,000	2.05	1.56	7.48	27.8
-40	136,000	2.21	1.61	6.50	27.2
-60	93,000		2.33	8.50	29.0
-78	79,000		1.87	7.78	22.7
		Average	1.80	7.34	26.5

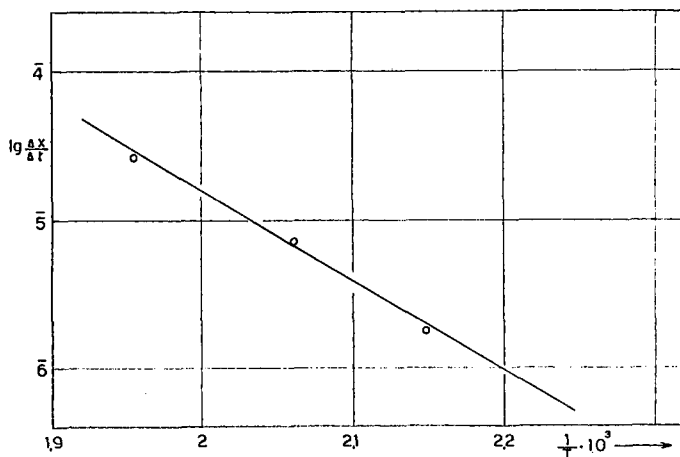


Fig. 5. Logarithm of the average dehydrochlorination rate for the polymers of Table II versus reciprocal temperature. $E_a = 28$ kcal.

dissolution in cyclohexanone. This was particularly true for the polymer prepared at -60°C . Therefore the discrepancy observed in the rate values is rather to be ascribed to the above considerations than to an actual difference in the thermal stability level. Thus it seemed a justifiable procedure to derive the activation energy from the average values at the three experimental temperatures, and from the Arrhenius plot (Fig. 5) a value of 28 kcal. was obtained.

DISCUSSION

In a polymer molecule the chain ends differ in nature from the internal structural units, since they are composed of the initiator residues and of other groupings arising, during polymerization, from disproportionation termination and chain transfer, the relative amount of each type, naturally, depending on the extent to which the corresponding reaction occurs.

The influence of chain ends on poly(vinyl chloride) thermal stability, as it appears from the dehydrochlorination experiments with the eight fractions of Table I, which cover a wide range of molecular weights, is to be considered negligible so far as their concentration is lower than a rather high value, but with higher concentrations it becomes more and more important.

With polymers which are prepared at several temperatures and which contain chain ends in concentration, according to the previous data, too low to affect thermal stability (see the molecular weight column in Table II), only those effects related to the increase of stereoregularity (Table II) and decrease of the degree of branching, with decreasing polymerization temperature, are conceivably to be expected.

Because of their low concentration, it must also be disregarded that the chain ends are of several types, the proportion of which varies with temperature (since the processes involved in their formation are characterized by different activation energies), and that an unequal importance with respect to thermal stability, is assigned to the various types by the proposed dehydrochlorination mechanism.

From the results shown in Figures 2-4 no indication is given of an influence by the stereoregularity and, more important, by the tertiary chlorides (at least in the range of values involved in the polymers under test). Also the discoloration was very nearly the same in all cases after a degradation of 3 hr. for each of the dehydrochlorination temperatures.

As to the reliability of the data here obtained, it must be mentioned that, in a preliminary work, normal poly(vinyl chloride) obtained suspension polymerization at 50°C . gave the same dehydrochlorination rates as in Table II, which it may be noted, are in fair agreement with the values quoted in the literature.¹¹⁻¹³ Obviously, the same can be said of the activation energy value resulting from the plot of Figure 5.

In conclusion, all the experimental evidence obtained in the course of this work is not in favor of the zipper dehydrochlorination mechanism,

starting from the so-called weak points of the polymer molecule. The tertiary chlorides, the actual existence of which is only inferred by the occurrence of branching, do not affect thermal stability. The chain ends, which among other things comprise initiator residues and terminal double bonds, the other points from which dehydrochlorination is assumed to initiate, do show an influence on the dehydrochlorination kinetics only at relatively high concentration and where its features are difficult to explain. As to the respective contributions, we are of the opinion that most of the effects, if not all, are not to be ascribed to the terminal double bonds, since we have observed an analogous kinetic behavior with unpurified poly(vinyl chloride) polymers containing impurities similar in type to the initiator residues.

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Résumé

On a étudié la déshydrochloration thermique du chlorure de polyvinyle sur des échantillons, d'une part obtenus par fractionnement d'un PVC commercial, d'autre part préparés à diverses températures de polymérisation. Les résultats ne s'accordent pas avec le concept d'une déshydrochloration continue d'un groupe à l'autre, qui nécessite des anomalies de structure dans la macromolécule comme points d'armorage.

Zusammenfassung

Es wurde die thermische Chlorwasserstoffabspaltung aus Fraktionen eines technischen PVC und aus einigen bei verschiedenen Temperaturen hergestellten PVC-Polymerisaten untersucht. Die Ergebnisse stimmen nicht mit einem Zipper-Mechanismus der Chlorwasserstoffabspaltung überein, der strukturelle Unregelmäßigkeiten in der Makromolekel als Ausgangspunkte verlangt.

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