

On the Thermal Degradation of Poly(vinyl Chloride). I. An Apparatus for Investigation of Early Stages of Thermal Degradation

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Synopsis

A dehydrochlorination apparatus is described for studies of the early stages of the thermal degradation of poly(vinyl chloride) (PVC), combining good reproducibility, high accuracy, and a low detection limit. The evolved hydrogen chloride is absorbed in water and the electrical conductivity is continuously recorded. Measurements of the rate of dehydrochlorination repeated over an extended period of time showed a standard deviation of 2% of the mean value. The activation energies for the dehydrochlorination in nitrogen for two commercial suspension-polymerized samples were found to be 27.9 ± 1.5 and 26.2 ± 0.6 kcal/mole.

INTRODUCTION

If PVC were a polymer consisting of vinyl chloride units linked together in an unbranched chain, it ought to be resistant to temperatures exceeding 200°C. The degradation starts, however, already at about 120°C. This has been suggested to be due to the presence of irregular structures of lower thermal stability, such as different types of unsaturated groups and structures with tertiary chlorine atoms.^{1,2} So far, the relative contribution of these structural anomalies to the instability of the polymer has not been elucidated.

In order to improve the thermal stability of the polymer and to develop more efficient heat stabilizers, one needs a better knowledge of the initial stages of thermal degradation of PVC. Therefore, it has been our aim to construct an improved dehydrochlorination apparatus which combines quick response, high sensitivity, and good reproducibility.

EXPERIMENTAL METHODS

The effect of thermal degradation of PVC may be followed by studies of the remaining polymer or by analyses of the volatile decomposition products. The former procedure includes analyses by spectroscopy, gas chromatography, and measurement of evolved hydrogen chloride.

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At temperatures below 220°C, hydrogen chloride is the only volatile decomposition product. When studying PVC degradation within this temperature range, measurement of evolved hydrogen chloride is a simple and accurate method. The amount of hydrogen chloride evolved compared to the total amount available is usually called the degree of dehydrochlorination or the conversion. It is denoted by x and expressed in percentages. An intermittent titration of absorbed hydrogen chloride (in water) by alkali was one of the first methods used.³⁻⁷ Later, other titration procedures were utilized. They include titration on chloride ions according to Mohr⁸ or Volhard⁹ and potentiometric titration using silver nitrate.¹⁰⁻¹³ Such analyzing systems with detection limits about 10⁻²% have been reported.

Compared with titration, pH measurement is much more sensitive and versatile. This method has frequently been used.¹⁴⁻¹⁹ A detection limit of 10⁻⁴% has been claimed,¹⁴ but in that case no correction for activity coefficients or carbon dioxide absorption was applied. Conductometric measurements are more reliable and at least as sensitive as pH measurements.²⁰⁻²⁴ Recently, Guyot has developed a differential technique resulting in higher stability and precision.²⁰ Using a sensitive conductometric measuring system and a special dehydrochlorination apparatus, we have reached a detection limit of 10⁻⁴% even with 0.1-g samples.

Apparatus Design

Besides high sensitivity of the hydrogen chloride detector, a properly constructed reaction vessel is necessary for studies of the early stages of the degradation. Long loading time, large dead volumes, and unsatisfactory temperature control have often contributed to unacceptably long times of reaching temperature equilibrium. Apparent induction periods of 10-30 min have frequently been reported. During dehydrochlorination in nitrogen at 180°C, this will result in a conversion of 0.1-0.2% before equilibrium is attained.

These facts were taken into account in the design of the dehydrochlorination apparatus shown in Figure 1. To avoid the undesirable effect of metals on PVC degradation, it was constructed entirely from glass. The lower part of the reaction vessel is immersed in a thermostat containing polyethylene glycol. The latter is covered by a brass plate, f , to which the reaction vessel is attached. The upper part of the reaction vessel can be removed. It is carefully protected from heat loss by a thick asbestos insulation layer, d , and an internal heating jacket, j . Through this jacket hot polyethylene glycol is circulated. The fluid is pumped from the bath through a Viton rubber tube and a glass coil immersed in the bath. It then enters into the jacket at g . The fluid returns via another Viton rubber tube connected at b (compare d in Fig. 2).

Although the upper part of the reactor is insulated, a heating jacket has been found to be essential in order to maintain temperature equilibrium. Without this arrangement, the reactor temperature was about 7°C lower

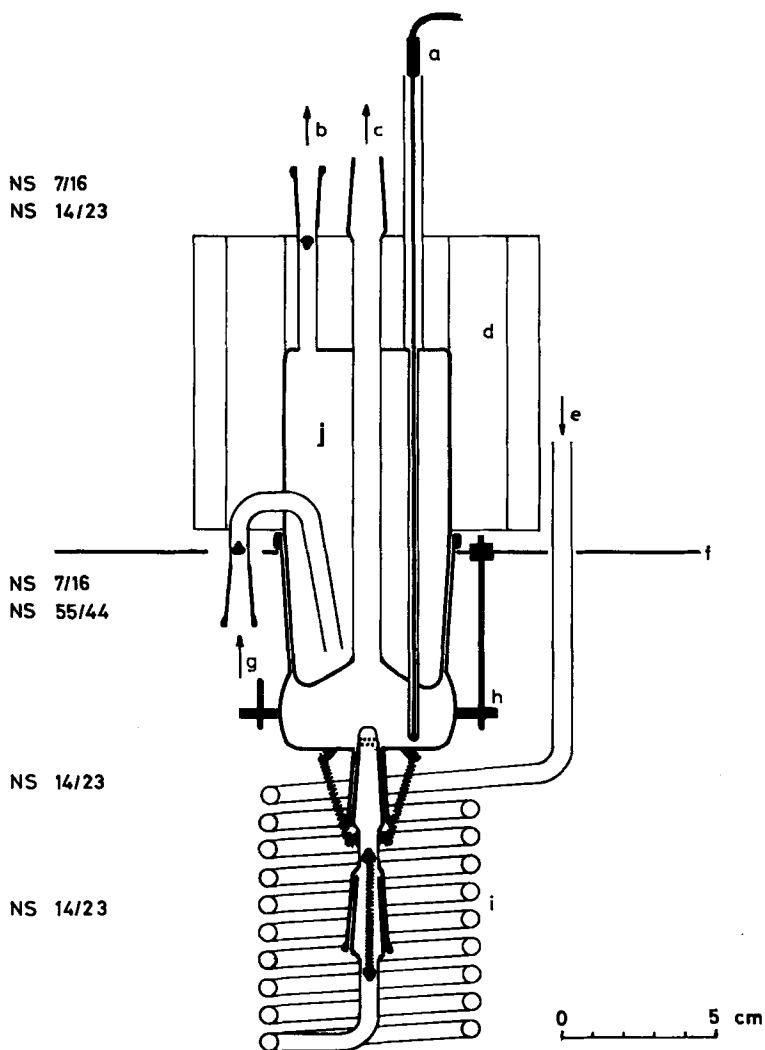


Fig. 1. Reaction vessel for PVC dehydrochlorination measurements: (a) thermocouple; (b) polyethylene glycol outlet; (c) carrier gas outlet; (d) asbestos insulation; (e) carrier gas inlet; (f) brass plate covering the thermostat; (g) polyethylene glycol inlet; (h) reaction vessel holder; (i) glass coil for preheating the carrier gas; (j) heating jacket.

than the bath temperature. When the heating jacket was used, this difference was limited to about 1.5°C . These values also include the temperature drop through the two glass walls between the bath and the thermocouple.

The carrier gas is preheated in a glass coil, *i*, and is then introduced into the reaction vessel via perforations in the bottom. The hydrogen chloride evolved is carried away by the gas stream and leaves the system at *c*. The reaction temperature is measured by an iron-Constantan thermo-

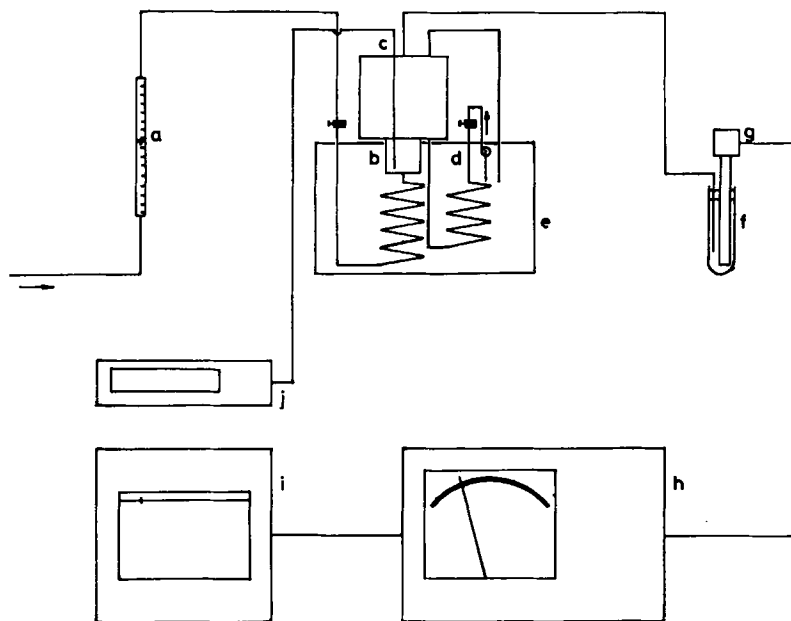


Fig. 2. Apparatus assembly: (a) rotameter; (b) lower part of the reaction vessel; (c) thermocouple; (d) heat exchanger connected to upper part of reaction vessel; (e) thermostat; (f) conductivity measuring cell; (g) probe; (h) conductivity meter; (i) recorder; (j) digital volt meter.

couple, *a*, placed in a glass pocket, which ends just above the polymer sample. All connections have been tightened by Teflon sleeves.

The reaction vessel is loaded by disconnection of the apparatus and addition of PVC powder from a weighing stick in a thin layer over the bottom of the reactor. After the desired degradation time, the powder is sucked into a round-bottomed flask and the reactor is carefully cleaned. It is also possible to use pieces of film, but in that case it is more practical to put the sample into a small platinum pan, which is then placed on the bottom of the reactor. Sample quantities of 1.0 g have been used, but 0.1 g was used for most of the experiments.

The units of the dehydrochlorination apparatus were combined as shown in Figure 2. The carrier gas flow was measured by a rotameter, Rota L1-1889, *a*. The temperature was measured by an iron-Constantan thermocouple, Termocoax TFA 15, *c*, connected with a digital volt meter, Philips digital multimeter PM 2421, *j*. A Haake thermostat type NBE with a R-20 relay was used, *e*. It was possible to maintain the set temperature within $\pm 0.2^\circ\text{C}$ with this equipment. Evolved hydrogen chloride was absorbed in a glass tube, *f*, containing 20 ml of water, and the electrical conductivity of the solution was measured by a Kemotron measuring cell, Type 20-002, *g*. The latter was connected to a conductometer with automatic temperature compensation, Tetramatic four-electrode mho-meter, *h*. The conductivity was recorded on a Philips PM 8100 recorder, *i*.

Sources of Error

When determining conversion and degradation rate, the following sources of error are possible: (1) inaccuracy in the electrical conductivity measurement; (2) incomplete absorption of hydrogen chloride; (3) the effect of carbon dioxide on the electrical conductivity of water; (4) temperature variations; (5) variable sample loading time; and (6) inaccuracy in the sample weight determination.

The conductometer has 18 different settings ranging from 10 to 4×10^6 μmho and will automatically correct for temperature variations. Concentration variations of about $10^{-7}M$ can be measured. This corresponds to a detection limit of about $10^{-4}\%$ when a 0.1-g sample is used. The measuring accuracy for the conductivity measurement was estimated at $\pm 1\%$, which includes the effect of the volatilization of water from the conductivity cell.

To check if the absorption of hydrogen chloride in water is complete, another conductivity cell was coupled in series with the ordinary one. A 100-mg PVC sample was degraded in nitrogen for 12 hr at a gas flow rate of 200 ml/min. No increase in conductivity could be observed in the second cell. Thus, no correction for incomplete absorption has been applied.

At low degrees of dehydrochlorination, the effect of absorption of carbon dioxide on the conductivity of water has to be taken into consideration. Complete absorption of carbon dioxide in water will cause a conductivity of 1.1 $\mu\text{mho/cm}$; but as the solution becomes more acidic, this contribution will decrease. pH Measurements on deionized water indicated that the conductivity was caused both by carbon dioxide absorption and by remaining inert ions. Directly after the purification by ion exchange, the conductivity of water was about 0.8 $\mu\text{mho/cm}$, but it gradually increased to more than 1 μmho . A representative value for the water used was 1.4 $\mu\text{mho/cm}$. For calculation of the amount of evolved hydrogen chloride, the measured conductivity thus has to be reduced by the effects of inert ions and carbon dioxide. Such corrections are often omitted but, as shown in Figure 3, this may cause nonnegligible errors even at comparatively high conversions. Figure 3 also shows that a subtraction of the conductivity of the inert ions will give satisfactory small errors at degrees of dehydrochlorination exceeding about 0.02%.

Sample loading does not take more than about 10 sec, which implicates that temperature equilibrium is attained very rapidly. At 190°C, temperature equilibrium is reached within 3–4 min, after 2 min a temperature of about 189°C is attained. To a limited degree, loading time variations will not alter the rate of dehydrochlorination but may cause a minor shift of the position of the degradation curve. After the induction period, the temperature is constant within $\pm 0.1^\circ\text{C}$. This is valid for temperatures of 200°C and lower. Temperature variations will implicate an error of about $\pm 1\%$.

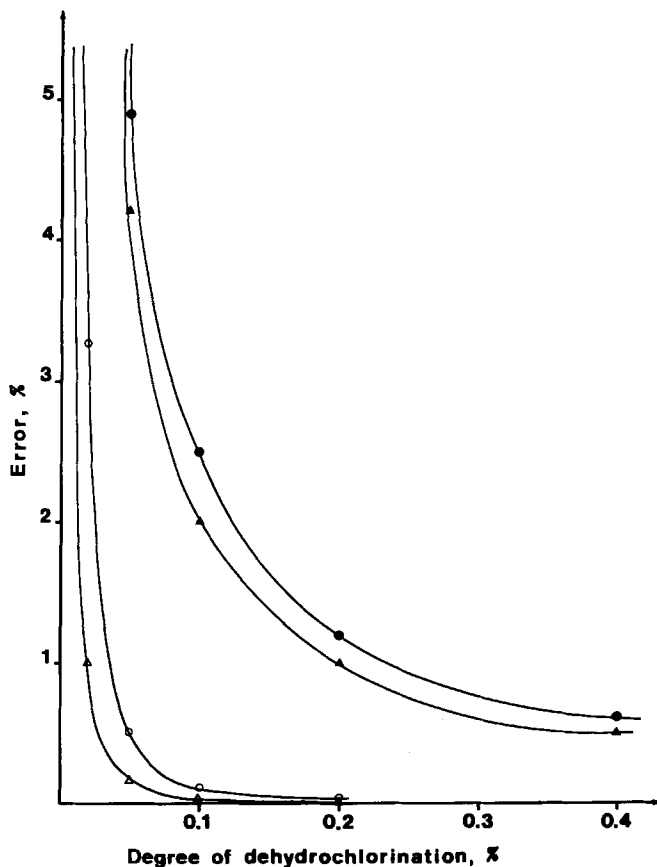


Fig. 3. Different ways to calculate the conductivity due to evolved hydrogen chloride. Resulting errors are expressed as a function of conversion. The measured conductivity has been reduced by: (●) the conductivity due to absorbed carbon dioxide according to pH measurements; (▲) the conductivity of the deionized water ($1.4 \mu\text{mho/cm}$); (○) the theoretically calculated conductivity due to quantitative absorption of ambient carbon dioxide; (△) the conductivity of inert ions.

There is always some PVC powder left in the weighing stick after loading. The remaining amount of polymer is very small, however. From a number of tests, it was estimated to be less than 0.4 mg, which corresponds to 0.4% for a 100-mg sample.

A constant deviation from the set carrier gas flow does not alter the rate of degradation, but changes the time scale with a constant value. Flow variations during a degradation test were found to be less than $\pm 1.3 \text{ ml/min}$. The effect on the rate of dehydrochlorination will be less than $\pm 0.7\%$. The accuracy of the flow rate setting was $\pm 1.3\%$.

The maximum deviations from a number of reproducibility tests are collected in Table I. The measurements were carried out in a conversion range from 0.1% to 1.0%. The sample size throughout this investigation was 0.1 g. Table II shows the experimental data from a reproducibility

TABLE I
Maximum Deviations Calculated at Different Reproducibility Tests

Sample	Degradation temp., °C	Degradation atmosphere	Number of tests	Rate of dehydrochlorination, maximum deviation, %	Calculated maximum deviation, %	Test period, days
Pevikon R-341	180	Nitrogen	3	±1.9	±3.2	4
Pevikon R-45	190	Air	4	±1.4	±3.2	2
Pevikon R-45	190	Nitrogen	4	±3.2	±3.4	25
Pevikon R-45	190	Nitrogen	7	±1.9	±2.0	2
Pevikon R-45	190	Nitrogen	11	±4.0	±4.7	100

TABLE II
Rates of Dehydrochlorination Obtained from Repeated Measurements of Pevikon R-45 at 190°C in Nitrogen

Rate of dehydrochlorination, %·min ⁻¹	
0.0191	0.0202
0.0189	0.0196
0.0199	0.0197
0.0202	0.0196
0.0195	0.0195

Ave. 0.0196

Standard deviation = 0.0004
or 2% of mean

test extended over three months. The rates of dehydrochlorination were determined from measurements on Pevikon R-45 at 190°C in nitrogen.

Materials

Two commercial PVC qualities have been tested. They were generously supplied by KemaNord AB, Sweden. Pevikon R-45 ($\bar{M}_n = 49,000$; $\bar{M}_w = 113,000$) was used without further purification (see next paragraph). Pevikon R-341 ($\bar{M}_n = 48,000$; $\bar{M}_w = 114,000$) was precipitated before use: 20 g PVC was dissolved in 1 l. peroxide-free tetrahydrofuran (THF), freshly distilled. The solution was kept in dark overnight under inert atmosphere. The polymer solution was poured into methanol (puriss). The precipitated polymer was filtered off, thoroughly washed with methanol, and left to dry in air. The polymer lumps were crushed and sieved.

For both polymers, a 0.200–0.315 mm fraction was used. The samples were stored under vacuum for at least 24 hr before use.

The Effect of Sample Preparation

Precipitated Pevikon R-341 was compared with an untreated sample. The rates of dehydrochlorination were almost identical. The difference was smaller than the current reproducibility test. This implies that precipitation will not cause any change in the rate of dehydrochlorination although it supposedly gives a more pure polymer. This indicates that the

effect of external impurities and polymerization residues was negligible for this type of suspension PVC.

Large differences in particle size have been found to influence the course of PVC degradation.^{25,26} To avoid such effects, a specific particle fraction was used throughout the experiments.

When large amounts of polymer are used, diffusion and thermal effects will cause incorrect results. Sample sizes of 200 mg or less are therefore preferred.

Determination of Activation Energies

The effect of temperature on the thermal degradation of Pevikon R-341 in nitrogen is shown in Figure 4. With the exception of a very short induction period, the rate of dehydrochlorination is constant. A temperature increase by 10°C will almost double the degradation rate.

Arrhenius plots for Pevikon R-341 and Pevikon R-45 are shown in Figure 5. The activation energies were found to be 27.9 ± 1.5 and 26.2 ± 0.6 kcal/mole, respectively. Earlier reported activation energy data for the dehydrochlorination of PVC have been collected in Table III. The

TABLE III
Reported Activation Energies for the Dehydrochlorination of PVC

Temp. range, °C	Polymer ^a	Activation energy, kcal/mole	Comments	Ref.
		34		27
160-200	Nippon Kasei Co. (E)	7.3		3
208-223		28		28
150-190	Vestolit S 70 (E)	29		29
160-200	Geon 101	34	powder and solution	19
		36		30
235-260	AIBN-initiated PVC	26		31
235-260	BP-initiated PVC	30		31
235-260	γ -initiated PVC	32		31
140-180		19		32
>180		39		32
200-250	Sicron 548 (S)	33	$\bar{M}_n = 51,000$	21
150-190		20		33
>200		33		33
178-212		22.8		5
210-250		31.0		34
170-190		34.4		6
190-230		28		35
160-215		15		36
178-243		22-30	solution	37
150-210	Vestolit SK 55 (S)	29.5 ± 1.5		38
160-200	BASF (S)	30 ± 2	solution	39
170-200	Sicron 548 FM (S)	32.8		40
170-200	Pevikon R-341 (S)	27.9 ± 1.5		this work
160-200	Pevikon R-45 (S)	26.2 ± 0.6		this work

^a S = suspension-polymerized; E = emulsion-polymerized.

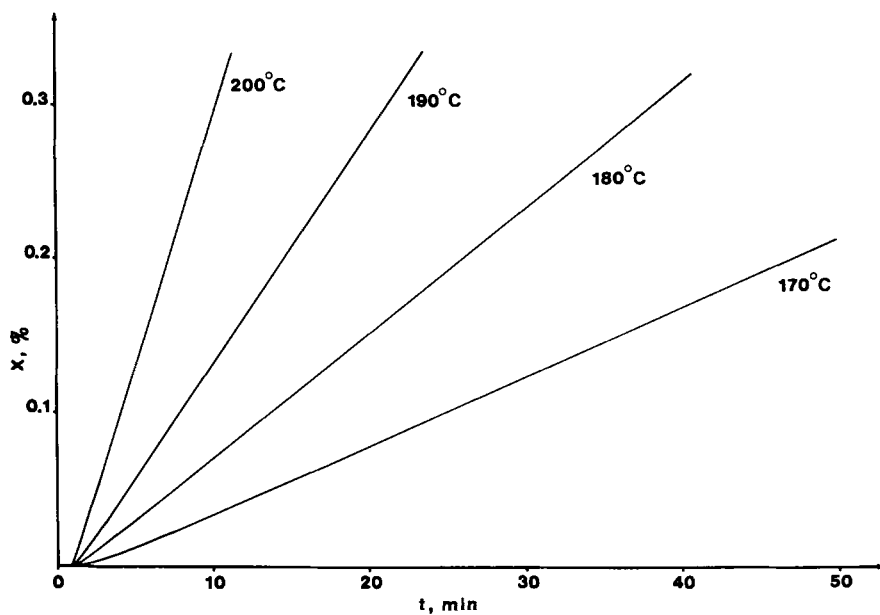


Fig. 4. Degree of dehydrochlorination as a function of time at different temperatures. Measurements for Pevikon R-341 in nitrogen.

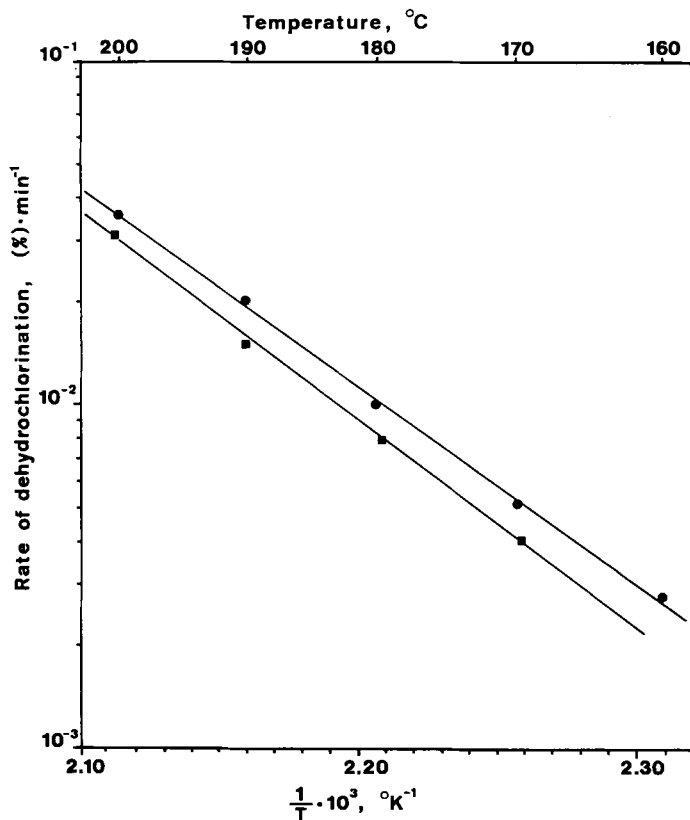


Fig. 5. Arrhenius plots for Pevikon R-341 (■) and Pevikon R-45 (●) degraded in nitrogen.

discrepancies are not only due to the use of different experimental techniques but also to differences in polymer qualities.

Further results on the thermal degradation of PVC will soon be reported.

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