Peroxide in Poly(vinyl Chloride) Ozonlzation

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ABSTRACT

Four samples of PVC polymerized in suspension (S) or emulsion (E) or in bulk at two different temperatures (M_1 and M_2) have been treated by ozone between -20 and 120°C, either in the solid state or in tetrachloroethane solution. Chain scission and peroxidation are observed with a clear parallel between the two processes. The polymer which contains the smaller amount of internal double bond (broken down at -20°C) is less sensitive to peroxidation and further chain scission at higher temperatures. Chemical or thermal peroxide decomposition experiments show that there are no residual peroxide structures in the backbone of the chain and the presence of ozone is necessary to cause chain scission. Ozonization in the solid state shows that, under T_g, the peroxidation process involves a dehydrochlorination step. A tentative mechanism for the ozonization process is suggested.

INTRODUCTION

Lebel and Landler [1] have shown that poly(vinyl chloride) (PVC) peroxidized with ozone can be used to initiate radical polymerization of vinyl monomers. They observed no variation of the molecular

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weight of PVC due to ozonization. In a previous paper, however, we
showed [2] that upon ozonization in solution at temperature higher
than 0°C, PVC oligomers with carboxylic end groups may be prepared
by chain scission of the high polymers PVC. At low temperatures,
only internal double bonds are broken [3]. We observed that the PVC
oligomers contain some peroxide structures [2]. The main purpose
of the present paper is to study more thoroughly the peroxidation
process and its relation to the chain scission process.

EXPERIMENTAL

Four poly(vinyl chloride) samples were studied: sample S, polym-
erized in suspension, sample E, polymerized in emulsion, were ex-
perimental samples kindly supplied by PC-Ugine Kuhlmann. Samples
M_1 and M_2, which were polymerized in bulk, were commercial PVC
samples, Lucovyl GB 9550 and Lucovyl RB 8010, respectively. The
ozonization of PVC was performed either in the solid state or in a
tetrachloroethane solution of polymer prepared at 80°C in the pres-
ence of nitrogen.

In both cases the ozone was generated from an oxygen stream with
a Trailigaz apparatus, model LABO 70. The vessel in which ozoniza-
tion occurred was a double-walled glass reactor; the oxygen stream
with ozone was passed through a glass-frit at the bottom of the reac-
tor and bubbled through the solution or through the powder of solid
polymer.

For experiments in solution, the production of ozone was 7.4 g/hr
and in the solid state, 9.5 g/hr. For experiments carried out in
solution, the polymer was subsequently precipitated with a great
excess of heptane and dried in vacuo at room temperature.

All samples were characterized by intrinsic viscosity, as deter-
mined in tetrahydrofuran (THF) at 25°C with a FICA viscometer
and $\overline{M}_n$ calculated from the Mark-Houwink relation: $[\eta] = 1.5 \times 10^{-2}$
$\overline{M}_n^{0.822}$, was established by gel permeation chromatography. The
peroxide titration was performed by using the iodide process [4] in
THF, this solvent being previously distilled in presence of $LiAlH_4$ to
destroy peroxides. A blank determination was performed on the pure
solvent before every titration. The initial amount of peroxide in
every sample was deduced to determine the amount of peroxides due
to the ozonization. For the experiments carried out in the solid state,
the ozonized oxygen was bubbled through water after the reactor so
that the total acidity of the aqueous solution could be determined by
using a potentiometric method with 0.1 N NaOH, although the hydrogen
chloride evolved from the reactor could be titrated simultaneously by
using a chlorine specific electrode and 0.1 N $AgNO_3$.
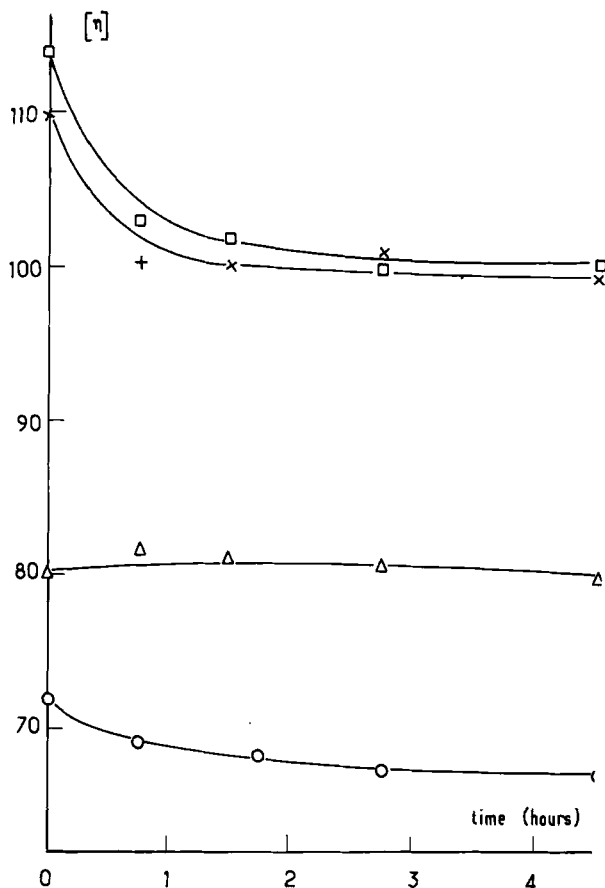
FIG. 1.   Ozonolysis of PVC at -20°C: (□) suspension PVC (S);
(×) emulsion PVC (E); (△) bulk PVC (M$_1$); (○) bulk PVC (M$_2$).

RESULTS AND DISCUSSION

When the ozonolysis of PVC is performed at -20°C, the molecular
weight decreases only if there are double bonds in the chains [2].
Figure 1 gives the variation of intrinsic viscosity at -20°C. Only the
sample M$_1$ is not degraded at this temperature. Samples S, E, and M$_2$
should contain double bonds in the chains.

But if the ozonization is performed at above 0°C, all samples are
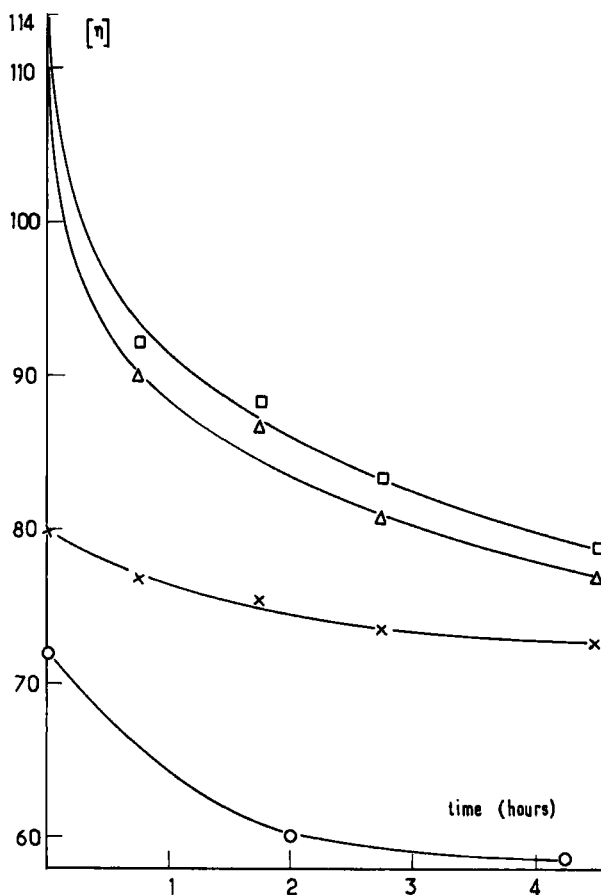
FIG. 2. Ozonization of PVC at 20°C: (□) suspension PVC (S);
(△) emulsion PVC(E); (×) bulk PVC (M_1); (○) bulk PVC (M_2).

degraded by the autoxidation process (Fig. 2) which we think is due
to a previous peroxidation of the polymer.

Tables 1-4 summarized the conditions of ozonization of different
samples and the evolution of their peroxidation essentially between
-20°C and +20°C.

The average number of breaks per chain $\overline{X}$, is deduced from the
relation

$$\overline{X} = ([\eta_0]/[\eta])^{1/\alpha} - 1$$

TABLE 1. Ozonization of a Bulk PVC, Sample M_1, at Different
Temperatures T

T (°C)	Time (min)	$[\eta]$ (ml/g)	$\overline{M_n} \times 10^{-3}$	$\overline{X}$	Peroxide (mmole/100 g of polymer)	N_{OP} (mole)	N_{RP} (mole)
-20	0	80	34.2	0	1.5		
	45	81.8	34.2	0	2.5	0.34	0.34
	90	81.3	34.2	0	2.5	0.34	0.34
	165	80.6	34.2	0	2.5	0.34	0.34
	270	79.8	34.2	0	2.5	0.34	0.34
-10	45	81.0	34.2	0	2.5	0.34	0.34
	90	80.8	34.2	0	2.5	0.34	0.34
	165	81.0	34.2	0	2.5	0.34	0.34
	270	81.5	34.2	0	2.5	0.34	0.34
0	45	80.9	34.2	0	2.5	0.34	0.34
	90	80.9	34.2	0	2.5	0.34	0.34
	165	80.9	34.2	0	2.5	0.34	0.34
	270	80.7	34.2	0	3.0	0.51	0.51
+20	45	76.8	32.5	0.05	4	0.81	0.90
	90	75.6	31.9	0.07	5	1.22	1.27
	165	73.4	30.8	0.11	6.5	1.54	1.82
	270	72.6	30.4	0.12	7	1.67	2.00

where $[\eta_0]$ and $[\eta]$ are intrinsic viscosities before and after ozoniza-
tion, respectively, and α is the coefficient of the Mark-Houwink equa-
tion.

N_{OP} is the number of residual peroxide groups per mole of polymer
after ozonization. This value is directly deduced from peroxide titra-
tion on 100 mg of ozonized polymer. N_{RP} is the number of residual

peroxide groups per initial chain of polymer, and

$$N_{RP} = N_{OP}\,(\overline{X} + 1) \tag{1}$$

TABLE 2. Ozonization of Suspension PVC, Sample S

T (°C)	Time (min)	$[\eta]$ (ml/g)	$\overline{M_n} \times 10^{-3}$	$\overline{X}$	Peroxide (mmole/100 g of polymer)	N_{OP} (mole)	N_{RP} (mole)
-20	0	114	52.4	0	3		
	45	103	46.6	0.13	7	1.86	2.34
	90	102	46.0	0.14	7.5	2.07	2.50
	165	100.0	44.9	0.17	8	2.24	2.80
	270	100.4	45.0	0.16	8	2.24	2.80
-10	45	104	47.1	0.11	6	1.41	1.70
	90	104	47.1	0.11	6	1.41	1.70
	165	102.4	46.1	0.13	7	1.84	2.2
	270	101.4	45.6	0.15	7.5	2.05	2.5
0	45	100	44.9	0.17	9	2.69	3.3
	90	97.7	43.5	0.20	11.5	3.78	4.6
	165	95.4	42.3	0.24	13.5	4.43	5.7
	270	91.6	40.4	0.30	14.5	4.62	6.3
+20	45	92.2	40.6	0.29	10	2.84	3.91
	90	88.5	38.6	0.35	19.5	6.37	9.02
	165	83.4	36.0	0.46	25.0	7.93	12.0
	270	78.8	33.5	0.56	28.5	8.54	13.9

The results in Table 1 show clearly that sample M_1 reacts with ozone at temperatures above 0°C and peroxidation of the polymer and chain breakage take place simultaneously. As shown in Table 2, the peroxidation of sample S begins at -20°C, but the autoxidation process begins only at about 0°C. For sample E, the peroxidation of this PVC is observed also at -20°C, and the autoxidation process begins at about 0°C. It seems clear from these results that the peroxidation of PVC is connected with the presence of double bonds in the chain, and consequently also, in the presence of allylic hydrogen atom which can react with ozone or oxygen, gives hydroperoxide which can initiate the autoxidation process.

The molecular weight of polymer M_2 is lower than that of sample M_1 because the temperature of polymerization is higher, since

TABLE 3. Ozonization of Emulsion PVC, Sample E

T (°C)	Time (min)	$[\eta]$ (ml/g)	$\overline{M_n} \times 10^{-3}$	$\overline{X}$	Peroxide (mmole/100 g of polymer)	N_{OP} (mole)	N_{RP} (mole)
-20	0	110	50.4	0	5		
	45	110	44.9	0.12	10	2.30	2.70
	90	100	44.9	0.12	11	2.76	3.21
	165	101.2	44.5	0.10	11	2.73	3.11
	270	99.2	44.5	0.13	11.5	2.89	3.40
-10	45	97.5	43.6	0.15	12.5	3.26	3.94
	90	97.0	43.6	0.16	13.5	3.68	4.41
	165	98.2	43.8	0.14	13.5	3.72	4.43
	270	97.0	43.3	0.16	14.0	3.90	4.77
0	45	97.6	43.3	0.15	15.0	4.35	5.2
	90	97.2	43.3	0.16	15.5	4.56	5.4
	165	95.0	42.2	0.19	16.5	4.85	6.0
	270	94.2	41.7	0.20	18.0	5.41	6.7
+10	45	90.0	39.4	0.27	12.0	2.76	3.80
	90	86.8	37.8	0.33	17.5	4.72	6.6
	165	81.0	34.7	0.44	22.0	5.89	9.0
	270	76.8	32.5	0.54	28.5	7.64	12.3

this PVC contains some double bonds in the chains. To elucidate
the mechanism of the autoxidation process, peroxidation was
studied from -20°C to +120°C (Table 4). As for the previous
samples S and E, this polymer is peroxidized from -20°C
but to a smaller extent because the number of double bonds par chain
is smaller (Fig. 1). As suggested in a previous paper [2], if the chain
scission is directly related to the peroxide decomposition, it is pos-
sible to calculate from the above results the theoretical number of
peroxide groups (N_p) which can appear in an initial chain of poly(vinyl

chloride). This value N_p represents the peroxidizability of the PVC

and it is equal to the number of residual peroxide groups per initial
chain (N_{RP}) plus the number of breaks per chain $\overline{X}$.

TABLE 4. Ozonization of Bulk PVC, Sample M_2

T (°C)	Time (min)	$[\eta]$ (ml/g)	$\overline{M}_n \times 10^{-3}$	$\overline{X}$	Peroxide (mmole/100 g of polymer)	N_{OP} (mole)	N_{RP} (mole)
-20	0	72	30.1	0	1.0		
	45	69.3	28.6	0.04	3.0	0.57	0.64
	105	68.4	28.2	0.06	3.25	0.63	0.73
	165	67.2	27.7	0.08	3.75	0.73	0.91
	270	67.0	27.5	0.09	4.0	0.82	1.00
-10	87	64.8	26.4	0.13	4.5	0.92	1.20
	150	63.2	25.7	0.17	6.5	1.41	1.81
0	120	63.3	25.7	0.17	10.0	2.31	2.90
	265	62.2	25.1	0.19	11.0	2.51	3.20
	1140	61.7	24.9	0.20	11.25	2.55	3.30
20	120	60.0	24.1	0.24	12.5	2.77	3.70
	255	58.5	23.4	0.28	14.0	3.04	4.20
	900	50.0	19.3	0.55	14.5	2.60	4.60
50	120	40.2	14.8	1.02	16.5	2.29	5.6
	270	30.8	10.7	1.79	22.5	2.29	8.2
	915	17.3	5.3	4.61	26.0	1.32	12.0
70	60	33.2	11.7	1.55	22.5	2.52	8.0
	285	12.6	3.6	7.24	28.5	0.99	15.4
	540	8.1	2.1	13.06	32.5	0.66	22.3
90	15	31.4	11.8	1.73	6.0	0.54	3.20
	35	18.6	5.8	4.43	19.5	1.07	10.2
	60	14.25	4.2	6.1	30.5	1.21	14.6
	120	7	1.8	15.8	40.0	0.69	27.2
100	15	29.15	10.0	1.98	6.5	0.55	3.63
	35	15.5	4.6	5.41	27.5	0.98	11.70
	60	12.3	3.5	7.48	37.5	1.28	18.3
	120	5.4	1.3	21.97	50.0	0.50	33.4
120	15	93.8	16.4	0.82	7.5	1.06	2.76
	35	13.8	4.0	6.38	25.0	0.97	13.50
	60	7.8	2.0	13.72	47.5	0.93	27.4
	120	6.3	1.5	18.06	50	0.76	32.5
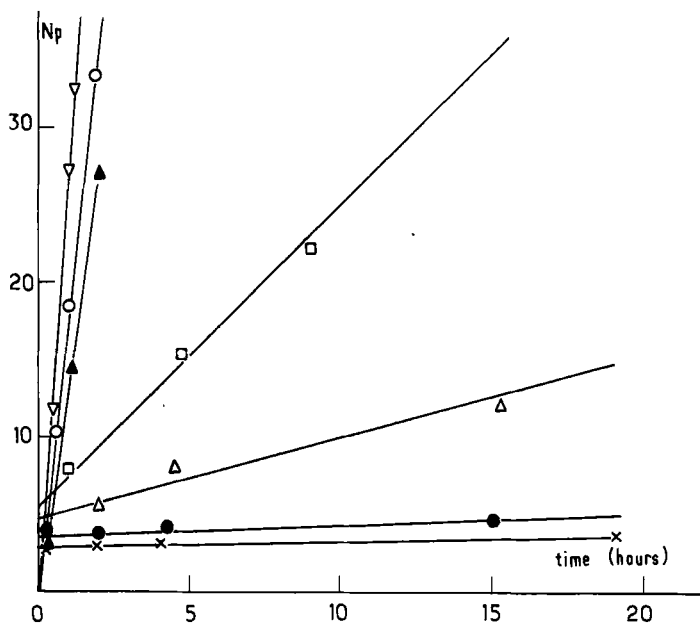
FIG. 3. Peroxydation of bulk PVC RB 8010 at different temperatures (M₂): (x) 0°C; (•) 20°C; (△) 50°C; (□) 70°C; (▲) 90°C; (○) 100°C; (▽) 120°C.

$$N_P = N_{RP} + \overline{\overline{X}} \qquad\qquad (2)$$

For sample M₂, Fig. 3 illustrates the variations of N_P versus time for different temperatures. All plots are straight lines, and the peroxidation rate is constant in isothermal conditions as well as the rate of chain scission. The ratio of these two rates is constant but always in favor of the peroxidation reaction. For this reason the total amount of peroxide groups in the polymer increases continuously with time and temperature.

Figure 4 shows the variations of N_p. The corresponding data for $\overline{X}$ (Table 4) are shown in Fig. 5 to illustrate the great similarity of the curves and the autoacceleration of the processes in the same range of temperature between 50 and 70°C. These results are in agreement with the data of Lebel and Landler [1], who have shown that the rate constant of decomposition of peroxide groups introduced in PVC by ozonization increases from 4.6×10^{-7} to 1.3×10^{-4} sec⁻¹ when the
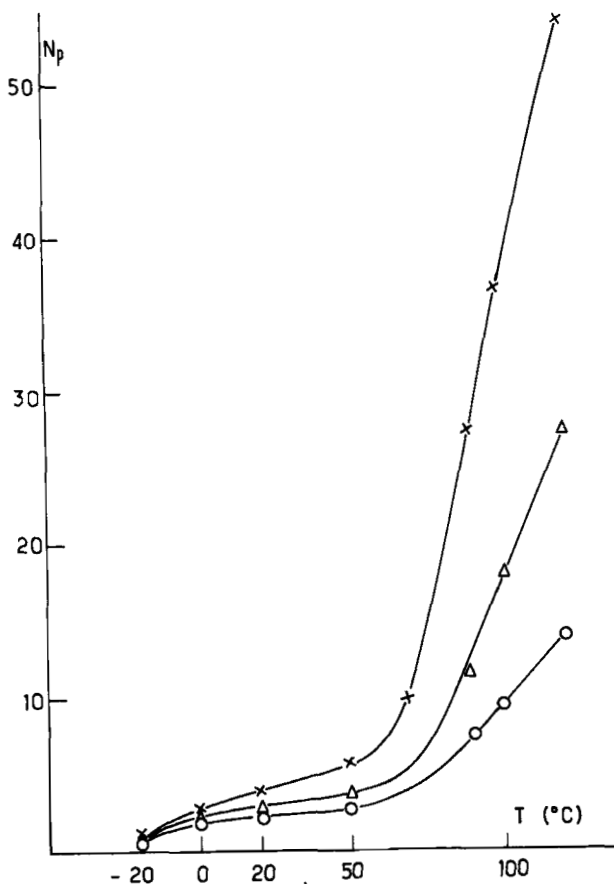
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FIG. 4. Peroxidation of bulk PVC (M_2) vs. time and temperature: (o) 30 min; (△) 1 hr; (×) 2 hr.

temperature is elevated from 25°C to 80°C. For sample M_2, the number of peroxides per chain after ozonization goes through a maximum at a temperature of 20-30°C.

From all above results for the different PVC samples studied it is possible to compare their peroxidizability and their degradability in the presence of ozone by comparing N_p (Figs. 6 and 7) or $\overline{X}$ (Fig. 8) versus the time under the same isothermal conditions. At 20°C the PVC is degraded more than it is peroxidized, and it is clear that the
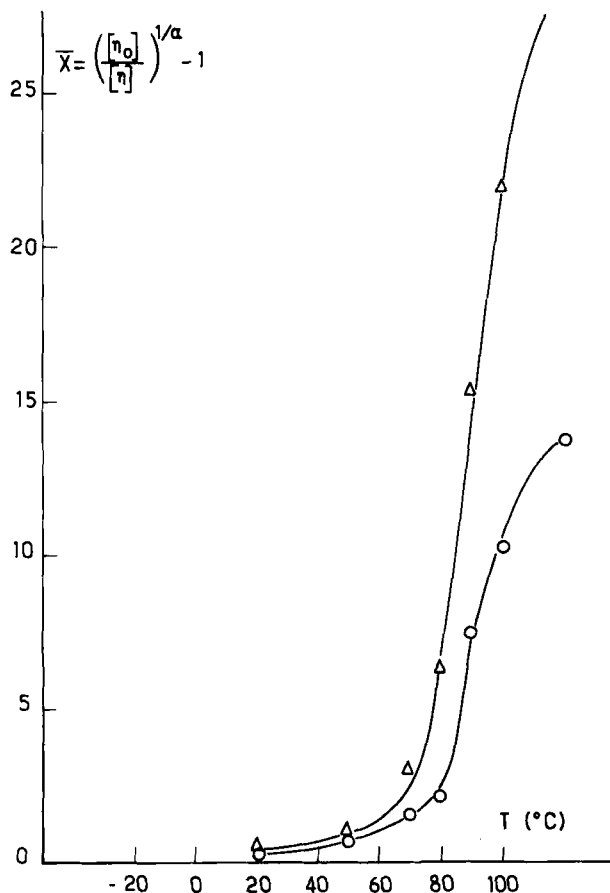
$$\overline{X} = \left(\frac{[\eta_0]}{[\eta]}\right)^{1/\alpha} - 1$$

T (°C)

FIG. 5. Chain scission of bulk PVC (M_2) vs. time and temperature
in the presence of ozone: (○) 1 hr; (△) 2 hr.

least peroxidized polymer is the polymer which contains the smallest
amount of double bonds. This is also very clear at -20°C (Fig. 7). On
the contrary, those polymers which contain the largest number of
these structures are the most sensitive to peroxidation and degrada-
tion in the presence of ozone.

Finally, Table 5 summarizes the study of ozonization of bulk PVC
(sample M_1) in the solid state at different temperatures.

All these results show that the PVC is attacked by ozone at tem-
peratures as low as -20°C with elimination of hydrogen chloride,
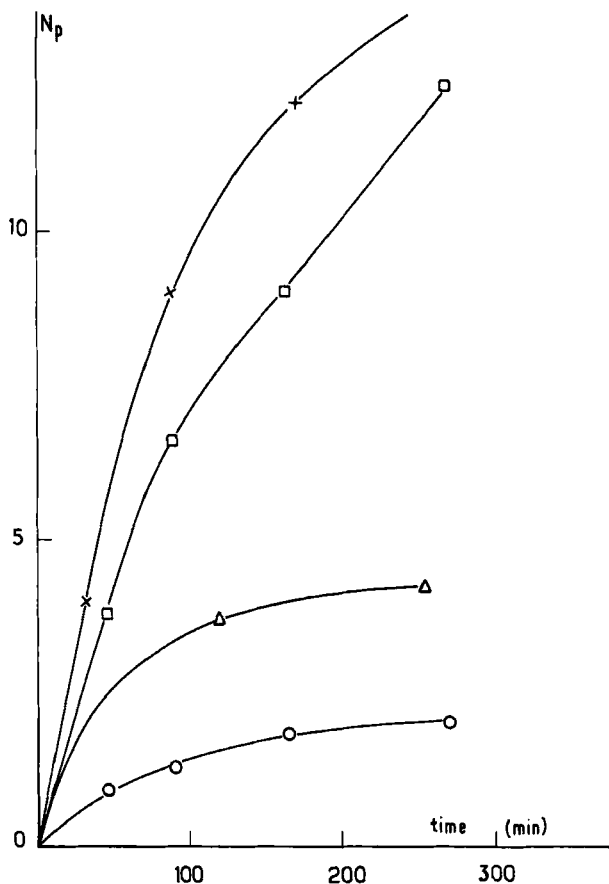
FIG. 6. Peroxidability (N_p) of different PVC at 20°C: (○) bulk PVC (M_1); (△) bulk PVC (M_2); (□) emulsion PVC (E); (×) suspension PVC (S).

which constitutes between 50 and 85% of the acids liberated during the ozonization in the temperature range 0-70°C. At -20°C it represents only 0.2% of the total acidity.

In the solid state the chain scission process is much less efficient than in solution, and the number of peroxide groups N_{RP} is very much larger than $\overline{X}$. It is interesting to note that, between 50 and 70°C, there is a quite good correspondence between the number of HCl
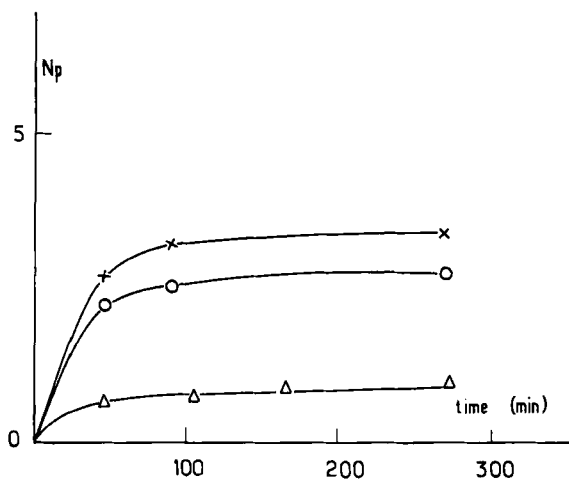
FIG. 7. Peroxidability (N_p) of different PVC at -20°C: ($\triangle$) bulk PVC (M_2); ($\circ$) emulsion PVC (E); ($\times$) suspension PVC (S).

molecules evolved per polymer chain and the total number N_p of peroxidizable sites. At lower temperatures we suspect that there may be some retention of HCl which may remain dissolved in the PVC at temperatures under T_g [6], so that the results strongly suggest that the peroxidation process involves the loss of one mole of hydrochloric acid. Above T_g, of course, dehydrochlorination of the polymer takes place by the zipping mechanism, probably initiated by the thermal decomposition of peroxides, and the amount of HCl evolved increases very much.

This fact suggests that the rate of dehydrochlorination from a radical introduced in the PVC chain is greater than the rate of peroxidation, even in presence of ozone.

The slight differences observed between the number of moles of HCl evolved from the reactor and the total acidity determined in the gas-washing bubbler may be explained by the formation of dihydrated perchloric acid. The melting point of this acid is -17.8°C, and a very strongly acidic product which melts about in the same range temperature is condensed in the trap (-78°C) inserted between the reactor and the gas-washing bubbler.

The thermal stability of the peroxides has been studied at 80°C, using the sample (M_2) ozonized at 20°C for 15 hr either in the solid state or in solution. The thermal degradation experiments have been carried out either under nitrogen or oxygen. It is clear from the

$$\bar{X} = \left(\frac{[\eta_o]}{[\eta]}\right)^{1/\alpha} - 1$$

time (hours)
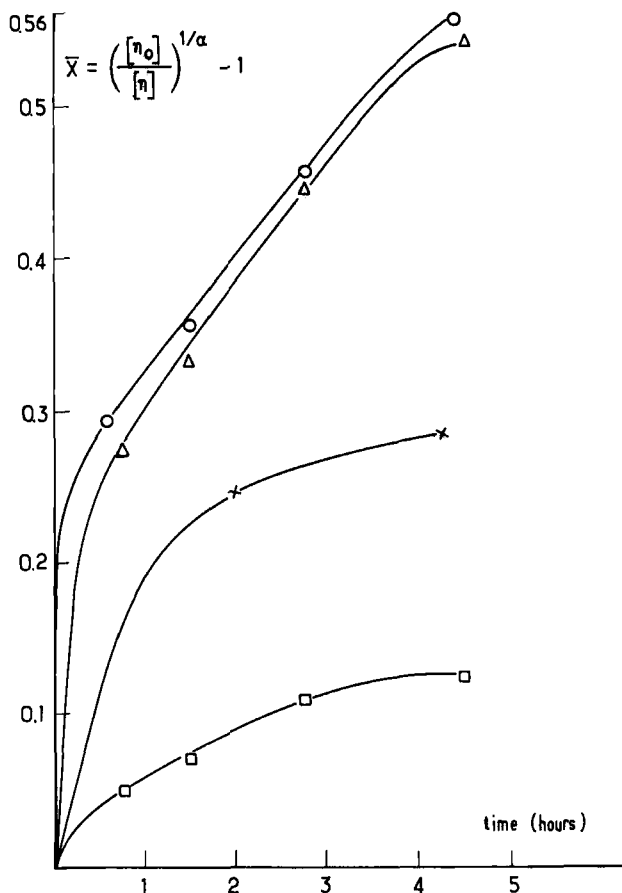
FIG. 8. Chain scission vs. time at 20°C for ozonization of PVC at 20°C: (□) bulk PVC (M₁); (×) bulk PVC (M₂); (△) emulsion PVC (E); (○) suspension PVC (S).

typical results reported in Table 6 that, whatever the atmosphere, the decomposition of peroxide does not cause chain scission. On the other hand, thermal autoxidation occurs under the oxygen atmosphere, while the amount of peroxide decreases with time under the nitrogen atmosphere with a rate which is in line with the data of Lebel and Landler [1]. These results show that the peroxides are grafted, and not in the backbone of the PVC chain. On the other hand, the presence of ozone is necessary to cause chain scission. The first of these two

TABLE 5. PVC Peroxidation in Solid State

T (°C)	Time (hr)	$[\eta]$ (ml/g)	$\overline{M}_n \times 10^{-3}$	$\overline{X}$	Peroxide (mmole/100 g of polymer)	N_{RP} (mole)	N_P (mole)	Total acidity (mole/ initial chain)	HCl (mole/initial chain)
-20	22.25	80	34.2	0	0.5	0.17	0.17	0.49	1.12×10^{-2}
0	22.50	73.6	31.2	0.11	5	1.70	1.8	0.92	0.62
20	21.50	60.6	24.2	0.40	8	2.73	3.1	2.46	1.24
50	22.50	43.8	16.4	1.09	13	4.44	5.5	6.10	4.39
60	22.0	39.0	14.2	1.40	15.5	5.30	6.7	8.00	6.55
70	22.25	30.5	10.4	2.24	25.5	8.72	10.9	13.67	11.54
90	22.5	18.2	5.6	5.09	40.0	13.85	18.80	59.7	49.5

TABLE 6. Thermal Decomposition of PVC Peroxidized at 80°C

Atmosphere	Condition	Time (min)	$[\eta]$ (ml/g)	Peroxide (mmole/100 g of polymer)
Nitrogen	Solid state	0	50	14.5
		90	51.6	10.0
		180	54.6	5.0
Nitrogen	Tetrachloroethane	0	50	14.5
	solution	90	49.7	11.5
		180	49.3	8.5
Oxygen	Tetrachloroethane	0	50.0	14.5
	solution	90	50.4	15.0
		180	-	17.5

points is supported by experiments of chemical deactivation of peroxides using either potassium iodide or triphenylphosphine in THF solution. Typical results reported in Table 7 show that in these conditions there are only a small number of chain scissions. The chemical deactivation by KI would give the reaction (3):

$$R-O-O-R' + 2\ I^- + 2\ H^+ \longrightarrow I_2 + ROH + R'OH \tag{3}$$
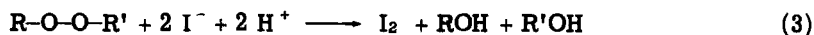
These alcoholic functions have been qualitatively characterized by reaction of different PVC samples ozonized in the solid state at different temperatures with phenyl isocyanate or diphenylmethane diisocyanate in tetrachloroethane at 110°C for 6 hr. The results are summarized in Table 8.

As shown in Table 8, the molecular weight does not vary with phenylisocyanate; in the infrared spectra two new bands at 1600 cm^{-1} and 1520 cm^{-1} appear which may be attributed to C_6H_5-N-H groups

[7] and R–NH–C=O groups [8], respectively. On the contrary, in the presence of diphenylmethane diisocyanate the molecular weight increases, indicating the coupling of different chains.

The previous results lead us to propose the following mechanism.

The initiation of the ozone reaction takes place on the double bonds as well as on the allylic structure in the alpha position [Eq. (4)].

In a second step, ozonide decomposition takes place [Eq. (5)]

TABLE 7. Chemical Deactivation of PVC Peroxide

Sample	Ozonization conditions		Peroxide per residual chain (mole)	$[\eta_0]$ (ml/g)	Deactivation method	T (°C)	Time (min)	Residual peroxide	$[\eta]$ (ml/g)
	Time (hr)	T (°C)							
M_1	22.0	60	2.42	39.0	KI, THF	60	5	0.0	37
M_1	22.25	70	2.82	30.5	$P(C_6H_5)_3$, THF	room	1020	0.0	26.5

TABLE 8. Interaction of Ozonized PVC after Peroxide Deactivation with Mono- or Diisocyanate

Sample	Ozonization conditions in solid state		$[\eta]$ after peroxide deactivation with KI (ml/g)	$[\eta]$ after reaction with phenyl isocyanate (ml/g)	$[\eta]$ after reaction with diphenylmethane diisocyanate (ml/g)
	T ($^\circ$C)	Time (hr)			
M_1	20	21.5	59.6	61	ND[a]
M_1	50	22.5	42	45	ND
M_1	60	22.0	37	39.3	ND
M_1	75	23.0	20.5	24	30.5

[a]Not determined.

$$\sim\!CHCl\!-\!CH_2\!-\!CH\!=\!CH\!-\!CH\!-\!CH_2 \sim \xrightarrow{O_3} \quad \sim\!CHCl\!-\!CH\!-\!CH \overset{O-O}{\underset{O}{\diamond}} CH\!-\!CH\!-\!CH$$

(4)

$$\sim\!CHCl\!-\!CH\!-\!CH \overset{O-O}{\underset{O}{\diamond}} CH\!-\!CH\!-\!CH_2 \sim \longrightarrow$$

$$\sim\!CHCl\!-\!CH\!-\!C\overset{OH}{\underset{OOH}{\diagup}} \quad + \quad \overset{O}{\underset{H}{\diagdown}}C\!-\!CH\!-\!CH_2 \sim$$

(5)
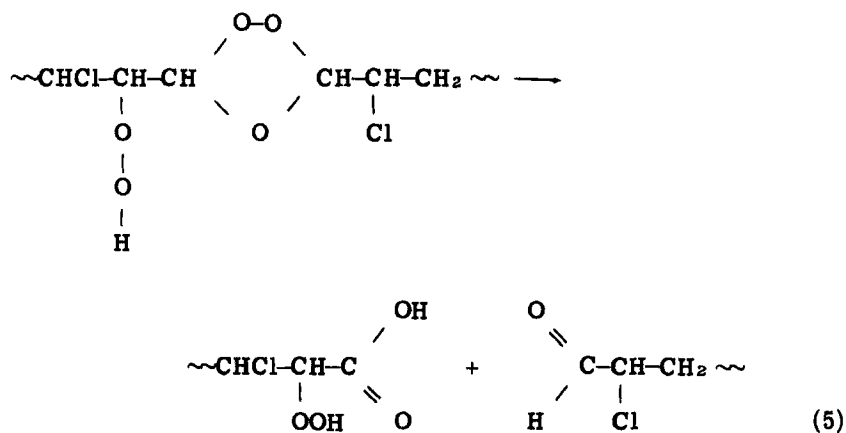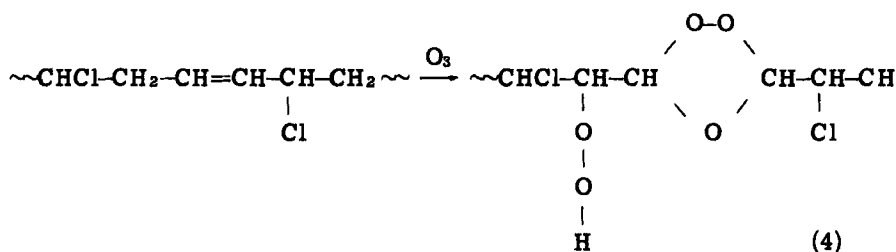
and, at the same time, there is a cyclization of the hydroperoxide structure in a branched peroxide and dehydrochlorination [Eq. (6)].

$$\sim\text{CHCl--CH}_2\text{--CHCl--CH}_2\text{--CHCl--CH--C} \overset{O}{\underset{\underset{\underset{H}{|}}{\underset{O}{|}}}{\overset{/\!/}{\diagdown}}} \text{OH} \longrightarrow$$
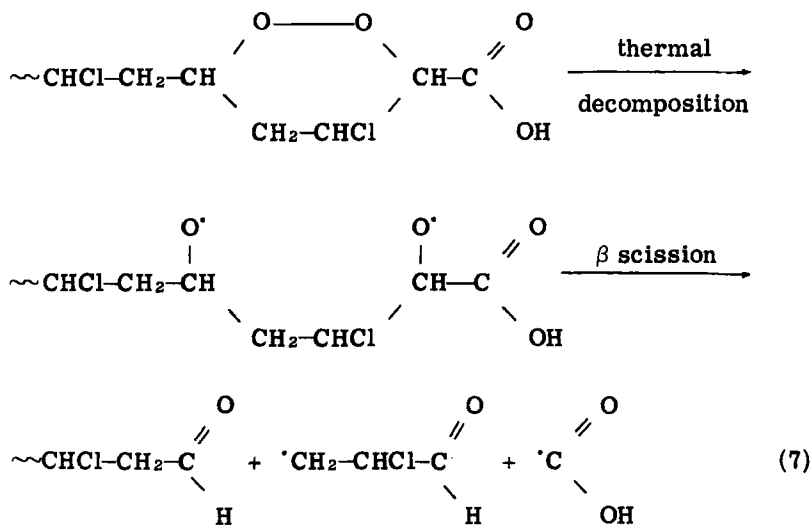
$$\sim\text{CHCl--CH}_2\text{--CH} \overset{\text{CH}_2\text{--CHCl}}{\underset{\text{O}\text{------}\text{O}}{\diagup\diagdown}} \text{CH--C} \overset{O}{\overset{/\!/}{\diagdown}} \text{OH} \quad + \text{ HCl} \qquad (6)$$
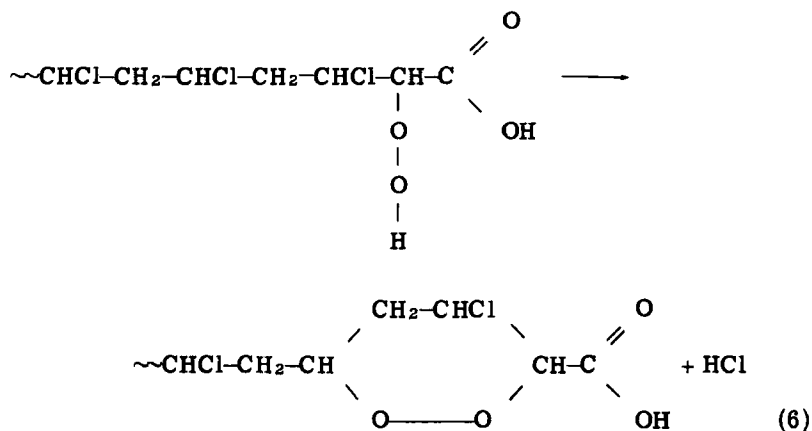
Thermal decomposition of alkoxy radicals and their β scission causes chain scission with appearance of aldehyde end groups on PVC and low molecular weight radicals which can lead to different oxidative products and peroxy radicals.

$$\sim\text{CHCl--CH}_2\text{--CH} \overset{O\text{------}O}{\underset{\text{CH}_2\text{--CHCl}}{\diagup\diagdown}} \text{CH--C} \overset{O}{\overset{/\!/}{\diagdown}} \text{OH} \quad \xrightarrow[\text{decomposition}]{\text{thermal}}$$

$$\sim\text{CHCl--CH}_2\text{--CH} \overset{\overset{O^{\bullet}}{|}}{\underset{\text{CH}_2\text{--CHCl}}{}} \text{CH--C} \overset{\overset{O^{\bullet}}{|}}{}\overset{O}{\overset{/\!/}{\diagdown}} \text{OH} \quad \xrightarrow{\beta \text{ scission}}$$

$$\sim\text{CHCl--CH}_2\text{--C} \overset{O}{\underset{H}{\overset{/\!/}{\diagdown}}} \quad + \quad {}^{\bullet}\text{CH}_2\text{--CHCl--C} \overset{O}{\underset{H}{\overset{/\!/}{\diagdown}}} \quad + \quad {}^{\bullet}\text{C} \overset{O}{\underset{OH}{\overset{/\!/}{\diagdown}}} \qquad (7)$$

It is interesting to note that at least six volatile products formed
during the ozonization of PVC have been separated by gas chroma-
tography but not identified up to now.

In the presence of oxygen and ozone the aldehyde end groups are
transformed into acid groups; this mechanism explains the formation
of α and β chlorinated acid end groups on PVC [2]. Peroxy radicals,
such as

```
   O              H
    \\             |
      C–CHCl–COO·
    /             |
   H              H
```
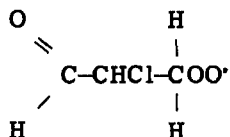
participate in the propagation reaction by hydrogen transfer from
the PVC chain, and the dehydrochlorination takes place from this new
macroradical. Because of the presence of ozone there is further
ozonide formation, and then the process may be continued up to very
high level of chain scission depending on the temperature of the
reaction.

CONCLUSION

This study shows that the PVC chain scission by ozone is due to
an autoxidation process initiated specifically by this product with
elimination of hydrogen chloride and formation of peroxide groups
at temperatures as low as -20°C. The weak points in PVC chains
which are peroxidized at this temperature seem to be the double bonds
and the allylic hydrogen atom, and the number of defects can depend
on the history of the samples and probably at first on the polymeri-
zation conditions (polymerization process, thermal history after
polymerization, storage).

The difference between the peroxadizability of PVC samples in
the presence of ozone can have important consequences on natural
aging; Marechal [9] has shown that PVC peroxidized in presence of
ozone is more sensitive to photoxidation beyond 320 nm than virgin
polymer. Besides Scott [10] has observed also that PVC is degraded
during photoxidation with decrease of molecular weight and appearance
of end groups such as α and β chlorinated acids that we have observed.
There may be an analogy between photoxidation of PVC and degradation
in the presence of ozone.

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