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On the PVC Chlorination Mechanism

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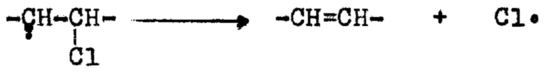
SUMMARY

A radiochemical method was used to study PVC chlorination. A reaction mechanism was proposed based on the results obtained from chlorination of ^{36}chlorine labeled PVC. A mechanism was proposed also for chain transfer reaction to polymer in vinyl chloride polymerization.

In our previous papers (CARACULACU et al. 1970, BURUIANA et al. 1980) we have demonstrated that there were no chlorine atoms at most of the tertiary carbons of PVC branches. By ^{13}C NMR (BOVEY et al. 1975) it has been established that the structure of the branching is principally $-CH_2Cl$, appearing by a rearrangement of the growing macroradical (RIGO et al. 1972). Therefore the chain transfer to polymer, which was considered for a long time to be responsable for the formation of the branches, could produce other types of structures, as well. Studying the behaviour of unsaturated end groups models at an intense radicalic attack (CARACULACU et al. 1978, BURUIANA, in press) we concluded that when a radical of type I appears, this expels the neighbouring chlorine atom forming a double bond (II):



$$-\underset{\bullet}{C}H-\underset{\substack{|\\ Cl}}{C}H- \longrightarrow -CH{=}CH- \quad + \quad Cl\bullet$$

I II

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If such a radical is formed as a result of chain transfer to polymer during the polymerization of vinyl chloride, it will produce internal double bonds on the polymer backbone. In order to verify this supposition we studied another radicalic process on the PVC chain, the chlorination.

Although thanks to its multiple applications chlorinated PVC (CPVC) has been known and studied long ago, the mechanism of the chlorination reaction was not wholly elucidated.

The problem of the grouping supporting the chlorination was discussed very much.

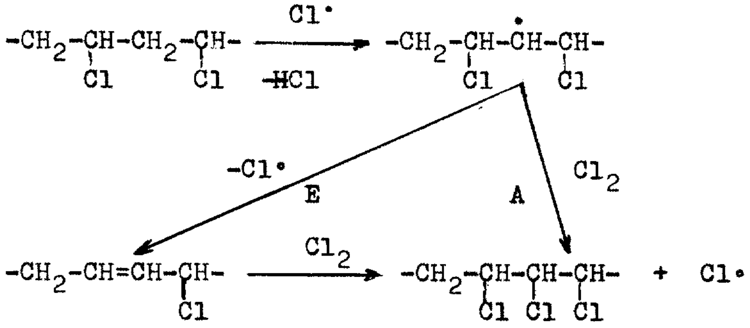
The substitution may take place at $-CH_2-$;  $-\underset{\substack{|\\ Cl}}{C}H-$ or at both of them.

IR (FUCHS et al. 1957, GERMAR, 1965, FREDRIKSEN 1967, KALTWASSER et al. 1966a, KALTWASSER et al. 1966 b), NMR (PETERSEN et al. 1967, SOBAJIMA et al. 1968, THO et al. 1968, SVEGLIADO et al. 1969) or pirolitic gas - chromatography (TSUGE, 1969) studies argued alternatively for one or other of these possibilities.

The newer researches show a greater reactivity of the $-CH_2-$ group than that of $-CHCl-$ during the chlorination reaction (KOLINSKY et al. 1971, BARTA et al. 1980).

If the chlorination takes place at $-CH_2-$ group, during the reaction would appear a radical in the vicinity of the carbon atom bearing chlorine. This would react with chlorine (as in classical chain reaction), or eliminate a chlorine radical, forming double bonds on the chain. Then chlorine would be added to these double bonds.

Based on thermodynamic considerations, (FUCHS et al. 1957) suggested that such an "aditive chlorination" can take place. Later on (CARACULACU et al. 1979) and other researchers (LUKÁS et al. 1979) took it into consideration:



EXPERIMENTAL PART

$Ag^{36}Cl$ was prepared from a $H^{36}Cl$ solution having specific activity λ_{sp} = 1,936,800 imp/g_{Cl} min., by precipitation with $AgNO_3$ solution.

$Al^{36}Cl_3$ was obtained by heating 1.1g $Ag^{36}Cl$ and 0.6g aluminium sheet under argon, until reaction mixture was molten. The formed $Al^{36}Cl_3$ sublimed.

Labeling of PVC with 36 - chlorine. A solution of 2% PVC in 1,1,2,2-tetrachloroethane was mixed with a solution of $Al^{36}Cl_3$ in tetrachloroethane. The mixture was kept 3 hr at 60°. The polymer was precipitated in petroleum ether, then washed with petroleum ether and then with water. Four reprecipitations from THF/EP solvent system were performed for complete purification.

Labeling of vinyl chloride with 36-chloride $Al^{36}Cl_3$ was sublimed in a polymerization vial, under argon. Then 20 ml vinyl chloride were condensed. The vial was closed under argon and stired for 96 hr at 40°. The labeled vinyl chloride was distiled in the polymerization vessel.

Polymerization of vinyl chloride - ^{36}Cl was carried out in glass vials, in block, under argon, using AIBN as initiator, at a concentration of 1%. The polymer was purified by reprecipitation from tetrahydrofuran-petroleum ether. Specific activity of the polymer was λ_{sp} = 752 imp/g min.

Chlorination of PVC - ^{36}Cl Aproximativelly 1g PVC, 25 ml CCl_4 and 2g Cl were introduced in clossed glass vials, under argon. The reaction was performed at room temperature with stiring. To interrupt the reaction, the vials were cooled at 75°, opened and left to get to room temperature. The chlorine excess and formed hydrogen chloride were caught in a traps system with KOH solution (25%). Carbon tetrachloride was warmed at 60°C in order to remove the chlorine completelly, there was distiled at reduced pressure.

The measurements of activity were performed with a liquid counter. The activities of polymers were measured in tetrahydrofuran solutions.

The chlorine content in polymers was determined according to Schöninger procedure, followed by titration.

The chlorine content in the gases was determined by their catching in KOH solution and by measurement of the Cl^- + ClO^- with methyl-orange.(LITEANU, 1969).

NMR spectra were recorded with a JEOL - 60 MHz spectrometer, using o-dichlorobenzene as solvent.

RESULTS AND DISCUSSIONS

The polyvinylchloride labeled with 36-chlorine isotope was obtained both by direct isotopic exchange with $Al^{36}Cl_3$ (PVC^{36}Cl A) and by polymerization of labeled vinyl chloride (PVC^{36}Cl B) (Table I).

TABLE I

Sample	λ_{sp}^{PVC} imp/g min.	Cl%	λ_{sp}^{Cl} imp/g min.
PVC^{36}Cl A	2194	56.5	3980
PVC^{36}Cl B	752	56.5	1330

$PVC^{36}Cl$ A = polymer labeled by direct exchange with $AlCl_3$;
$PVC^{36}Cl$ B = polymer labeled by synthesis;
λ_{sp} = specific activity;

The chlorination was performed in closed system, using PVC and Cl_2 at a molar ratio of 1:4. When reaction was interrupted the chlorine excess and formed hydrogen chloride were quantitatively catched in KOH solution.

After performing the chlorination, extent of chlorination was determined, on the basis of the ratio of the characteristic bands for the -CHCl- and $-CH_2-$ groups from NMR spectra. A chlorine content of 72% for $PVC^{36}Cl$ A and of 67.5% for $PVC^{36}Cl$ B was found (Table II). The same results were obtained by elemental analysis and IR spectroscopy.

The measurements of radioactivity on the polymer before and after chlorination showed a decrease of total radioactivity, as presented in Table II.

Simultaneously almost whole radioactivity lost from polymer was found again in the gases resulted from reaction. Normally these must not be radioactive.

The presence of the radioactive chlorine in the gases is an experimental proof for the producing of chlorination by a mechanism involving an unsaturated intermediate.

Preliminary calculations made with the formula:

$$E\% = \frac{Cl_1(\lambda_1 - \lambda_2)}{\lambda_1(Cl_2 - Cl_1)} \times 100$$

where:

E% = the proportion of reaction going on elimination;

Cl_1 = the total content of chlorine in the sam-

TABLE II

Sample	PVC ^{36}Cl A	PVC ^{36}Cl B
Polymer before chlorination, g	0.6277	0.88
λ_1, **imp/min.**	1343	662
Polymer after chlorination, g	0.9753	1.25
λ_2, **imp/min.**	537	539
Cl% in chlorinated polymer	72.0	67.5
λ_{gases}, **imp/min.**	664	97
Chlorination by mechanism with elimination, E%	25.1	61.0

ple before chlorination;

Cl_2 = the total content of chlorine in the chlorinated sample;

λ_1 = the total activity of the polymer before chlorination;

λ_2 = the total activity of the polymer after chlorination;

indicate that the process takes place by a mechanism with elimination in an extent of 21.1% for PVC^{36}Cl A and of 61% for PVC^{36}Cl B. In this calculation was not considered the possibility for radioactive chlorine to return in the polymer. This would lead to an increase of the values mentioned above.

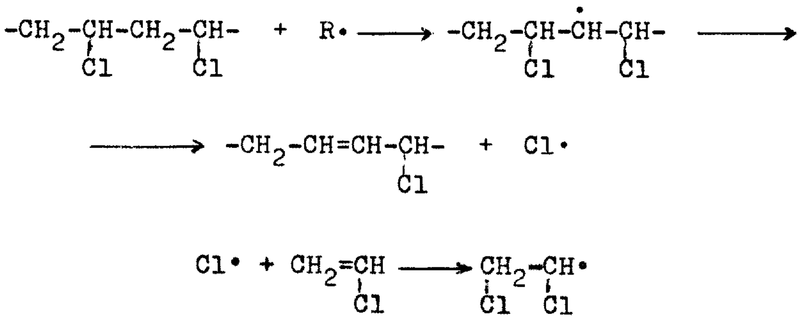
It may be seen that with increasing the chlorination degree, the proportion of mechanism with elimination increases, too.

It is very propbably that the temperature of reaction will influence the course of reaction by one or other of mechanisms.

In conclusion, we proved experimentally that the chlorination reaction of the polyvinylchloride proceeds at least partially by a step of elimination of chlorine followed by its readdition to the formed double bond.

The increase of chlorination extent determines the grouth of the elimination in the chlorination mechanism.

Extending the above results on the polymerization of vinyl chloride, the following schema could be formulated for the chain transfer to polymer:



$$\mathrm{-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-} \quad + \quad \mathrm{R\cdot} \longrightarrow \mathrm{-CH_2-\underset{Cl}{CH}-\dot{C}H-\underset{Cl}{CH}-} \longrightarrow$$

$$\longrightarrow \mathrm{-CH_2-CH=CH-\underset{Cl}{CH}-} \quad + \quad \mathrm{Cl\cdot}$$

$$\mathrm{Cl\cdot} + \mathrm{CH_2=\underset{Cl}{CH}} \longrightarrow \mathrm{\underset{Cl}{CH_2}-\underset{Cl}{CH}\cdot}$$

In this way the formation of isolated double bonds on the polymer backbone without emitting of hydrogen chloride is explained by means of chain transfer to polymer.

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