CHEMICAL AND MOLECULAR STRUCTURE OF POLY(VINYL CHLORIDE)

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Abstract - Poly(vinyl chloride) presents a number of defects per 1,000 monomer units (m.u.), as follows: 4 - 6 chloromethyl branches; 0.4 - 2.4 chloroethyl branches; 0.4 - 1.6 butyl branches (uncertain value); 0.18 - 2.4 long branches (uncertain value); 6 - 7 head-to-head structures (uncertain value); 1.4 - 3 total double bonds; 0.07 - 0.27 internal double bonds. The structure of internal unsaturation as allylic and ketochloroallylic chlorides is discussed. Labile chlorine atoms, 0.6 - 2.5 per 1,000 monomer units, were found, from which: 0.5 - 2.5 allylic chlorine (Cl_A) or ketochloroallylic chlorine (Cl_{COA}) and 0.16 - 1 chlorine at tertiary carbon (Cl_T) (uncertain value). A general mechanism is proposed which explains the formation of unsaturated groups found in ^1H NMR and ^{13}C NMR spectra. During polymerization some defects can undergo further transformations. The chlorination process of poly(vinyl chloride) involves partially the chlorine addition reaction to the intermediary formed double bond. Raman spectroscopy supplies comparative data with NMR and IR regarding the chain configuration. Rotation isomery and its consequences upon the reactions of the poly(vinyl chloride) in solide state are discussed.

This paper presents the main worldwide progresses which have been made since the last International Symposium on PVC in Lyon (1976), towards the elucidation of the chemical and molecular structure of this polymer.

Branching

In 1977 it seemed that with the works published by Rigo (1), Abbas (2) and Bovey (3), the branching problem has been elucidated, as it was established that the preponderent structure of branchings is of chloromethyl type, $-CH_2-CHCl-CH(CH_2Cl)-CH_2-$. This structure is repeated on the macromolecular chain with a frequency of 5 branches per 1,000 monomer units (5/1,000 m.u.) along with a low frequency of long branches, about 0.5/1,000 m.u. (Ref.4). The main direct data were based on ^{13}C NMR measurements on PVC reduced with lithium aluminum hydride ($LiAlH_4$).

Analysing by gas chromatography the products formed as a result of the γ-radiolysis of polyethylene obtained by $LiAlH_4$ reduction of PVC, Schröder and Byrdy (5 & 6) reported that in emulsion polymerization intramolecular 1,5 transfer leading to the formation of butyl branches is more pronounced than in bulk or suspension polymerization, and this fact could explain the higher concentration of butane found in the radiolysis products.

Later on Starnes (7) demonstrated that the reduction with $LiAlH_4$ presents serious disadvantages caused by the incomplete removal of chlorine, by the lack of reproductibility and side reactions leading to supplementary double bonds, as well as by the appearance of some ^{13}C NMR signals of unknown origin. A NS_2 mechanism was proposed, in which the reaction rate of different chain segments is not equal. Monade CHCl group reacts 3.8 times faster with $LiAlH_4$ than r-dyade CHCl group. This behaviour was explained by the diffe-

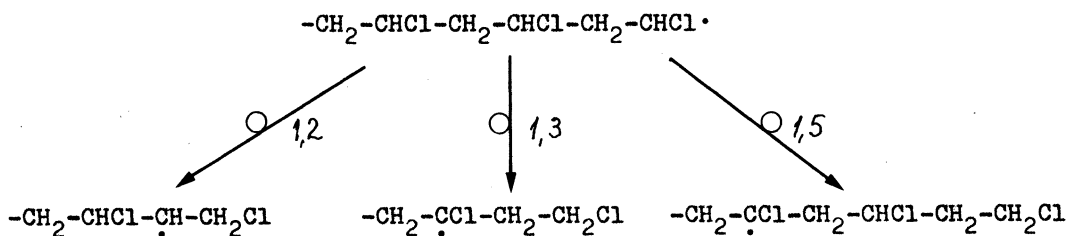rence of the configuration of the transition state.

The hypothesis of the formation of a transition complex, which was not possible to be proved in earlier works (Ref.8), is supported by our observations (Ref.9). Thus, by mixing clear solutions of PVC and $LiAlH_4$ in tetrahydrofuran (THF), under inert atmosphere, we separated the complex PVC - - $LiAlH_4$, insoluble in THF but decomposed by acids. The fact that this complex is very unstable when heated, generating polyolefins, supports the arguments regarding the formation of suplementary double bonds during the reduction of PVC.

To avoid these disadvantages, Starnes (7) came up with new arguments in favour of the reduction of PVC with tri-n-butyltin hydride (Bu_3SnH). The new measurements on branching under these conditions modified somewhat the previous knowledge. According to recent data the following branchings could be identified (Ref.10 & 11): 1 - 2.4 long branches/1,000 m.u.; 0.4 - 2.4 chloroethyl branches/1,000 m.u.; 4 - 6 chloromethyl branches/1,000 m.u.; 0.4 - - 1.6 2,4-dichlorobutyl branches/1,000 m.u. (uncertain value).

Unfortunately, a series of doubts on the new reduction method with Bu_3SnH has appeared. Analysing the products resulted from γ-radiolysis of polyethylene obtained in this way, Bowner (12) found a strong increase of butane concentration, that supports the existence of side butylation reactions.

The results obtained by Schwenk (13) on low molecular PVC fractions catalytically reduced, at 200 at, with Ni Raney, followed by NMR measurements, supports partially the results obtained by the measurements performed on PVC reduced with metallic hydrides. The extrapolation of these results to normal PVC leads to values which are comparable with those presented above, except that regarding the ethyl branches.

The mechanism proposed for the formation of branches (Ref.5 & 11) including a "backbitting" internal transfer of hydrogen from α , β or δ positions inside the head-to-tail macroradical:

$$-CH_2-CHCl-CH_2-CHCl-CH_2-CHCl\cdot$$

$$1,2 \qquad\qquad 1,3 \qquad\qquad 1,5$$

$$-CH_2-CHCl-CH-CH_2Cl \qquad -CH_2-CCl-CH_2-CH_2Cl \qquad -CH_2-CCl-CH_2-CHCl-CH_2-CH_2Cl$$

could not be proved for the formation of chloromethyl groups (Ref.14). But it should be taken into account the fact that in the case of internal 1,3 and 1,4 transfers, the situation is somewhat different, since radicals more stable than in the case of 1,2 transfer are formed.
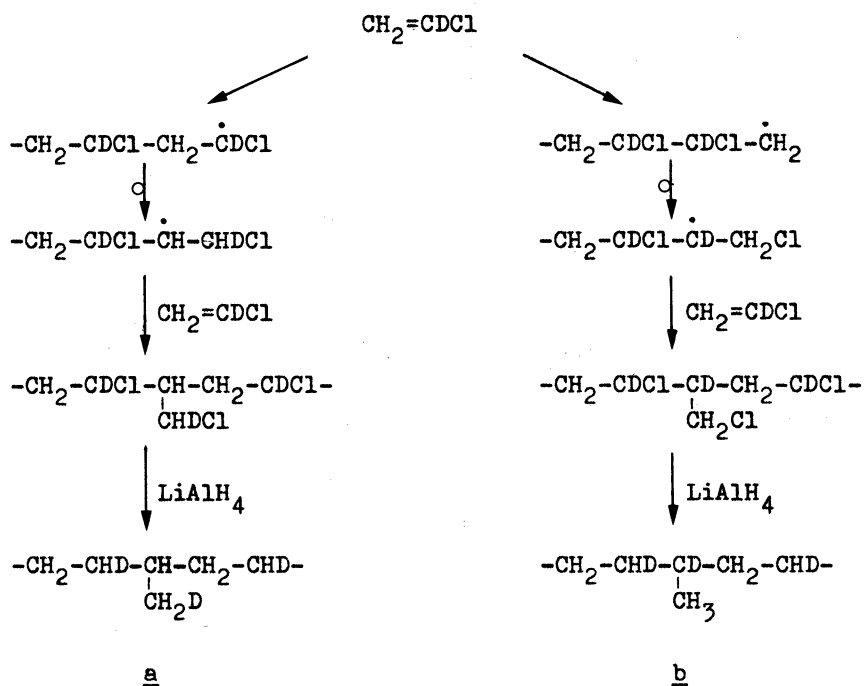
If these doubts will be eliminated, the detection by ^{13}C NMR spectroscopy of up to 2.4 long branches/1,000 m.u. (Ref.10) or of 0.18 - 1.5/1,000 m.u. by viscometry (Ref.15), which might contain chlorine at the tertiary carbon of branching (Ref.10), reopens the problem of the contribution of these structure types to the initiation process of PVC destruction. The above values are comparable with that of the allylic chlorine possibly to be bound to 1.5 - 3.0 double bonds/1,000 m.u. found in PVC (Ref.16 - 18). In this case it will be necessary to clarify more precisely to which type of structure belongs the labile chlorine (Cl_L), about 2.0/1,000 m.u. determined by phenolysis (Ref.19) or 0.4 - 3 determined by thyophenolysis (Ref.20).

Regarding the appearance of long branches, we tried to come up with new arguments (Ref.9) that would render evident the self-grafting process of PVC. Thus, a low molecular weight PVC fraction, soluble in benzene, has been labelled with 36-chlorine isotope (^{36}Cl) and reintroduced in the polymerization process of vinyl chloride. After the completion of the polymerization, the labelled fraction has been extracted with benzene, without the finding of any supplementary shifting of the radioactivity towards higher molecular

weights, in comparison with the control sample, where the labelled fraction was mixed with similar PVC by co-precipitation. Even in the case of a single grafting on the macromolecule, one should have observed a pronounced shifting of the molecular weight to higher values.

From all these facts one can conclude that the possible long branches are probably formed by copolymerization of the monomer with different unsaturated end groups, as experimentally demonstrated (Ref.21). In this case the presence of chlorine atom at the branching point is not always obligatory.

The validity of the mechanism suggested by Rigo (1), regarding the formation of short branches as a result of the head-to-head collision, has been elegantly demonstrated experimentally by Starnes (14) who investigated the structure of short branches formed during the polymerization of α-deutherated-vinyl chloride.

$$CH_2=CDCl$$

-CH$_2$-CDCl-CH$_2$-ĊDCl

-CH$_2$-CDCl-ĊH-CHDCl

    ↓ CH$_2$=CDCl

-CH$_2$-CDCl-CH-CH$_2$-CDCl-
    |
    CHDCl

    ↓ LiAlH$_4$

-CH$_2$-CHD-CH-CH$_2$-CHD-
    |
    CH$_2$D

__a__

-CH$_2$-CDCl-CDCl-ĊH$_2$

-CH$_2$-CDCl-CD-CH$_2$Cl

    ↓ CH$_2$=CDCl

-CH$_2$-CDCl-CD-CH$_2$-CDCl-
    |
    CH$_2$Cl

    ↓ LiAlH$_4$

-CH$_2$-CHD-CD-CH$_2$-CHD-
    |
    CH$_3$

__b__

The exclusive formation of the __b__ type structure, evidenced in ^{13}C NMR spectra, confirms the Rigo's mechanism (Ref.1)i.e. that starting from accidental head-to-head structures.

Head-to-head structures
These structures have drawn scientists'attention since long time (Ref.22 & & 23), but their close similarity with the normal structure of the PVC makes difficult the investigations. Thus, except the rather old work of Mitani (24) which indicates 6 - 7 head-to-head structures/1,000 m.u., there is not other paper to bring new evidences on this matter.

Indirect informations have been obtained using macromolecular models synthesized by chlorination of 1,4-polybutadiene. Crawley (25) demonstrates that head-to-head structures have important effects on the dehydrochlorination process. Therefore, more efforts should be done to improve the direct methods for the investigation of these structures.

Unsaturation
Recent investigations continue to bring new evidences which confirm the hypotheses of the important role played by unsaturated structures on the PVC stability.
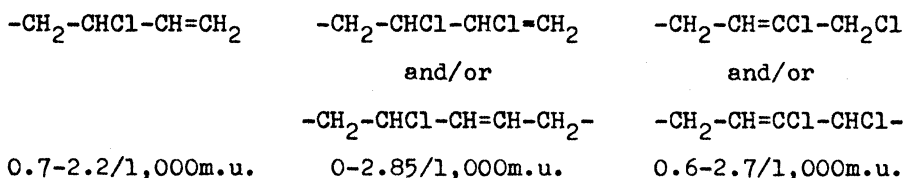
Total unsaturation. The main direct method to estimate the total unsatura-
tion is that of bromination. The determined values are in the range of
1.5 - 3 double bonds/1,000 m.u. (Ref.26).

Recently a new method based on the ozone absorption by solid PVC cast as a
thin layer on aerosyl has been developed (Ref.27). The values given by this
method are comparable with that determined by bromination.

The above mentioned chemical methods give only an information regarding the
double bonds content, but they do not allow us to obtain any indication on
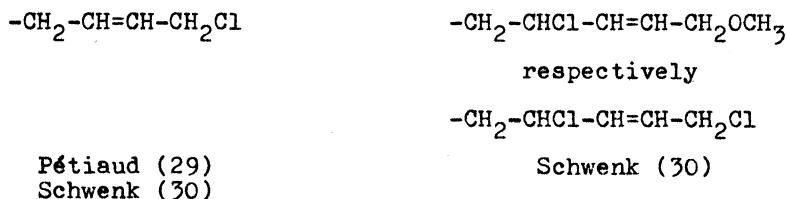their structure.

Continuing our investigations on unsaturated structures by ^{1}H NMR method,
we tried to apply the results obtained on model compounds to the PVC (Ref.28).

Using FT ^{1}H NMR technique we found a series of very low signals at 5.35;
5.55; 5.95; 5.68 and 5.78 ppm. The first three signals which were somewhat
stronger could be assigned to the following structures, respectively:

$-CH_2-CHCl-CH=CH_2$ $-CH_2-CHCl-CHCl=CH_2$ $-CH_2-CH=CCl-CH_2Cl$

                                  and/or   and/or

                             $-CH_2-CHCl-CH=CH-CH_2-$ $-CH_2-CH=CCl-CHCl-$

0.7-2.2/1,000m.u.   0-2.85/1,000m.u.   0.6-2.7/1,000m.u.

Owing to the low concentration, the measuring difficulties, as well as the
possibilities of partial interference with $^{13}CHCl$ signals, these results
should be considered for the time being only as a begining. Future develop-
ments of measuring techniques for weak NMR signals are expected to give more
precise informations.

Using the same method, other authors (Ref.29 & 30) tried to increase the
precision, by measuring of only low molecular fractions which present a hi-
gher degree of unsaturation. They were able to evidence signals assigned to
the following structures:

$-CH_2-CH=CH-CH_2Cl$ $-CH_2-CHCl-CH=CH-CH_2OCH_3$

                                           respectively

                                       $-CH_2-CHCl-CH=CH-CH_2Cl$

        Pétiaud (29)   Schwenk (30)
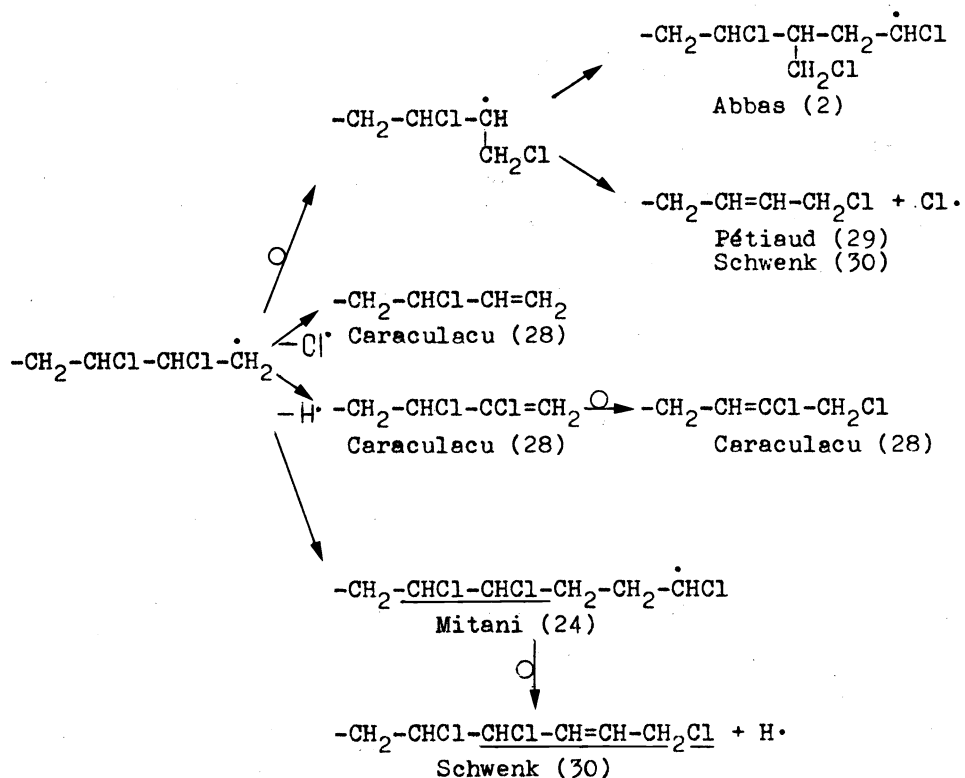   Schwenk (30)

NMR signals thus observed came with more probability from the unsaturation
at the end of the chain, as the concentration of the internal unsaturation
is too low to be deceleated by this technique (Ref.16 & 18).

The internal unsaturation determined on polyethylene obtained by reduction
of PVC with $LiAlH_4$, using ^{1}H NMR, ^{13}C NMR and IR techniques, must be cautio-
nary considered, due to the possibility of formation of additional double
bonds by side reactions during the reduction process (Ref.7).

In the case of reduction with Bu_3SnH followed by ^{13}C NMR measurements,
Starnes et al. (7) found too low values, under 1 double bond/1,000 m.u.,
which can not be correlated with the values found on other ways. The authors
do not exclude the possibility of the disappearance of double bonds by side
reactions during the reduction process.

Regarding the formation of the above mentioned unsaturated structures obser-

ved by us and by other authors, a reaction scheme has been proposed, starting from the hypothesis that defects of this type appear from unstable radicals resulted from accidental head-to-head collisions (Ref.31).

$$-CH_2-CHCl-\overset{\cdot}{C}H-CH_2-\overset{\cdot}{C}HCl$$
$$\underset{CH_2Cl}{|}$$
Abbas (2)

$$-CH_2-CHCl-\overset{\cdot}{C}H$$
$$\underset{CH_2Cl}{|}$$

$$-CH_2-CH=CH-CH_2Cl \; + \; Cl\cdot$$
Pétiaud (29)
Schwenk (30)

$$-CH_2-CHCl-CH=CH_2$$
Caraculacu (28)

$$-CH_2-CHCl-\overset{\cdot}{C}HCl-CH_2$$

$\overset{O}{\diagup}$

$\underset{Cl\cdot}{\diagup}$

$-H\cdot$

$$-CH_2-CHCl-CCl=CH_2 \overset{O}{\longrightarrow} -CH_2-CH=CCl-CH_2Cl$$
Caraculacu (28)   Caraculacu (28)

$$-CH_2\underline{-CHCl-CHCl}-CH_2-CH_2-\overset{\cdot}{C}HCl$$
Mitani (24)

$\overset{O}{\downarrow}$

$$-CH_2-CHCl\underline{-CHCl}-CH=CH-\underline{CH_2Cl} \; + \; H\cdot$$
Schwenk (30)

Internal double bonds. The ozonolysis method (Ref.18), continues to give valuable information on internal double bonds. Thus recent determination shows an amount of the concentration of 0.09 - 0.27 internal double bonds//1,000 m.u. (Ref.16).

On the basis of a complex consideration, starting from kinetical measurements of dehydrochlorination of PVC and Onozuka's observations (32) regarding the oxidation of chlorinated derivatives, as well as on the basis of extrapolation of certain reactions of $P(OR)_3$ on small molecule compounds, Minsker (33 - 35) elaborated the hypothesis that internal unsaturated groups do not have a simple chloroallylic structure as it was proposed by the majority of authors. In his opinion the chloroallylic structures appeared in the first stage are rapidly oxidized into carbonyl-chloroallylic structures (Ref.33 & 35) -CO-CH=CH-CHCl-.

These structures are very unstable and they could be exclusively the initiation point of PVC dehydrochlorination. In his opinion, which could be hardly accepted, allylic chlorides and other labile structures would not influence the stability of the PVC (Ref.33 - 35).

Taking into account the scission of ketovinylic structures as a result of the alkaline hydrolysis, the same author developed a method for the quantitative analysis of ketochloroallylic structure based on the variation of the molecular weight brought about by the hydrolytic scission. The method is based on the hypothesis that the usual chloroallylic structures are stable at this treatment.
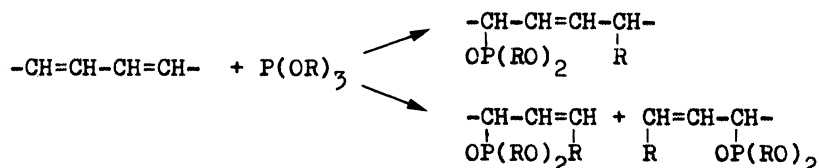
In the case of usually manufactured PVC the number of scissions obtained by ozonolysis and that found by hydrolysis are practically the same, indicating that the hypothesis of the exclusive presence of ketochloroallylic structures is right. In the case of the PVC synthesized and treated in the total absence of the oxygen, the values are quite different, most of the structu-

res being chloroallylic (Ref.16).

However, two problems remain to be answered. First, why the model substances consisting of 4-chlorohexene-2, together with its transposed derivative 2-chlorohexene-3, are not oxidized to corresponding ketochloroallylic structures even after one year of standing in air or oxygen, since only a partial dehydrochlorination and the consequent formation of the hexadiene has been observed (Ref.9). Second, to what extend the alkaline hydrolytic scission is peculiar only to ketochloroallylic structures supposed to be present.

It seems interesting other oxidated structures to be taken into consideration, such as hydroperoxidic groups containing structures which could explain the absence of the characteristic carbonyl band in the IR spectra. It is expected that such a structure to be transformed by hydrolysis into ketonic group and subsequently the neighbouring C=C double bonds to be broken bringing about the diminution of the molecular weight.

Polyenic structures. When polyenes are reacted with $P(OR)_3$, Minsker et al. (33) shows that there are two possible reactions:

$$-CH=CH-CH=CH- \ + \ P(OR)_3 \ \left\langle \begin{array}{l} -CH-CH=CH-CH- \\ \ \ \ \underset{OP(RO)_2}{|} \qquad \underset{R}{|} \\ \\ -CH-CH=CH \ + \ CH=CH-CH- \\ \ \underset{OP(RO)_2}{|}\underset{R}{|} \qquad \underset{R}{|} \qquad \underset{OP(RO)_2}{|} \end{array}\right.$$
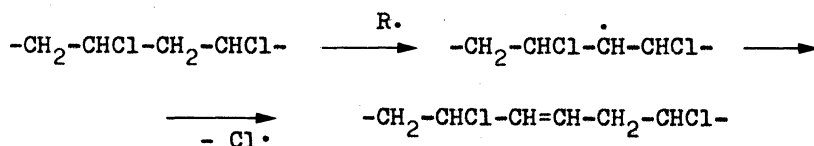
In both cases, after this treatment and subsequent ozonolysis, the macromolecular chain is broken. From the preservation of the molecular weight of the polymer after these succesive treatments Minsker et al. concluded that freshly synthesized PVC did not contain polyenic structures (Ref.33).

Verdu et al. (36) improved the UV methods for the determination of polyenic structures by measurement of the transmittance before and after photooxidative destruction of polyenes. Very low values of polyenes of the order of 4×10^{-4} tetrades/1,000 m.u., and even much lower values for longer polyenic sequences in different PVC samples, are precisely determined from the difference of these two transmittances.

Recently Dobrescu et al. (37) established a new method for the investigation of the PVC stability based on the modification of absorptions from electronic spectra, due to the formation of polyenic sequences, which appear by heating during DSC analysis of the polyenes. In this way the precision of the analysis has been significantly enhanced.
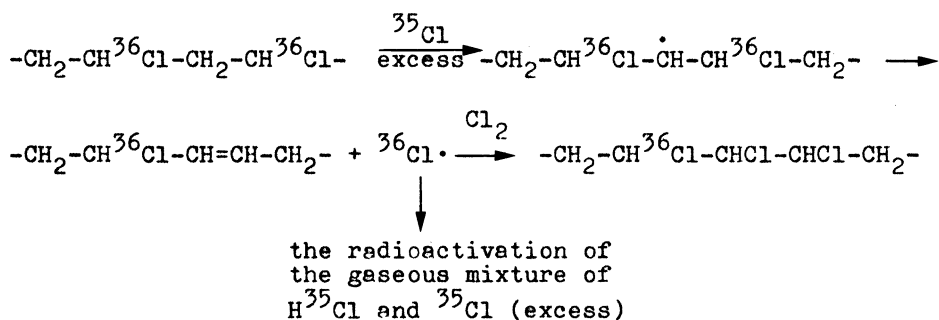
Regarding the way in which the double bonds can appear on the PVC backbone we believe that they are formed during the polymerization as a consequence of the transfer reaction to the polymer, as follows (Ref.31):

$$-CH_2-CHCl-CH_2-CHCl- \ \xrightarrow{\ R\cdot\ } \ -CH_2-CHCl-\overset{\cdot}{C}H-CHCl- \ \longrightarrow$$

$$\xrightarrow[-\ Cl\cdot]{} \ -CH_2-CHCl-CH=CH-CH_2-CHCl-$$

As shown by Kolinsky et al. (38), the radicalic attack on PVC in the case of chlorination occurs to a large extent at $-CH_2-$ group, generating in the first step a $-\overset{\cdot}{C}H-$ type radical. According to our observations (Ref.39), as shown above, such a radical expels the neighbouring chlorine atom forming an internal double bond. During the chlorination process this step can not be observed due to the addition of excess chlorine molecule at the just formed double bond.

In order to verify this mechanism we used a radioactive chlorine (^{36}Cl) la-

belled PVC which was chlorinated in a closed vessel with a certain amount in excess of non-radioactive chlorine (^{35}Cl). Subsequent to the reaction the gaseous mixture, i.e. excess of chlorine and hydrochloric acid formed, was collected and a significant amount of radioactive chlorine (^{36}Cl) originating from the PVC chain has been evidenced in it. The following series of reactions could explain the radioactivation of the post-reaction gaseous mixture (Ref.40).

$$-CH_2-CH^{36}Cl-CH_2-CH^{36}Cl- \xrightarrow[\text{excess}]{^{35}Cl} -CH_2-CH^{36}Cl-\overset{\bullet}{C}H-CH^{36}Cl-CH_2- \longrightarrow$$

$$-CH_2-CH^{36}Cl-CH=CH-CH_2- + \ ^{36}Cl\cdot \xrightarrow{Cl_2} -CH_2-CH^{36}Cl-CHCl-CHCl-CH_2-$$

$$\downarrow$$

the radioactivation of
the gaseous mixture of
$H^{35}Cl$ and ^{35}Cl (excess)

Ketonic groups

It has been shown by Bauer and Sabel (41) that carbon oxide is formed when vinyl chloride is polymerized in presence of air oxygen, according to the following reactions:

$$-CH_2-\overset{\bullet}{C}HCl + O_2 \longrightarrow -CH_2-CHCl-O-O\cdot \longrightarrow CH_2O + HCl + CO + R\cdot$$
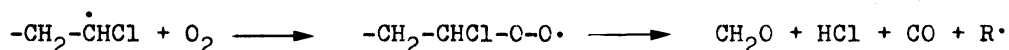
Starting from this observation Braun and Wolf (42) demonstrated practically that carbon oxide could copolymerize with vinyl chloride leading to unstable carbonyl structures in the PVC chain, evidenced in IR spectra by absorption maxima between 1710 and 1740 cm^{-1}.

$$-CH_2-CHCl-CO-CH_2-CHCl-$$
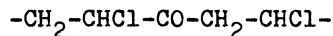
Minsker et al. considers that all internal chloroallylic structures are spontaneously oxidized forming ketochloroallylic groups which should be observed in IR spectra at 1600 and 1675 cm^{-1}, bands characteristic to mutually conjugated CO and vinyl groups, respectively (Ref.33 & 35). These bands should be visible at the concentration indicated by Minsker et al.

Several authors tried to determine the content of CO groups in PVC samples obtained industrially or in laboratory (Ref.43 & 44). The results of the investigations carried out on industrially manufactured PVC are not conclusive due to the possibility of the overlaping of the carbonyl band with bands pertaining to the initiator or other different additives used in the polymerization process.
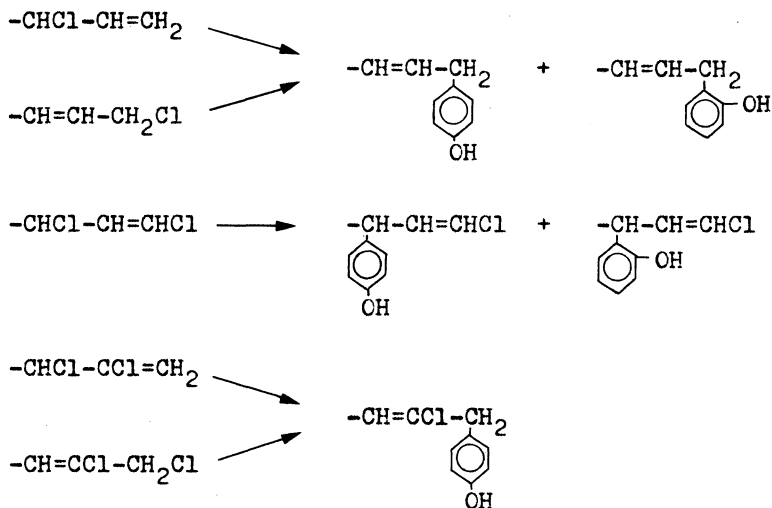
The investigations carried out by different authors on identical samples supplied by IUPAC Working Party on PVC Defects, evidenced the existence of CO groups. However there are large differences between the results obtained by different authors, so that a certain conclusion can not be drawn yet (Ref. 43 & 44).
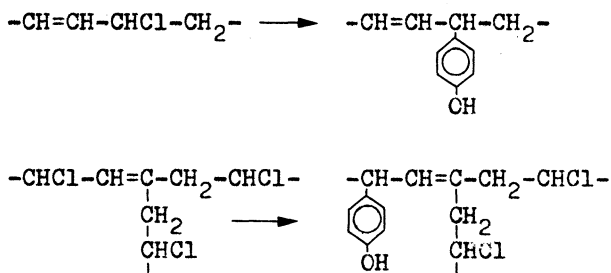
Total labile chlorine

As generally admitted, the dehydrochlorination process starts at different structural defects which contain labile chlorine atoms (Cl$_L$), able to be broken and to initiate the chain reaction. Some time ago, we succeeded in

establishing a method for evidencing of these structures by phenol selective reaction which has been verified both on tertiary and allylic chlorides considered as model substances (Ref.19 & 45). Different types of Cl_L containing structures react with phenol according to the following scheme (Ref. 46):
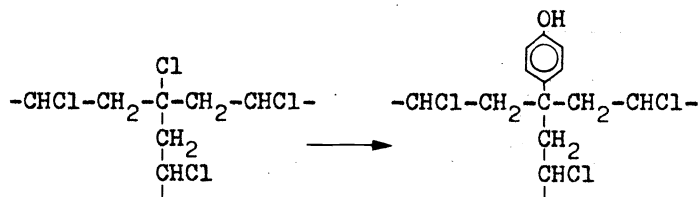
Unsaturated end groups:

$-CHCl-CH=CH_2$

$-CH=CH-CH_2Cl$

$\longrightarrow$

$-CH=CH-CH_2$ (with phenol ring, OH para) + $-CH=CH-CH_2$ (with phenol ring, OH ortho)

$-CHCl-CH=CHCl \longrightarrow$ $-CH-CH=CHCl$ (with phenol ring, OH para) + $-CH-CH=CHCl$ (with phenol ring, OH ortho)

$-CHCl-CCl=CH_2$

$-CH=CCl-CH_2Cl$

$\longrightarrow$

$-CH=CCl-CH_2$ (with phenol ring, OH para)

Unsaturated internal groups:

$-CH=CH-CHCl-CH_2- \longrightarrow$ $-CH=CH-CH-CH_2-$ (with phenol ring, OH)

$-CHCl-CH=C-CH_2-CHCl-$
        $|$
       CH_2
       $CHCl$
$\longrightarrow$
$-CH-CH=C-CH_2-CHCl-$ (with phenol ring, OH)
        $|$
       CH_2
       $CHCl$

Branching:

        Cl
       $|$
$-CHCl-CH_2-C-CH_2-CHCl-$
       $|$
      CH_2
      $CHCl$
$\longrightarrow$
      (phenol ring, OH)
$-CHCl-CH_2-C-CH_2-CHCl-$
       $|$
      CH_2
      $CHCl$

Taking into consideration the fact that in all these reactions the labile chlorine was entirely substituted by a phenol rest, a new quantitative analytical method has been developed for the measuring of Cl_L by UV determination of the number of aromatic rings attached after phenolysis.

The correlation of the number of total double bonds found by bromination with the number of Cl_L atoms determined by phenolysis supports the hypothesis that most of Cl_L atoms are of chloroallylic nature, or according to Minsker et al. of ketochloroallylic nature (Table 1),(Ref.9).

TABLE 1. Content of double bonds and labile chlorine atoms

No.	Double bonds/1,000 m.u.	Cl_L atoms/1,000 m.u.
1	1.47	1.17
2	3.05	2.50
3	1.97	1.58
4	2.05	1.24
5	1.53	0.55
6	1.48	0.57
7	1.51	0.96
8	1.80	0.76

As recently shown by Bovey et al. (2 & 10) and by us (Ref.9) the presence of the labile chlorine in the ramification points of long PVC branches is not excluded but their concentration is generally small.

Chlorine on tertiary carbon and allylic chlorine

By bromination of PVC its double bonds are saturated and consequently chloroallylic (Cl_A) structures disappear. If a brominated PVC is subjected to analysis by phenolysis, it is expected that the small concentration of structures containing a chlorine atom bound to the carbon atom bearing long branches to be put in evidence (Cl_T).

Indeed, applying this method to a series of 8 samples we obtained the results listed in Table 2 (Ref.47).

TABLE 2. Content of different types of labile chlorine in PVC correlated with the concentration of long branches

No.	Cl_L atoms/ /1,000m.u. (phenolysis)	Cl_T atoms/ /1,000m.u. (phenolysis after bromination	Long branches/ /1,000m.u. viscometry, (Ref.15)	Cl_A atoms/ /1,000m.u. ($Cl_L - Cl_T$)	Cl_A atoms/ /1,000m.u. ($SO^{36}Cl_2$)
1	1.17	0.18	0.18	0.99	0.89
2	2.51	1.17	1.50	1.34	2.15
3	1.58	0.48	0.15	1.10	1.34
4	1.64	0.28	0.94	1.36	0.59
5	0.56	0.27	0.38	0.29	0.80
6	0.57	0.16	0.46	0.41	0.53
7	0.96	0.47	0.62	0.49	0.88
8	0.76	0.18	0.18	0.58	0.97

The somewhat lower values of the tertiary carbon bound chlorine in comparison with the concentration of long branches could be explained either by the fact that not every long branch has a chlorine atom at the tertiary carbon atom or by analytical differences.

Based on ^{13}C NMR measurements, Bovey et al. (10) concluded that a small number of long branches, containing chlorine at the ramification point, could be detected, observation which is supported by the comparison of Cl_T values with the frequence of the appearance of long branches in PVC, Table 2.

Regarding Cl_A we succeeded to find for this kind of chlorides a selective isotopic exchange reaction through the agency of radioactive $SO^{36}Cl_2$. The values obtained for a series of PVC samples are comparable, in the error limits, with that obtained by phenolysis. This fact proves that with few exceptions most of the labile chlorine is of allylic type (Ref.48).

Using thiophenol instead of phenol Michel et al. (20) found a new selective reaction which takes exclusively place with allylic chlorides and not with tertiary chlorides. A single kind of products of thioetheric structure is formed, as follows:

$$-CH=CH-CHCl- \quad + \quad \text{(SH-phenyl)} \quad \longrightarrow \quad -CH=CH-CH- \quad + \quad HCl$$
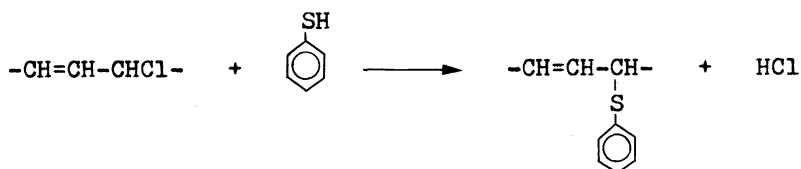
In the usual PVC the obtained values are of the order of 1.53 - 2.54 Cl_A/ /1,000 m.u. while for benzene soluble low molecular PVC fraction the value is higher, i.e. 3.07 Cl_A/1,000 m.u.

Parasite structures of the second generation

Generally, the studies made till now developed successfully different methods for the detection of certain structural defects which were primarily assumed, in most cases, on the basis of logical theoretical considerations. These considerations usually end with the formation of certain primary structures,without any assumption on the fact that,once formed, these structures remain in the reaction medium until the polymerization is over and that consequently could undergo different transformations, which could be denominated as transformations of the second generation.

In order to verify the possibility of these transformations we started with the investigation of the behaviour of certain unsaturated group models at an intense radicalic attack generated by a large amount of initiators (Ref.39). We found that in stainless steel vessels all the models are transformed forming a mixture of very complex derivatives, while in glass vessels vicinally substituted unsaturated structures of the type

$$R-CH=CH-R' \quad and \quad R-CH=C\begin{cases} R' \\ R'' \end{cases}$$
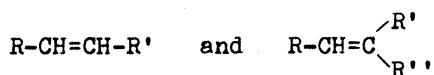
such as 1,3-dichloro-1-pentene, 1,4-dichloro-1-pentene, 1,1-dichloro-2-pentene, 1,2-dichloro-2-pentene and 1-chloro-2-pentene do not react.

Unsymmetrically substituted unsaturated end groups could be more or less transformed during the polymerization, as a result of the radicalic attack, in the following structures shown in Table 3 (Ref.31).

We consider that in industrial conditions, at large reaction volumes, the influence of the metallic wall is very much diminished, so that the conditions are similar to that from the glass vessel.

In the second stage we studied with the aid of model substances the behaviour of these defects in the conditions of a normal polymerization. In this manner we found that 3-chloro-1-pentene, 2,4-dichloro-1-pentene and 4-chloro-1-pentene models could copolymerize with the vinyl chloride (Table 3), (Ref.2).

The inhibition effect and the molecular weight decrease observed in the case of 2,4-dichloro-1-pentene were explained by the possibility of the appearance of internal abnormal structures, presented in Table 3, which interrupt the growth of the macromolecule (Ref.21 & 49).

We are now confronted with a new phenomenon, which indicates that at the vinyl chloride polymerization certain internal structures leading to autoinhibition of the polymerization process could appear, without the interference of any other strange agent.

It is possible that the rate of these transformations, which may occur pro-

bably in a heterogeneous medium, after the coming out of PVC from solution, is low. However, even if these defects do not call our attention from the begining, they should be taken into account for the general discussion of the problem.
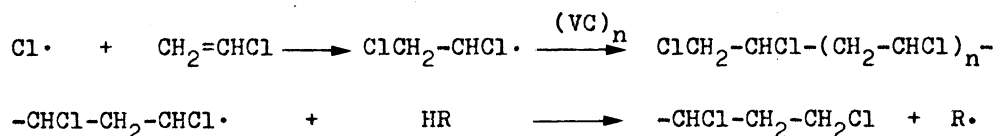

TABLE 3. Structural defects of the second generation in PVC

Unsaturated end groups	Possible transformation products	
	Long branches	Abnormal internal structures
$-CH_2-CHCl-CCl=CH_2$	–	$-CH_2-CCl=CH-CH_2-$
$-CH_2-CHCl-CH=CH_2$	$-CH_2-CH-CH_2-$ $\quad\quad\mid$ $\quad\quad CHCl$ $\quad\quad\mid$ $\quad\quad Cl$	$-CH_2-CH=CH-CH_2-$
$-CH_2-CHCl-CH_2-CCl=CH_2$	$-CH_2-C-CH_2-$ $\quad\quad\mid$ $\quad\quad CH_2$ $\quad\quad\mid$	$-CH_2-CHCl-CH_2-CCl=CH-CHCl-CH_2-$
$-CH_2-CHCl-CH_2-CH=CH_2$	$-CH_2-CH-CH_2-$ $\quad\quad\mid$ $\quad\quad CH_2$ $\quad\quad\mid$	

Saturated end groups

In general, these structures were less studied because of the unanimous supposition that they have a smaller influence upon the PVC stability. We will mention here only two NMR works (Ref.7 & 29). Thus, with the aid of measurements of FT ^{1}H NMR on the PVC fractions of low molecular weight, Pétiaud and Pham (29) found a signal which could be assigned to 1,2-dichloroethyl type structure. In a more recent paper Starnes et al. (Ref.7) confirmed with the aid of ^{13}C NMR spectra the existence of these saturated end groups together with other saturated end groups of 1,3-dichloropropane type, the last one being in a lower concentration.

The scheme which could explain the appearance of these two structures is as follows:

$$Cl\cdot \quad + \quad CH_2=CHCl \longrightarrow ClCH_2-CHCl\cdot \xrightarrow{\ (VC)_n\ } ClCH_2-CHCl-(CH_2-CHCl)_n-$$

$$-CHCl-CH_2-CHCl\cdot \quad + \quad HR \quad \longrightarrow \quad -CHCl-CH_2-CH_2Cl \quad + \quad R\cdot$$

Initiator fragments and transfer agents

Few investigators paid attention to this problem. Thus, Stanaback (50) studied the effect of various halogenated derivatives as transfer agents regarding their capacity as chain regulators. The fragments of the transfer agents at the ends of the macromolecules were not directly evidenced, but their presence could be ascertained by viscometry. Halogenated derivatives, such as pentabromomethan, carbon tetrabromide, dibromodichloromethane, bromodichloromethane, and dibromotetrachloroethane, are easily fixed at PVC ends by transfer reactions in comparison with trichloroethylene, taken as standard derivative.

It seems interesting to study the effects of these groups upon the PVC stability, since their reactivity is much different than that of other known

structures in PVC.

Tacticity

In the last time the interest upon the PVC tacticity decreased, this fact being explained to a great extend by difficulties met in the solution of this problem.

Sörvik (51) presents an extensive comparative study upon the quantitative determination of the PVC tacticity, getting to the conclusion that NMR spectroscopy is a more precise tool for these measurements that IR or Raman spectroscopy. For quantitative determination the NMR spectra of methylenic group were graphically solved in six bands which were assigned to syndiotactic, isotactic and combined sequences, respectively. By comparison of the signal area of syndiotactic bands with the total area, syndiotactic dyades of 0.52 - 0.56 order was obtained. It has been also shown that the decrease of the polymerization temperature leads to a slight increase of the syndiotacticity.

In a more recent paper Robinson et al. (52) tried to improve the known NMR methods for quantitative determination of the tacticity. A series of PVC samples were analysed in different conditions: at 60 MHz with α -proton undecoupled, at 90 MHz with β -proton undecoupled, and at 90 MHz with α - and β -proton decoupled. The authors observed that the reproducibility of the values from different solutions of a given polymer sample is significantly worse than that between a series of runs on a particular solution, showing that sampling errors are larger than those from instrumental sources. Although the 60 MHz spectra were found to be unsatisfactory when interpreted on a first order basis, curve fitting methods gave results of comparable precision to those from the two types of decoupling spectra and superior to those from the undecoupled 90 MHz spectra. The preferred approach is to combine the results from α- and β -proton spectra and to examine more than one solution of a given material. The lack of the reproducibility of the NMR data when different solutions of the same sample are investigated, explained by the difficulty in the detachment of macromolecular aggregates, diminishes somewhat the accuracy of the measurements (Ref.52).

We should also mention the investigations made by Starnes et al. (7), regarding the correlation of the reactivity of chlorine atom from the PVC chain in the reduction reaction with $LiAlH_4$ or Bu_3SnH, where an enhanced stereoselectivity has been observed.

The investigation of the C-Cl stretching vibration region from Raman spectra of PVC, carried out by Robinson et al. (54), points out to a new method for the determination of the polymer tacticity. The region of the C-Cl stretching vibration of the Raman spectrum of the PVC comprises nine Lorentzian maxima partially overlaped. Two of them are attributable to the A_g and B_{3g} species vibrations of crystalline material while the remaining seven may be assigned to specific structure in the amorphous region. Three maxima from these are associated with isotactic configuration and may be used to estimate the polymer tacticity. The values obtained both from Raman and NMR spectroscopy are very close. The advantage of the Raman method in comparison with other spectral methods consists in the fact that no special sample preparation is required, which might alter the conformation content or cristallinity.

In the Martinez and Millán's paper (55), which studied the influence of the tacticity on thermal degradation of PVC, UV-Visible spectroscopy was used to follow the relative tacticity of different samples.

Chain conformation

The studies upon the PVC chain conformation carried out by IR spectroscopy, evidenced the existence of an equilibrium between different rotational structures (Ref.54,56 & 57).

Koenig and Antoon (58), on the basis of the above cited works, published a detailed study on the atactic PVC conformation modifications, measured by FT IR spectroscopy. The modifications of the chain conformation were studied with respect to the "gauche" defects as a function of temperature and recovering capacity. The intensity of the specific bands γ (ClCl) and δ (CH_2) varies with temperature, a fact which allows to calculate the activation e-

nergy of the rotation, similar to the work of Caraculacu (56) on models. Therefore, there were detected the conformational modifications for the cold PVC, due to the annealing produced around the glass transition temperature, T_g.

The investigation of the chain conformation had particularly up to now a theoretical aspect. There are some attempts to put in evidence the reactivity difference of various rotational structures, especially for the labile tertiary chlorine in PVC (Ref.59). As it was observed, the tertiary chlorides are presented as three rotational isomers in equillibrium, belonging to different symmetry types: T'_{CHH}, T_{CHH} and T'_{HHH}.

C₁ symmetry   Cₛ symmetry   C₃ symmetry
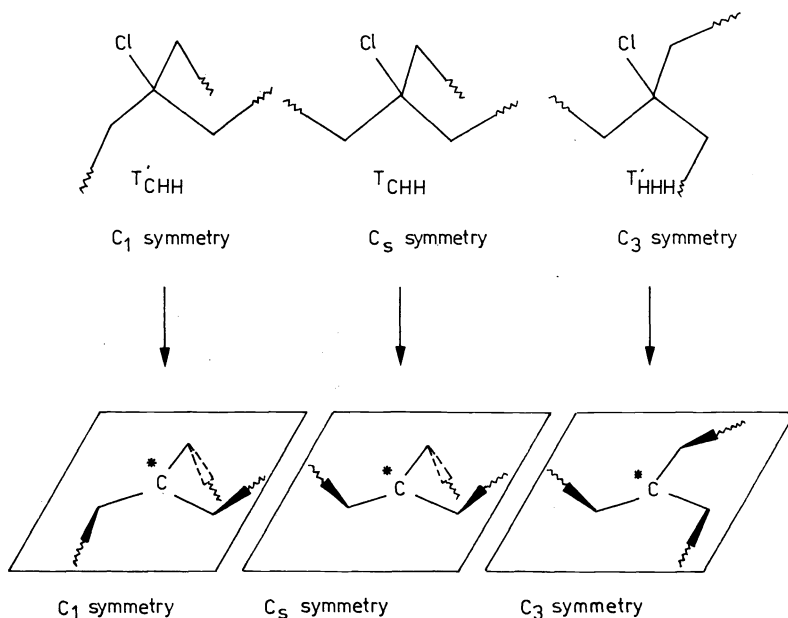
The possibility of the reaction between the chlorine atom and the reactant in the case of solvolysis involving bulky reactants such as phenol or thiophenol varies from structure to structure according to the screening effect on the chlorine atom. At the same time, each isomer will give rise to certain active species, radicals or ions, of different planar structures, as a result of the homolytic and heterolytic dissociation, respectively. The substituents of active species could be situated both on each side of the plane leading to two different symmetries, C_1 and C_s, and on the same side of the plane giving a C_3 symmetry arrangement.

Different screening effects have been observed by kinetical measurements in solvolysis reactions of tertiary chlorides of increasing volume of their substituents. A dramatic change of the screening effect was found when the agents used for solvolysis were of small or large volume, e.g. ethanol-water mixture (80 : 20, v/v) or phenol, respectively. This screening acts effectively both in the dissociation step and the addition to the active species formed. In spite of the fact that both the alcoholysis and the phenolysis proceed by a similar SN_1 reaction, the change of the anchimeric assistance at the alcoholysis and phenolysis, respectively, is illustrated (Fig.1) by the reversal of the slope (value of ρ *) in the plot of the Taft function: $lg(k/k_o) = \sigma * \rho *$

As a consequence of the fast passing from a rotational isomer to another, which occurs in geseous or liquid state in the case of small molecules, the equilibrium concentration of the active species does not significantly a-

ffect the reaction rate.

In the case of macromolecules the change of the backbone conformation by ro-
tation around single bonds is hindered by the lenght of the chains and by
solid state itself. This change is practically prohibited when the polymers
are "frozen" in solid state, but it takes place near the glass transition,
e.g. 80 to cca. 120 ^{o}C for PVC (Ref.58). Even at these temperatures Koenig
and Antoon (58) found that the differences of energetic levels of different
rotational isomers in PVC are 2.5 - 3 times higher than that reported by
Caraculacu for small molecule model substances (56). The "frozen" state of
different conformational structures will certainly influence the oxidation,
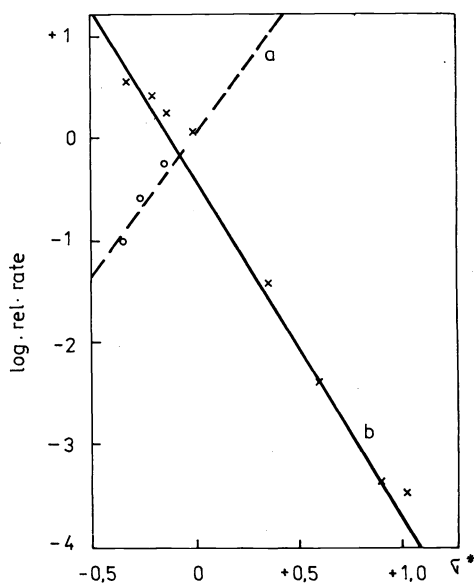destruction and recombination processes that occur at the degradation of PVC
in solid state.

Figure 1. Correlation of solvo-
lysis rate of tertiary halides
with polar substituent constants,
𝔯*: a. phenolysis; b. solvolysis
with 80% ethanol in water

Zipping propagation of the dehydrochlorination will proceed with different
rates in chain domains of different conformations. These phenomena can not
be unfortunatelly mimed using models of small molecules.

Up to now it was not possible to evidence the rotational isomers of various
chloroallylic structures. However, through the agency of stereomodels seve-
ral chloroallylic structures could be imagined, as a result of the combina-
tion of cis-trans double bond isomery and rotational isomery. It is expected
that certain rotations around single bonds to be entirely forbinden by the
voluminous neighbours, such as the chlorine atom, the allylic system or the
remaining part of the macromolecules. Consequently, various isomeric structu-
res could contribute in a different way to thermal or oxidative degradation
of the polymer. We believe that all these transformations occuring at the
degradation of solid polymers are specifically determined by the solid state
itself and it is this state, of limited ordonation, to which we should paid a
greater attention in order to have a better understanding of phenomena.

In conclusion, it should be pointed out that there is a general tendency for
the simplification of phenomena affecting the PVC stability by looking for
a simple and as much as possible a linear biunivocal interdependence between
this stability and a particular defect. Even if this fact is possible in a
few situations, in our opinion the stability of this particular polymer de-
pends on the whole ensemble of defects, the state of the material and the
degradation conditions. Such a correlation rooting from a complex multitude
of informations should be described by an intricate function where the na-
ture and the concentration of individual defects should affect more or less
the stability. These informations could be obtained only by a common effort
and should be gained from standard samples, according to the well establish-
ed co-operation between the members of the IUPAC Working Group on PVC De-

fects.

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