BRANCHING CHARACTERISTICS OF POLY(VINYL CHLORIDE)

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Abstract – Different ways to determine branched structures in PVC were discussed and a brief review of recent studies by ^{13}C NMR was given. The latter method has not only proved capable of elucidating the branching structure in PVC, but it also exhibited higher accuracy than conventional procedures. Common PVC grades were found to contain 2-3 pendant chloromethyl groups per 1,000 C and about 0.5 long branches per 1,000 C. Calculations showed that if long branches were associated with tertiary chloride, this concentration of labile sites would suffice to account for most of the observed degradation in the polymer. Reduced PVC exhibited annealing effects similar to those observed for LDPE, although the number of branches was closer to that characteristic of HDPE. Degraded PVC, which was reductively dehalogenated, exhibited a lower tendency to crystallize. This was believed to be the result of cross-linking reactions which decreased molecular mobility.

INTRODUCTION

The thermal stability of poly(vinyl chloride), PVC, is critically dependant on the frequency of certain defect structures in the polymer. These irregularities are generally present at very low concentrations, which complicates their analysis. Consequently, there is a great demand for powerful experimental techniques, which are capable of elucidating the microstructure of PVC in detail. In this context it would be important to determine the nature and concentration of branches in PVC and clarify to what extent they may contribute to the instability of the polymer. Significant information about these structures have been obtained through studies of reduced PVC by ^{13}C NMR (1-8). It is the purpose ot this paper to discuss results obtained by this and other experimental techniques and try to give further insight into the branching structure och PVC.

EXPERIMENTAL

Materials
Virgin and thermally degraded PVC samples of Pevikon R-45 were employed in this study (9). The original polymer was generously supplied by Kema Nord AB, Sweden. The polyethylenes used for the DSC measurements are listed in Table 1 (10).

TABLE 1. Investigated polyethylenes

Trade name	$\bar{M}_N$	$\bar{M}_W$	$\bar{M}_W/\bar{M}_N$	LCB/1,000 C	Density, g/cm^3
Marlex 6001	16,000	150,000	9.4	0.1 - 0.2	0.96
Sclair 2914	16,000	45,000	2.8	–	0.96
Sclair 2514	15,000	46,000	3.1	0.2 - 0.3	0.94
Unifos DFDS 6600	31,000	97,000	3.1	1.0	0.93

Thermal analysis
The thermal analyses were performed on a du Pont 990 Differential Thermal Analyzer using a sample weight of 6.3 mg and a heating rate of 10°C/min.

Poly(vinyl chloride) reduction
The reductive dehalogenation of PVC has commonly been carried out with LiAlH$_4$, (1, 9). This procedure is very time consuming and may lead to incomplete removal of chlorine as well as undesirable side reactions. These drawbacks can be avoided by using Bu$_3$SnH as the reducing agent. This was first suggested by Starnes, who has demonstrated that essentially all

chlorine could be eliminated by such a procedure (4, 6). ^{13}C NMR data have shown that the stereoselectivity of LiAlH$_4$ and Bu$_3$SnH reagents are quite different (6). After about 99 % reduction with LiAlH$_4$, PVC is converted into products containing vinyl chloride monads and racemic dyads in ratios of about 1.1 - 1.4. If the reduction was carried out in Bu$_3$SnH only vinyl chloride monads were observed. The lower reactivity of racemic structures in LiAlH$_4$ is in agreement with earlier studies (11, 12).

The presence of internal <u>trans</u> double bonds in LiAlH$_4$-reduced PVC has been shown by IR and ^{13}C NMR (2, 6). However, no groups of this type were detected in the polymers reduced by Bu$_3$SnH (6). The unsaturated structures, which obviously were formed during the LiAlH$_4$-reduction, did not change in concentration after a successive Bu$_3$SnH-reduction. It is evident that the vigorous conditions employed during the LiAlH$_4$-reduction (7 days at 100°C) may easily cause undesirable side reactions.

Miscellaneous
The molecular weight determinations and the dehydrochlorination measurements were carried out as previously described (13, 14).

RESULTS AND DISCUSSION

Long chain branching
A deviation from linearity of log $[\eta]$-log $\bar{M}_W$-plots has frequently been observed in the high molecular weight region. This deviation has often been considered to be the result of long chain branching, which preferentially occurred in the larger molecules (15, 16). However, it is now well known that the observed deviation is mainly caused by molecular aggregation and not by long chain branching (17-19).

The undesired influence of these supermolecular structures could be prevented by heat treatment of the PVC solutions. Evidently, the extent of long chain branching is much lower than indicated by the above observations. A rough estimate of the concentration of long branches may be obtained from a relationship proposed by Graessley (20):

$$\frac{\bar{M}_W}{\bar{M}_N} = 2 \ (1 + \bar{B}_N), \tag{1}$$

where $\bar{B}_n$ is the number average branching density. For a set of commercial PVC samples Lyngaae-Jörgensen (18) observed polydispersities between $2.0 \le \bar{M}_W/\bar{M}_N \le 2.2$. By the use of eq. (1), he then estimated the maximum branching frequency to 0.06 per 1,000 C. Again, it should be emphasized that the accuracy of this calculation is very low and only related to a certain collection of PVC grades. A more careful analysis was performed by the use of GPC and light scattering. This resulted in a maximum branching frequency of 0.3 per 1,000 C (18). de Vries et al. compared the intrinsic viscosity of reduced PVC with the corresponding data for LDPE and HDPE (19). The intrinsic viscosity of the reduced PVC resin was in excellent agreement with the values calculated from the empirical relationship for HDPE. From these results they concluded that most PVC polymers contain very few long branches, if any.

The long chain branching of polymers is usually determined by comparing the molecular size of branched molecules to that of linear polymers having the same molecular weight. This procedure was used in one of our earlier studies (17). This resulted in branching frequencies of about 0.4 per 1,000 C. As this method is commonly used for the determination of branching in LDPE, it might be of interest to analyze its potentials when applied at lower branching concentrations. These calculations are based on Zimm-Stockmayer's theory (21). The relationship for trifunctional branch points has been given as follows:

$$<g_3> = \frac{6}{\bar{n}_w} \left[0.5 \ (\frac{2 + \bar{n}_w}{\bar{n}_w})^{0.5} \ \ln\left\{\frac{(2 + \bar{n}_w)^{0.5} + \bar{n}_w^{0.5}}{(2 + \bar{n}_w)^{0.5} - \bar{n}_w^{0.5}}\right\} - 1 \right] \tag{2}$$

where $\bar{n}_w$ is the weight average number of branch points per molecule and $<g_3>_w$ is a factor related to the intrinsic viscosities for branched, $[\eta]_{br}$, and linear $[\eta]_l$ polymers as indicated by eq. (3).

$$<g_3>^{0.5} = [\eta]_{br}/[\eta]_l \tag{3}$$

The exponent in eq. (3) is not a true constant, but a value of 0.5 has been shown to be valid for star-shaped branched polymers (22). The intrinsic viscosity of a linear polymer is calculated using the appropriate Mark-Houwink equation.

$$[\eta] = K \cdot M^a \tag{4}$$

A number of relationships are given in the literature, but there are only a few valid for PVC in THF at 25°C (15, 19, 23). These are collected in Table 2.

TABLE 2. Viscosity – Molecular Weight Relationships for PVC in THF at 25°C

$K \cdot 10^4$, dl/g	α	No. of fractions	Mol. wt. range, $M \cdot 10^{-3}$	Polydispersity range for fractions, $\bar{M}_W/\bar{M}_N$	Reference No.
1.63	0.766	23	25 – 300	1.12 – 1.90	15
1.50	0.770	31	10 – 300	1.04 – 1.87	23
1.63	0.760	25	6.5 – 650	1.12 – 1.32	19

The Mark-Houwink equation derived by Freeman and Manning is the one recommended in Polymer Handbook (15). However, this relationship is the result of experiments where the potential molecular aggregation is not taken into account. We have therefore used the equation proposed by de Vries et al. (19), which covers the widest molecular weight range and is based on very solid experimental data.

Let us assume that the average estimated error in the Mark-Houwink relationship is in the order of 2 %. We may then determine the resulting error in wieght average number of branches per molecule. The calculation has been performed without considering variations in $[\eta]_{br}$. The results are given in Figure 1.
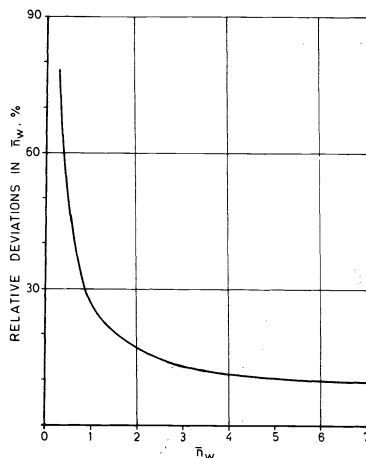

Fig. 1. Relative deviations in $\bar{n}_W$ at various levels of branching

It is evident that the error in $\bar{n}_W$ is extremely large at low branching frequencies but decreases rapidly with an increasing value of $\bar{n}_W$. However, it is important to notice that the number of long branches rarely exceeds 2 per molecule. At $\bar{n}_W = 1$ there is a relative deviation of $\pm$ 26.5 %. A more thorough error analysis has also been carried out. It is based on a truncated Taylor expansion of $<g_3>_W$ as expressed in eq. (3). The variance of $<g_3>_W$ may then be obtained as follows:

$$\text{Var} <g_3>_W = \frac{4 \cdot [\eta]^4_{br}}{[\eta]^4_1} \left\{ \frac{\text{Var} [\eta]_{br}}{[\eta]^2_{br}} + \frac{\text{Var} [\eta]_1}{[\eta]^2_1} \right\} , \tag{5}$$

where $[\eta]_{br}$ and $[\eta]_1$ are the expected values for the intrinsic viscosities of branched and linear molecules respectively. The estimated errors then have to be translated into appropriate confidence levels. If we assume that the experimental error in $[\eta]_{br}$ is 2 %, which corresponds to 3 σ we obtain:

$$\frac{3 \sqrt{\text{Var} [\eta]_{br}}}{[\eta]_{br}} = 2 \% \tag{6}$$

or $\quad \dfrac{\text{Var } [\eta]_{br}}{[\eta]_{br}^2} = \dfrac{4}{90,000}$

Assuming the same conditions for $[\eta]_1$ eq. (5) may be expressed as follows:

$$\text{Var } <g_3>_w \approx \dfrac{4\,[\eta]_{br}^4}{[\eta]_1^4}\ \dfrac{8}{90,000}\ ; \tag{7}$$

$$\text{Var } <g_3>_w \approx \dfrac{4\cdot\sqrt{2}}{300}\left\{\dfrac{[\eta]_{br}}{[\eta]_1}\right\}^2\ ;$$

$$\dfrac{\sqrt{\text{Var } <g_3>_w}}{<g_3>_w} \approx 0.019$$

This result may then be interpreted on different levels of confidence. Table 3 summarizes the percent error in $<g_3>_w$ determined with various assumptions. These calculations bring

TABLE 3. Percent error in $<g_3>_w$ calculated at different confidence levels

Confidence level for $<g_3>_w$	$[\eta]_1$		$[\eta]_{br}$		Percent error in $<g_3>_w$
	Estimated error, %	Confidence level	Estimated error, %	Confidence level	
2σ	2	3σ	1	3σ	± 3.0
	2	3σ	2	3σ	± 3.8
	2	σ	1	2σ	± 8.0
	2	σ	2	3σ	± 8.4
3σ	2	3σ	1	3σ	± 4.5
	2	3σ	2	3σ	± 5.7
	2	σ	1	3σ	± 12.0
	2	σ	2	3σ	± 12.6

about errors in $<g_3>_w$ from ± 3 to ± 12.6 %, which may then be translated into variations in $\bar{n}_W$. Given a value of 0.85 for $<g_3>_w$ we obtain $\bar{n}_W = 0.95 \pm 0.2$ for the highest accuracy and a value of $\bar{n}_W$ which varies from 0.23 to 1.96 for $<g_3>_w \doteq 0.85 \pm 12.6$ %. The error in $[\eta]_{br}$ has been interpreted as 3σ but the error in $[\eta]_1$ is considered to correspond to 1σ (19).
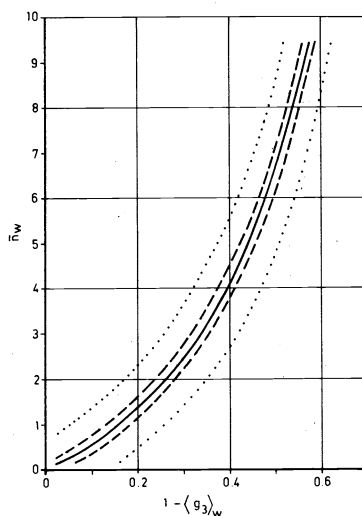

Fig. 2. $\bar{n}_W$ as a function of $1 - \{<g_3>_w\}$. Errors resulting from variations in $<g_3>_w$ of ± 3 % (---) and ± 12 % (......) are indicated.

Figure 2 shows $\bar{n}_W$ as a function of $\{1 - <g_3>_W\}$ as derived from eq. (2). The dashed lines correspond to an error in $<g_3>_W$ of $\pm$ 3 % and the dotted lines correspond to an error in $<g_3>_W$ of $\pm$ 12 %. It is obvious that only very small variations in $<g_3>_W$ are allowed if a high accuracy in $\bar{n}_W$ is desired. This is, of course, extremely important at low degrees of branching, where the deviations in percent will be larger (cf. Fig 2).

This study clearly shows the difficulties in determining $\bar{n}_W$ with high precision. The error limits indicated in Fig. 2 are calculated with the assumption that $[\eta]_1$ and $[\eta]_{br}$ could be obtained with very high accuracy. At low branching frequencies variations in $\bar{n}_W$ of about $\pm$ 40 % are thus quite realistic (cf. Fig. 2).

An alternative route to determine long chain branching in PVC is now available. It is based on ^{13}C NMR measurements on reduced PVC (1). The first data were obtained a few years ago and since then further refinement of the experimental techniques has improved reproducibility (1-8). Long branch points could not be identified in all LiAlH$_4$-reduced samples, apparently owing to side reactions occurring during reduction (6). When using the milder reducing agent, Bu$_3$SnH, long branches were found in all materials examined. By this procedure it is possible to detect branching frequencies in the order of 1 per 10,000 C, which is also the accuracy of the determination. A branching content of 0.5/1,000 C could be determined with an average error of less than 20 %. This is far better than what may be obtained by the previously discussed method. Furthermore, the sensitivity of the ^{13}C NMR technique will be highly improved when new instruments are introduced. Common use of this analytical procedure thus looks very promising and it is reasonable to believe that long branch contents in PVC may be determined with an estimated average error of less than 10 % at low branching frequencies.

Short chain branching

A couple of years ago we were able to demonstrate that the short branches in PVC are pendant chloromethyl groups (1, 2). These findings have later been confirmed and the mechanism for the formation of these structures has now been fully elucidated (1, 2, 8). The chloromethyl group is formed by an intramolecular process as suggested by Rigo et al. (24):
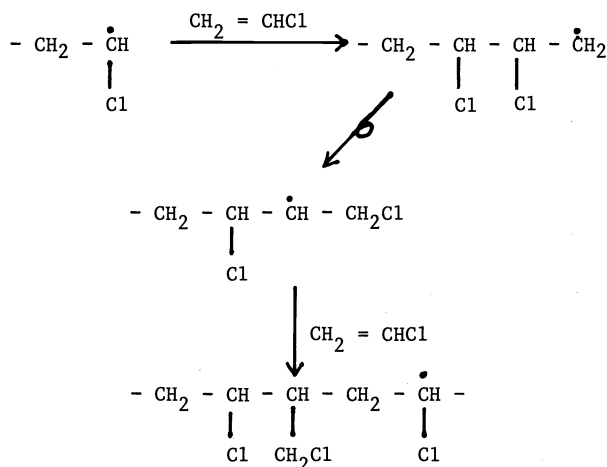
An occasional head-to-head monomer addition is followed by rearrangement of the resulting primary radical into a more stable secondary one via a 1,2-chlorine-atom shift. Normal propagation of this radical results in a chloromethyl branch (8). This structure (2-3/1,000 C) is most likely the main type of branching in all commercial grades, although smaller amounts of other short branches may also be present (24-27). Large discrepancies between the result from IR and ^{13}C NMR on reduced PVC have been observed (1). This is mainly caused by the use of erroneous extinction coefficients for the interpretation of infrared data (3). The extinction coefficient for the methyl deformation band (1378 cm^{-1}) is strongly dependent on the length of the side chain to which the methyl group is attached (28). Thus, infrared measurements of the total branching (methyl content) are only valid if the appropriate extinction coefficient is applied. The earlier assumption that all short branches in reduced PVC were butyl, led to an overestimation of the branching content by a factor of about two (3, 9, 28). Typical values of the extent of branching in suspension polymerized PVC are given in Table 4. IR data shown within brackets were calculated from the absorbance of the methyl deformation band at 1378 cm^{-1} on the assumption that most of the methyls were contained in pendant n-butyl groups. The other values from IR were obtained after correction for the extinction coefficients assuming the presence of one long branch per number-average molecule (6). The corrected IR-data

TABLE 4. Branches in reduced PVC

Reduced polymer	Polymeri-zation temperature °C	$\bar{M}_N{}^a$	$\bar{M}_W{}^a$	^{13}C NMR		
				CH$_3$/1,000C	LCB/1,000C	CH$_3$/1,000C
Nordforsk S-80	43	54,900	141,500	2.0	0.4	2.1 (4.1)
Pevikon R-23	56	37,700	86,700	2.6	-	2.9 (5.7)
Nordforsk S-54	75	24,700	53,300	2.8	0.5	3.9 (7.8)

a) Data for the original PVC

are comparable to those obtained by ^{13}C NMR, but give no information of the exact nature of the branches.

Thermal properties of reduced PVC

It is obvious that pendant chloromethyl groups have very little effect on rheological and conformational properties in comparison with long side chains. The effect of long branches in polyethylene on thermal and morphological properties is well known (29-31). Linear polyethylene (HDPE) exhibited a sharp melting peak (DSC), which was not very much affected by annealing below the melting point. This is demonstrated in Fig. 3.
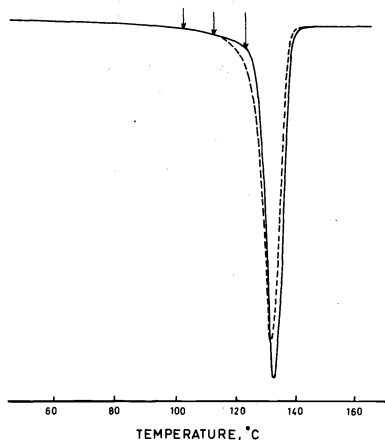

Fig. 3. Melting peaks for HDPE (Sclair 2914) before (---) and after annealing (———). The annealing temperatures are indicated by arrows.

To remove the thermal history of the sample, it was kept at 165°C for 15 min. before it was rapidly cooled down to room temperature. The polymer was annealed at successively lower temperatures (123, 112, and 102°C) as indicated by the arrows in Fig. 3. The annealed sample exhibited a slightly higher peak temperature and a somewhat sharper melting peak. Branched polyethylene (LDPE) is greatly affected by the previous thermal history and annealing at successively lower temperatures brings about a number of melting peaks – one for each annealing temperature (cf. Fig. 4). This behaviour has been used for the determination of LDPE-contents in polyethylene blends (32). In this connec-tion, it would be interesting to see how a reduced PVC performs in an identical test. The results of such a measurement are shown in Fig.4, where DSC traces of a LDPE (-·-) and a reduced PVC (———) are compared. The polymers were annealed as indicated above. The LDPE exhibited very distinct peaks at about 7°C above the annealing temperature. The reduced PVC was also affected by the thermal history, but the peaks appeared less regularly. A strong "extra" peak was observed at about 125°C. When the polymer samples were rapidly cooled a wide distribution of crystal sizes and irregular superlattices was formed. The annealing increased the order and size of the imperfectly formed crystallites, but this effect extended only to those which would ordinarily melt a few degrees above the annealing temperature. Rapidly crystallizing polymers like HDPE do not show these effects. Obviously, reduced PVC appeared to be more like LDPE than HDPE in this respect. LDPE contains about 1-2 long branches per 1,000 C and about 20 short branches per 1,000 C (mainly butyl). In general, a HDPE exhibits branching frequencies an order of magnitude lower, i.e. 0.1 - 0.2 long branches per 1,000 C and 1-3 short branches per 1,000 C. From Fig. 4, it may be concluded that the low branching frequencies observed in HDPE do not prevent rapid crystallization to any larger extent. The difference in DSC-data between
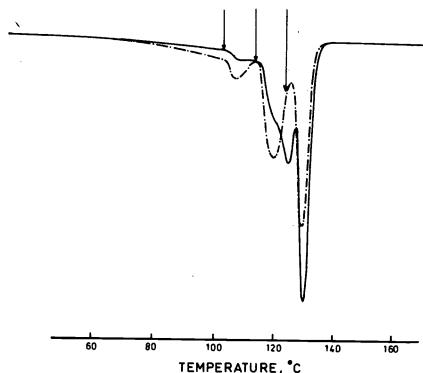
Fig. 4.   DSC traces of LDPE (−·−) and reduced PVC (———). The polymers
were annealed at 123, 112 and 102°C respectively (indicated by arrows).

HDPE and reduced PVC is most probably owing to a higher content of irregular structures
in the reduced PVC sample. The extent of short branches is the same in both polymers and
in addition the methyl groups in reduced PVC are smaller than the butyl groups in HDPE.
It thus seems reasonable to suggest that this difference in DSC data is the result of
the higher content of long branches in reduced PVC. Although the latter is fairly low
it is significantly higher than the very low contents observed for HDPE. However, it would
also be possible that residual chlorine (~1 %) in the reduced PVC affected the crystall-
izing behaviour of the polymer. This interaction was eliminated in a PVC, which was
reduced by a two-pass Bu_3SnH-reduction (33). Such a sample contained negligable amounts
of chlorine (not detectable). The DSC-trace was identical to the one shown in Fig. 4
(solid line). It is thus reasonable to believe that the observed effects were mainly
caused by the long branches in the polymer. During the thermal degradation of PVC in
inert atmosphere an increase in long chain branching is observed. This would indicate
that a PVC, which was first degraded and then reduced should exhibit annealing effects
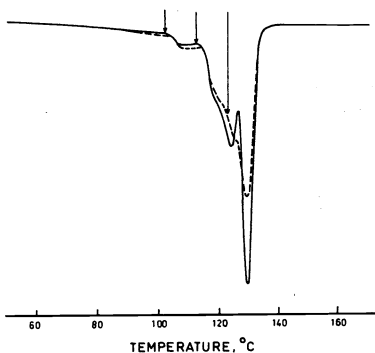even more pronounced. However, as may be seen form Fig. 5 this was not the case; on the

Fig. 5.   DSC traces of annealed, reduced PVC samples: (———) virgin polymer
and (−−−) polymer degraded to 1.5 % dehydrochlorination.

contrary the resulting peaks were smaller and less outspoken than for the original sample.
The changes in relative peak height and the number of tetrafunctional branch points per
1,000 C are shown in Fig. 6. The conversion is here defined as the ratio between the
hydrogen chloride evolved and the total available amount. The smaller peaks observed
after degradation are likely to result from crosslinking reactions which decreased mole-
cular mobility and crystallization. The sample at 1.5 % conversion contained about 6 %
insoluble material after treatment in tetrahydrofuran for 3 hr at 120°C (9).

Branched structures as labile sites in poly(vinyl chloride)
It is well known that PVC exhibits a lower thermal stability than would be expected from
its ideal composition. Thus, many investigators have tried to determine the concentration
and nature of various labile structures present in commercial PVC (4, 34-36). Chlorinated
hydrocarbons with tertiary chloride groups are known to exhibit limited thermal stability
and such structures are therefore frequently discussed as initiation sites for the
dehydrochlorination (4, 34-40). However, the presence of tertiary Cl in PVC has been
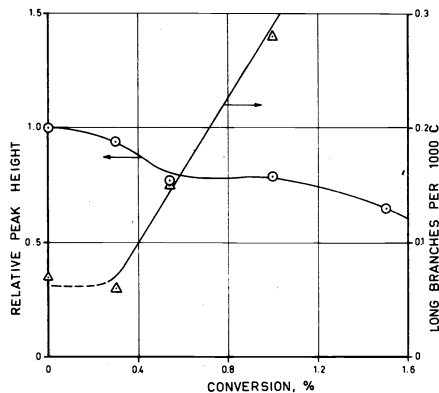
Fig. 6.   Changes in relative peak height (DSC) and number of long branches per 1,000 C plotted vs. conversion. Data for reduced (DSC) and virgin Pevikon R-45 (branching).

doubted mainly because its existance has not been experimentally proven (38-40). As mentioned above it has been conclusively shown that the branches in PVC are mainly pendant chloromethyl groups, which would not be expected to contribute to the thermal instability (1, 2, 8). Berens estimated the amount of tertiary Cl that would be sufficient to account for the observed degradation in PVC (37). His calculations suggested that a frequency of about 1 per 1,000 C may suffice. This means that although the concentration of a specific labile structure is very low it may strongly affect the stability of the polymer.

Long branches formed via hydrogen abstraction from the polymer should have tertiary chlorides at the branch points and appear at a frequency of about 0.5 per 1,000 C. From previous experiments it is likely that such labile structures are activated during the dehydrochlorination reaction (41). Starnes et al. have recently shown that tertiary chloride is present at all long-branch points and that PVC also contains a minor amount of 2-chloroethyl branches which are associated with tertiary halogen (27). The total content of such labile structures was determined to ca. 0.5 per 1,000 C. Previous studies on these materials have shown that polyene sequences formed during the dehydrochlorination in nitrogen contain at an average about 10 double bonds - somewhat depending on the experimental conditions (42). With the given assumptions it is possible to reach 1 % dehydrochlorination without activating any other labile sites but the tertiary chloride groups. The latter structures may thus account for a high fraction of the initiation sites although they are present in fairly low concentrations. This is supported by earlier studies (41).

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