On the Thermal Degradation of Poly(vinyl Chloride). IV. Initiation Sites of Dehydrochlorination

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Synopsis

A set of poly(vinyl chloride) samples were investigated with respect to their thermal stability. The dehydrochlorination rates were measured in nitrogen at 190°C by use of a very accurate, conductometric method. For all polymers studied, a significant molecular weight increase was observed after 0.4% conversion. With only one exception, samples exhibiting higher degradation rates showed higher absorptions (350–450 nm) after 0.4% dehydrochlorination. In addition, the relative amount of short polyene sequences was found to be higher for polymers with higher degrees of branching. The dehydrochlorination reaction was predominantly initiated at sites of internal unsaturation (allylic chlorines), but an initiation at tertiary chlorines and unstable end-groups could not be completely omitted. Head-to-head units, extraneous impurities, and syndiotactic sequences were found to be of minor importance in this respect.

INTRODUCTION

A basic disadvantage of poly(vinyl chloride) (PVC) is its limited thermal stability. Different structural defects in the polymer have been considered to cause this thermal instability. Many investigations have been carried out on this subject, but so far, the relative contribution of different structural anomalies to the instability of the polymer has not been elucidated. The initiation of the dehydrochlorination reaction has been related to parameters such as (1) extraneous impurities, (2) head-to-head units, (3) oxidation structures, (4) syndiotacticity, (5) initiator residues, (6) unsaturated chain ends, (7) tertiary chlorine atoms, and (8) allylic chlorines. It is the object of this study to investigate the relative importance of different initiation sites to the dehydrochlorination of PVC.

EXPERIMENTAL

Materials

Polymer data are given in Table I. Lucovyl GB 1150 is a bulk-polymerized sample, but all others were prepared from suspension polymerization. Nordforsk S-54 and Nordforsk S-80 were obtained from Kema Nord AB and have

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TABLE I
Data for Investigated Polymers

Polymer	$\overline{M}_n$	$\overline{M}_w$	H	Internal double bonds per 10,000 C	CH$_3$/ 1000[a]	$r \times 10^2$, %/min
Pevikon R-150	26,800	58,800	2.20	0.45	6.0	2.15
Pevikon R-25	33,300	76,300	2.29	1.90	5.8	2.08
Pevikon R-23	37,700	86,700	2.20	0.95	5.7	1.77
Pevikon R-24	39,600	90,300	2.28	0.87	5.5	1.76
Pevikon R-336	41,700	101,300	2.42	0.72	—	1.63
Pevikon R-45	48,400	109,400	2.26	0.54	5.1	1.82
Pevikon R-341	50,800	115,600	2.24	0.27	5.4	1.39
Nordforsk S-54	24,700	53,300	2.16	<0.10	7.8	2.00
Nordforsk S-80	54,900	141,500	2.56	0.18	4.1	1.25
Lucovyl GB 1150	38,900	90,800	2.34	0.30	5.1	1.33
Ravinil R 100/65D	40,200	87,000	2.16	0.18	6.2	1.07
Norvinyl S4-68	40,700	98,300	2.41	1.12	—	2.00
Shin-Etsu TK 1000	43,100	98,600	2.29	0.83	5.6	1.85

[a] Measured on reduced samples.[10,11]

been used in a "round robin test" in Nordforsk (Polymer Characterization Group). All samples, except the latter ones, were commercial.

The tetrahydrofuran (THF) used was refluxed over sodium borohydride until no peroxides could be detected.[1] It was then distilled under nitrogen from metallic sodium. Methanol and acetone were puriss grade. All other reagents and solvents were analytical grade. Nitrogen containing less than 10 ppm (3.4 ppm) oxygen was used. The gas was supplied and analyzed by AGA Sweden.

Dehydrochlorination Kinetics

A description of the dehydrochlorination apparatus has been given earlier.[2,3] All experiments were carried out in nitrogen at 190°C to 0.4% conversion. The degree of dehydrochlorination or the conversion, x%, was determined as the ratio between the hydrogen chloride evolved and the total amount available in the polymer. The rate of dehydrochlorination, r, was expressed in %/min and was determined between 0.2% and 0.3% conversion. Fractions with particle diameters between 0.1 and 0.2 mm were used.

Ultraviolet-Visible Spectroscopy

Absorbance spectra of PVC solutions in THF were obtained by a Beckman DK-2A spectrophotometer. All PVC solutions (4 g/l.) were carefully prepared under nitrogen and were rotated in sealed glass tubes for 4–6 hr before analysis. As it is of great importance to have peroxide-free solutions,[4,5] the THF was treated as above (see Materials).

Gel Permeation Chromatography

A Waters Associates GPC Model 200 equipped with an automatic injection system was used for determination of molecular weights and molecular

TABLE II
Molecular Weight Averages Before and After 0.4% Dehydrochlorination.
Thermal Degradation in Nitrogen at 190°C

Polymer	$\bar{M}_n$ original	$\bar{M}_w$ original	$\bar{M}_n$ after 0.4% dehydro-chlorination	$\bar{M}_w$ after 0.4% dehydro-chlorination
Pevikon R-150	26,800	58,800	32,800	64,700
Pevikon R-25	33,300	76,300	40,200	80,900
Pevikon R-23	37,700	86,700	45,700	96,500
Pevikon R-24	39,600	90,300	48,500	98,200
Pevikon R-336	41,700	101,300	54,200	114,200
Pevikon R-45	48,400	109,400	54,500	110,100
Pevikon R-341	50,800	115,600	57,900	125,200
Nordforsk S-54	24,700	53,300	32,600	66,200
Nordforsk S-80	54,900	141,500	54,400	158,000
Ravinil R 100/65D	40,200	87,000	45,100	97,600
Skin-Etsu TK 1000	43,100	98,600	50,200	98,800

weight distributions. The experimental details have been described elsewhere.[2,6]

Determination of Internal Unsaturation

The technique used for the determination of internal unsaturation was based upon ozonolysis combined with GPC.[6] The ozonolysis was carried out at room temperature. No further decrease in molecular weight was observed after 2 hr. This is in agreement with earlier findings,[7,8] but contradictory to those of Michel et al.[9]

Determination of Methyl Content

PVC was hydrogenated by $LiAlH_4$, and the methyl content was then measured by a compensation method using infrared spectroscopy.[10] The procedure has been described in a previous paper.[11]

RESULTS AND DISCUSSION

All degraded samples showed an increase in molecular weight at 0.4% conversion. The degree of dehydrochlorination is, however, too low to give conclusive information about the relative extent of crosslinking reactions. The molecular weights before and after dehydrochlorination to 0.4% conversion are listed in Table II. Ultraviolet-visible spectra were recorded for most of the polymer samples. Some of them are shown in Figure 1. Ravinil R 100/65D and Nordforsk S-80 exhibited the lowest and Pevikon R-150 the highest absorption at most wavelengths. At low wavelengths, however, Ravinil R 100/65D showed a rather high absorption. In the region of 350 to 450 nm, the absorption of the polymer solution was higher for samples exhibiting high degradation rates. The only exception from this rule was Shin-Etsu TK 1000, which showed a surprisingly high absorption. The relative amount of
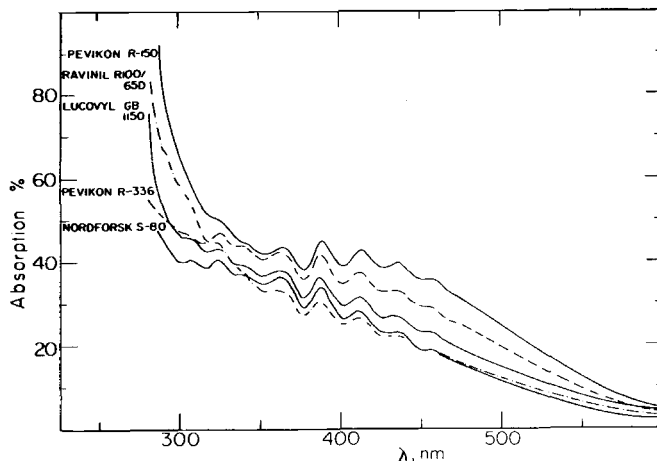
Fig. 1. UV-visible spectra of thermally degraded PVC samples. Degradation in nitrogen at 190°C to 0.4% conversion.

short polyene sequences was found to be higher for polymers with a higher degree of branching (measured as the methyl content of the reduced polymer).

Short branches acting as termination points for growing polyene sequences might explain this behavior[11] (see below).
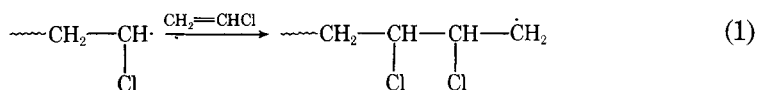
In the following, the importance of different irregular structures as initiation sites for the dehydrochloriniation reaction is discussed.
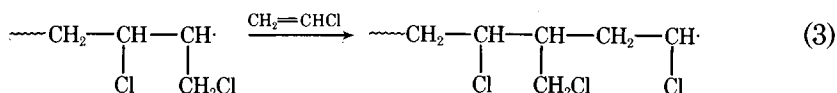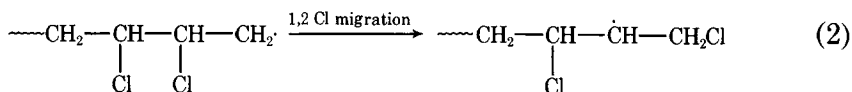
Extraneous Impurities

Polymer impurities do mainly come from polymerization additives. Talamini et al.[12] found that after reprecipitating the polymers twice, the dehydrochlorination rates decreased. The decrease in degradation rate was attributed to the removal of extraneous impurities and low molecular weight polymer. From other investigations, the effect of impurities as initiators for the dehydrochlorination has been considered negligible.[13,14] Our experiments showed that reprecipitation of polymers prepared by suspension polymerization did not affect the dehydrochlorination rate.[3]

Head-to-Head Units

Head-to-head units formed in a molecule have not only been considered as initiation sites for the dehydrochlorination, but also as termination points for the growing polyene sequences.[15–17] Head-to-head units can either be formed through termination by combination or by head-to-head addition during the propagation. Recently, studies by C-13 NMR have shown[18,19] that the short branches in PVC are pendent chloromethyl groups, which can be formed through an isomerization mechanism as suggested by Rigo et al.[20]:

$$\sim\!\!\sim\!\!CH_2\!-\!\!\overset{\displaystyle}{\underset{\displaystyle Cl}{CH}}\!\cdot \;\xrightarrow{\;CH_2=CHCl\;}\; \sim\!\!\sim\!\!CH_2\!-\!\!\overset{\displaystyle}{\underset{\displaystyle Cl}{CH}}\!-\!\!\overset{\displaystyle}{\underset{\displaystyle Cl}{CH}}\!-\!\dot{C}H_2 \qquad (1)$$

$$\sim\sim CH_2-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_2 \cdot \xrightarrow{\text{1,2 Cl migration}} \sim\sim CH_2-\underset{\underset{Cl}{|}}{CH}-\overset{\cdot}{C}H-CH_2Cl \qquad (2)$$

$$\sim\sim CH_2-\underset{\underset{Cl}{|}}{CH}-CH \cdot \underset{\underset{CH_2Cl}{|}}{} \xrightarrow{CH_2=CHCl} \sim\sim CH_2-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_2Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH} \cdot \qquad (3)$$

If the equilibrium in (2) is completely on the right side, no head-to-head units should be formed. Such structures were not observed by C-13 NMR.[18]

Oxidation Structures

The contribution of oxidation structures to the thermal instability of PVC has been studied very little. Virgin PVC may contain up to 500 ppm peroxide,[8] which together with hydroperoxides may act as initiation sites for the dehydrochlorination. Popova et al.[21] reported a higher dehydrochlorination rate for PVC polymerized in the presence of oxygen (0.1%). Decomposition temperatures were also 10–15°C lower. Sönnerskog[22] found that PVC could oxidize a number of phenols at room temperature in the absence of oxygen. In addition, a graft copolymer was formed when acrylonitrile was added to PVC. These results were taken as indications of the presence of peroxy groups in PVC. The effect of oxidation structures on the thermal degradation of PVC is not taken into account in this study, mainly due to the difficulties in their detection and characterization. However, from infrared studies on some of the samples, the amount of oxidation structures seems to be small.

Syndiotacticity

The effect of polymerization temperature on the thermal degradation of PVC has been studied by Talamini et al.[23] and by Guyot et al.[24] Neither group found any correlation between rate of dehydrochlorination and polymerization temperature (syndiotacticity). In a more recent study, however, Millan et al.[25] found that at low degradation temperatures (110–150°C), the rate of dehydrochlorination increased slightly with increasing syndiotacticity. At higher degradation temperatures (≥170°C), the rate of dehydrochlorination passed through a minimum and then showed high degradation rates at high degrees of syndiotacticity. Polymers prepared from −50° to +50°C were investigated. From this study, it is reasonable to conclude that syndiotactic sequences affect the propagation of polyene sequences, but can not be considered as specific initiation sites for the dehydrochlorination reaction. In our study, the difference in syndiotacticity between samples is very small.

Branched Structures

Figure 2 shows the relationship between the rate of dehydrochlorination and the number of CH_3 groups in reduced PVC. The latter property has been used as a measure of the total branching in the original PVC. It is also nearly the amount of short-chain branching (SCB) as the amount of long-chain branching (LCB) has been found to be very limited even for high mo-
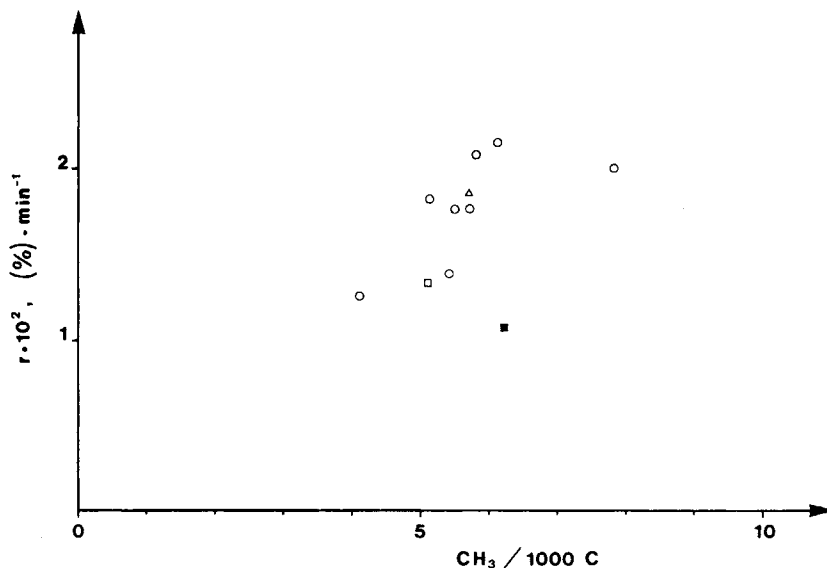
Fig. 2. Rate of dehydrochlorination vs. methyl content. Degradation in nitrogen at 190°C.

lecular weight polymers.[18,26-28] Short branches in PVC have usually been considered to be formed by back-biting mechanisms as for polyethylene. Such branches should have a tertiary chlorine at the branch point. Thus, in many earlier investigations, the methyl content was taken as a measure of the number of tertiary chlorines present in the polymer. In more recent studies, however, it has been found that the amount of tertiary chlorines in PVC is very low, but no conclusive explanation was given as to the exact structure of the branches.[29,30]

As mentioned above, it was recently shown by C-13 NMR that the short branches in PVC are mainly chloromethyl groups.[18,19] The methyl content is thus a measure of such structures, which are more stable than tertiary chlorines. For a model substance resembling the chloromethyl type of structure Suzuki and Nakamura[31] reported a decomposition temperature exceeding 180°C. Unstable tertiary chlorines can also be found at long-chain branches formed through chain transfer to polymer. A deviation from linearity in Kuhn-Mark-Houwink relationships at higher molecular weights has often been taken as an evidence for long-chain branching in PVC.[32] It has been shown, however, that this deviation is mainly due to aggregation of PVC molecules[2,33]; and, as mentioned above, it seems evident that there is less than one long branch per molecule.[18,26-28]

As can be seen from Figure 2, no obvious correlation between dehydrochlorination rate and methyl content in the reduced PVC could be observed. There is a slight trend toward higher degradation rates at higher amounts of branching, but the data are really scattered. Suzuki et al.[34] have found similar results for polymers of the same kind. For very high degrees of branching, they observed a much higher dehydrochlorination rate. They considered the degradation rate to be almost constant within the interval common for commercial polymers. During dehydrochlorination in oxygen, however, a greater dependence was observed.

Structures at Chain Ends

In earlier investigations, chain ends were suggested to be important initiation sites for the dehydrochlorination reaction. Some of them were unsaturated endgroups, but also initiator residues were considered. Thus, Cittadini and Paolillo found[35] that AIBN-initiated poly(vinyl chloride) was less stable than peroxide-initiated polymer. Similar results were also obtained by others.[36,37] In addition, Stromberg et al.[37] found that PVC prepared by gamma irradiation was still more stable. In these investigations no specific information was given about the polymers and the difference in stability is therefore, not necessarily due to the change in initiator. Talamini and co-workers[12] kept the molecular weight relatively constant and compared the rate of dehydrochlorination for samples obtained with different initiators. The results were consistent with the above mentioned. Park and Skene[38] determined the thermal stability for a series of PVCs prepared by *solution* polymerization with different initiators. They found an increase in degradation rate with increasing initiator content. The effectiveness of the initiator endgroups for causing dehydrochlorination was in the ratio lauroyl peroxide:isopropyl peroxydicarbonate:benzoyl peroxide:azoisobutyronitrile 9.7:5.8:4.4:1.6. These values were obtained at 220°C, and the degradation rates were taken as the mean value from 0% to 20% dehydrochlorination. However, the effect of initiator has been suggested to be less important, as model substances for such structures are much more stable than other possible structural irregularities.[16,17,39,40] In addition, it has been shown by kinetic studies that only approximately every fourth molecule contains an initiator residue.[41]

Talamini and Pezzin[42] have reported data on the degradation of PVC fractions in nitrogen. Four fractions were prepared from a polymer polymerized to a very low conversion. They observed a linear relationship between the rate of dehydrochlorination and the inverse molecular weight at 220°C. In a more extended study, Talamini et al.[23] verified these results for molecular weights lower than 45,000 (M_v); but at higher molecular weights, the degradation rate was approximately independent of molecular weight. Bengough and Sharpe[43] have conducted degradation experiments of PVC in ethyl benzoate solution at temperatures around 180°C. They obtained an inverse dependence of dehydrochlorination rate on molecular weight.

Arlman[44] found a linear relationship between rate of dehydrochlorination and the reciprocal of molecular weight, but he did not exclude other types of initiation sites, as extrapolation to infinite molecular weight resulted in a non-zero dehydrochlorination rate. The results were explained by the presence of unsaturated endgroups, which were considered to be the main initiation sites for the dehydrochlorination. Baum and Wartman[39] concluded from ozonolysis measurements on virgin PVC that the double bonds in PVC were located at chain ends. From IR measurements, they found that 60% of all endgroups were unsaturated. They considered the unsaturation at chain ends to be the main initiation site for the dehydrochlorination reaction. But as chlorination of the virgin PVC did not give zero dehydrochlorination rate, the residual instability was attributed to the tertiary chlorine atoms at branch points.

In Figure 3, the rate of dehydrochlorination is plotted versus the number-average molecular weight, $\bar{M}_n$ (inversely proportional to the number of end-
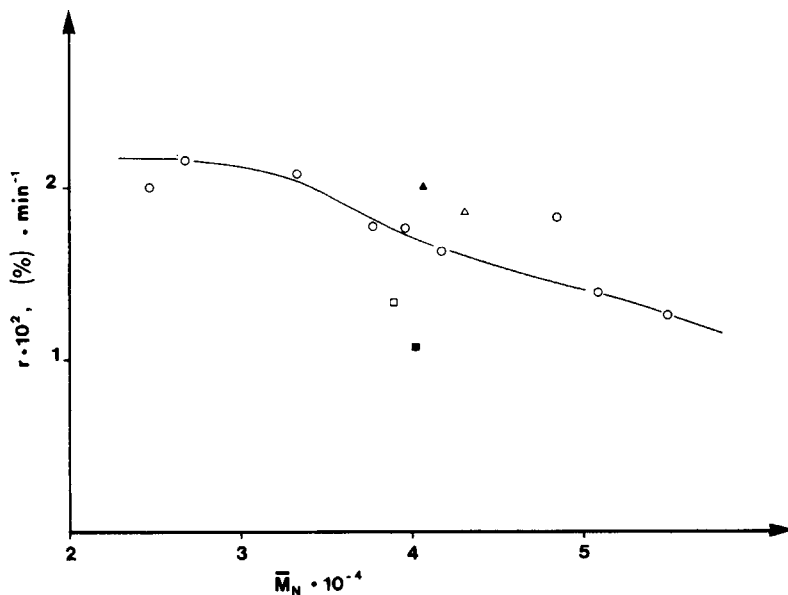
Fig. 3. Rate of dehydrochlorination vs. $\bar{M}_n$. Degradation in nitrogen at 190°C.

groups). For polymers from the same source (Pevikon), data points fall rather well on a single line. An exception is Pevikon R-45, which exhibited a dehydrochlorination rate higher than expected.

Allylic Structures

In Figure 4, the rate of dehydrochlorination is plotted versus the internal unsaturation as measured by ozonolysis.[6] It is seen that all points except
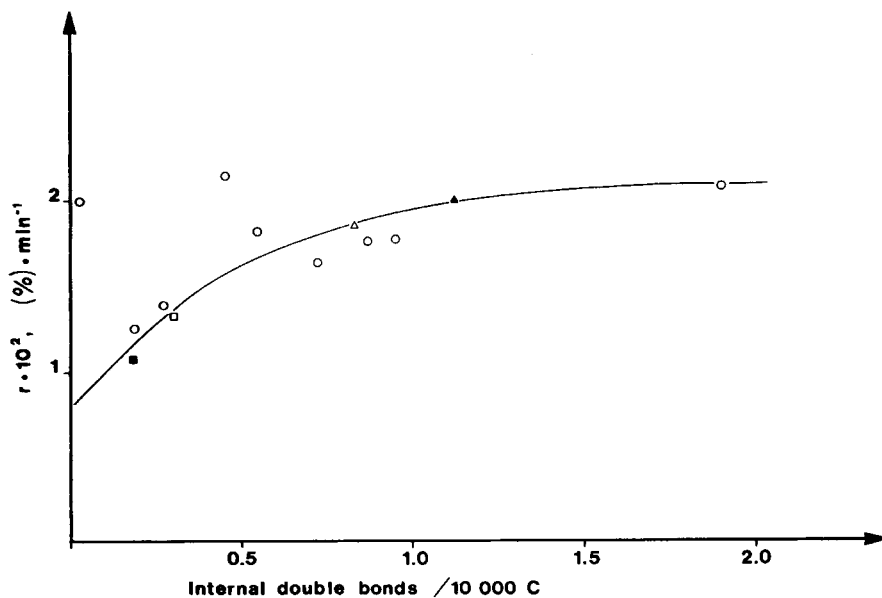

Fig. 4. Rate of dehydrochlorination vs. the content of internal double bonds. Degradation in nitrogen at 190°C.
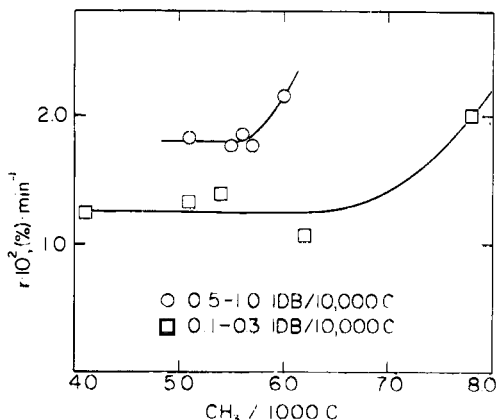
Fig. 5. Rate of dehydrochlorination vs. methyl content at constant degree of internal unsaturation. Degradation in nitrogen at 190°C.

those for the lowest molecular weights fall rather nicely on a single curve. At lower degrees of unsaturation, the rate of dehydrochlorination is more dependent on the internal double bonds than for a higher amount. Braun et al.[16] found a linear relationship between the rate of dehydrochlorination and the amount of internal unsaturation. In their first investigation, the rate was found to be zero at zero degree of unsaturation, which would indicate that the internal double bonds were the only initiation sites for the dehydrochlorination. The results from a more extended study published two years later,[45] however, showed a non-zero rate at zero internal unsaturation. Suzuki and Nakamura[28] obtained a linear relationship between the rate of dehydrochlorination and the total amount of double bonds present. They also found a non-zero rate at zero number of double bonds. The level of internal unsaturation from these investigations is much higher than in this work and in the work by Guyot et al., where ozonolysis was also employed.[46] In Guyot's and our work, commercial resins were used, while the others used laboratory products.
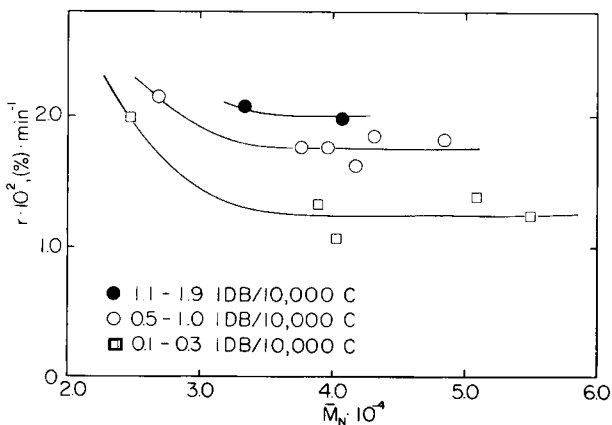

Fig. 6. Rate of dehydrochlorination vs. $\bar{M}_n$ at constant degree of internal unsaturation. Degradation in nitrogen at 190°C.
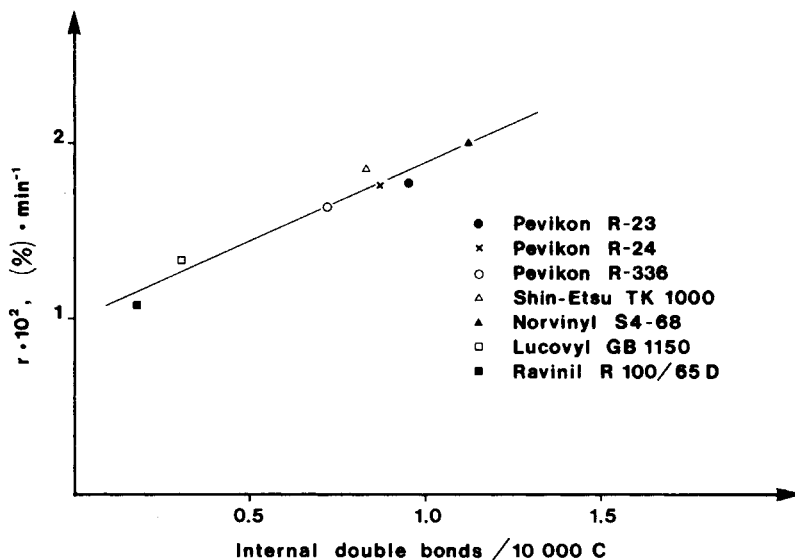
Fig. 7. Rate of dehydrochlorination vs. content of internal double bonds at constant $\bar{M}_n$. Degradation in nitrogen at 190°C.

Comparison Between Different Initiation Sites

To be able to reduce the effect of different variables, we tried to keep the amount of internal double bonds at a constant level. The results at various amounts of branching are shown in Figure 5. At a low level of unsaturation, the rate of dehydrochlorination is almost constant below 7 CH_3/1000 C, but then increases. For a higher degree of unsaturation, this dependence starts just below 6 CH_3/1000 C. A closer look at the deviating points shows that they represent data for the lowest molecular weight polymers. Therefore, the next step was to investigate the molecular weight dependence at different unsaturation levels. The results are shown in Figure 6. The dehydrochlorination rate is independent of molecular weight, except for number-average molecular weights lower than about 30,000. The onset of molecular weight dependence seems to be independent of the level of unsaturation, although the number of data points in this region is very limited. In Figure 7, the rate of dehydrochlorination is plotted versus the amount of internal double bonds at constant $\bar{M}_n$ (even the CH_3 content is almost constant). In this case, degradation rates correlate very well with the amount of internal unsaturation. As can be seen, a non-zero rate of dehydrochlorination is observed at zero unsaturation. This indicates the existence of additional initiation sites.

CONCLUSIONS

From this study, it seems obvious that the dehydrochlorination reaction is initiated predominantly at unsaturated structures (allylic chlorines) within the polymer chains. The importance of other possible initiation sites is less clear. As was recently shown,[18,19] branches in PVC are mainly pendent chloromethyl groups, which are less probable initiation sites. However, tertiary

chlorines might still exist in PVC at branch points formed through chain transfer to polymer (long branches). It has been observed that the number of unsaturation sites within the main chain increases as the degradation proceeds.[11] If a radical transfer is excluded, this must be caused by the activation of new initiation sites located within the polymer chain. The presence of tertiary chlorines explains this observation, but it might also be due to other unstable sites like oxidation structures, etc. The dehydrochlorination rate was found to be dependent on molecular weight (number of endgroups per unit weight) at low molecular weights only. As the molecular weight is determined by the polymerization temperature, the number of unstable endgroups might not be a constant fraction of the total amount present, but a function of polymerization temperature. This could explain the lower thermal stability for polymers prepared at higher polymerization temperatures, i.e., the lower molecular weight samples.

References

1. S. Siggia, *Quantitative Organic Analyses via Functional Groups*, 3rd ed., Wiley, New York, 1963, p. 258.
2. K. B. Andersson, Thesis, Chalmers University of Technology, Gothenburg, Sweden, 1973.
3. K. B. Abbås and E. M. Sörvik, *J. Appl. Polym. Sci.*, 17, 3567 (1973).
4. D. Braun and M. Thallmaier, *Makromol. Chem.*, 99, 59 (1966).
5. T. Matsumoto, I. Mune, and S. Watatani, *J. Polym. Sci. A-1*, 7, 609 (1969).
6. K. B. Abbås and E. M. Sörvik, *J. Appl. Polym. Sci.*, 17, 3577 (1973).
7. W. C. Geddes, *Eur. Polym. J.*, 3, 747 (1967).
8. Y. Landler and P. Lebel, *J. Polym. Sci.*, 48, 477 (1960).
9. A. Michel, G. Schmidt, and A. Guyot, *Polym. Prepr.*, 14, (2), 665 (1973).
10. A. H. Willbourn, *J. Polym. Sci.*, 34, 569 (1959).
11. K. B. Abbås and E. M. Sörvik, *J. Appl. Polym. Sci.*, 19, 2991 (1975).
12. G. Talamini, G. Cinque, and G. Palma, *Mat. Plast.*, 30(4), 317 (1964).
13. P. Carstensen, Thermal Degradation of PVC, paper presented at Nordiska Polymerdagarna, Göteborg, Nov. 1969.
14. W. C. Geddes, *Eur. Polym. J.*, 3, 267 (1967).
15. W. C. Geddes, *Rubber Chem. Technol.*, 40, 177 (1967).
16. D. Braun, *Pure Appl. Chem.*, 26(2), 173 (1971).
17. Z. Mayer, *J. Macromol. Sci. Rev.*, C10(2), 262 (1974).
18. K. B. Abbås, F. A. Bovey, and F. C. Schilling, *Makromol. Chem.*, in press.
19. F. A. Bovey, K. B. Abbås, F. C. Schilling, and W. H. Starnes, *Macromolecules*, 8, 437 (1975).
20. A. Rigo, G. Palma, and G. Talamini, *Makromol. Chem.*, 153, 219 (1972).
21. Z. V. Popova, N. V. Tikhova, and G. A. Razuvavev, *Polym. Sci. USSR*, 7(3), 588 (1965).
22. S. Sönnerskog, *Acta Chem. Scand.*, 13, 1634 (1959).
23. A. Crosato-Arnaldi, G. Palma, E. Peggion, and G. Talamini, *J. Appl. Polym. Sci.*, 8, 747 (1964).
24. A. Guyot, P. Roux, and P. Quang Tho, *J. Appl. Polym. Sci.*, 9, 1823 (1965).
25. J. Millan, E. L. Madruga, M. Bert, and A. Guyot, *J. Polym. Sci., Polym. Chem. Ed.*, 11 3299 (1973).
26. J. Lyngaae-Jörgensen, *J. Chromatogr. Sci.* 9, 331 (1971).
27. A. J. de Vries, C. Bonnebat, and M. Carrega, *Pure Appl. Chem.*, 25, 209 (1971).
28. K. B. Andersson and E. M. Sörvik, *J. Polym. Sci. C*, 35, 247 (1971).
29. A. Caraculacu, *J. Polym. Sci. A-1*, 4, 1829 (1966).

30. D. Braun and F. Weiss, *Angew. Makromol. Chem.,* **13,** 67 (1970).

31. T. Suzuki and M. Nakamura, *Jap. Plast.,* **4,** 16 (1970).

32. M. Freeman and P. P. Manning, *J. Polym. Sci.,* **A2,** 2017 (1964).

33. K. B. Andersson, A. Holmström, and E. M. Sörvik, *Makromol. Chem.,* **166,** 247 (1973).

34. T. Suzuki, M. Nakamura, M. Yasuda and J. Tatsumi, *J. Polym. Sci. C,* **33,** 281 (1971).

35. A. Cittadini and R. Paolillio, *Chim. Ind.* (Milan), **41,** 980 (1959).

36. C. Corso, *Chim. Ind.* (Milan), **43,** 8 (1961).

37. R. R. Stromberg, S. Straus, and B. G. Achhammer, *J. Polym. Sci.,* **35,** 355 (1959).

38. G. S. Park and C. L. Skene, *J. Polym. Sci. C,* **33,** 269 (1971).

39. B. Baum and L. H. Wartman, *J. Polym. Sci.,* **28,** 537 (1958).

40. M. Onozuka and M. Asahina, *J. Macromol. Sci., Rev,* **C3**(2), 235 (1969).

41. G. A. Razuvayev, G. G. Petukhov, and V. A. Dodonov, *Vysokomol. Soedin.,* **3**(10), 1549 (1961).

42. G. Talamini and G. Pezzin, *Makromol. Chem.,* **39,** 26 (1960).

43. W. I. Bengough and H. M. Sharpe, *Makromol. Chem.,* **66,** 31 (1963).

44. E. J. Arlman, *J. Polym. Sci.,* **12,** 547 (1954).

45. D. Braun and W. Quarg, *Angew. Makromol. Chem.,* **29/30,** 163 (1973).

46. A. Michel, G. Smith, and A. Guyot, *Polym. Prepr.,* **14**(2), 665 (1973).