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The Mechanism of the Formation of Chloromethyl Side Groups in Vinyl Chloride Polymerization

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SUMMARY

The dependence of the content of short branches on the monomer and initiator concentrations in vinyl chloride polymerization has been investigated by infrared examination of polymers reduced with tributyl tin hydride. The branch content increases with decreasing monomer concentration but appears to be independent of the initiator concentration. The findings best fit the mechanism of RIGO et al (1972) involving head-to-head addition followed by migration of the end chlorine atom.

INTRODUCTION

It has been known since 1953 (COTMAN ,1953) that PVC has a branched structure. Modern determinations suggest an average figure of about 5 branches per 1000 monomer units, while transfer constant measurements and intrinsic viscosity determinations give only about 0.5 long chain branches per 1000 monomer units (CARREGA,1977). It must be concluded therefore that nearly all the branches in PVC are very short and it was thought at one time that these arise from a back biting transfer reaction in a similar manner to the ethyl and butyl side chains in polyethylene. It is now recognised, however, that the short branches in PVC are predominantly only one carbon atom long and are probably chloromethyl groups (RIGO et al,1972, BAKER et al,1973, ABBÅS et al,1975 PARK,1977).

The presence of these groups poses a mechanistic problem and three suggestions have been proposed. These involve
(a) head-to-head addition followed by chlorine atom abstraction at the end of the polymer chain (RIGO et al,1972);
(b) hydrogen atom abstraction from an adjacent carbon atom at the end of the chain (ABBÅS et al,1975);
(c) interaction of two growing radicals involving double hydrogen transfer in a six-membered ring system (PARK,1977).

It was thought that investigation of the dependence of branch content on monomer and initiator concentration might help to decide between these three mechanisms.

THEORETICAL

(a) The mechanism of RIGO et al.(1972) is as follows

$$\sim\!\sim CH_2.\dot{C}HCl + CH_2{=}CHCl \rightarrow \sim\!\sim CH_2.CHCl.CHCl.\dot{C}H_2 \qquad (k_H)$$

$$\sim\!\sim CH_2.CHCl.CHCl.\dot{C}H_2 + CH_2{=}CHCl \rightarrow \sim\!\sim CH_2.CHCl.CHCl.CH_2.CH_2.\dot{C}HCl \qquad (k_G)$$

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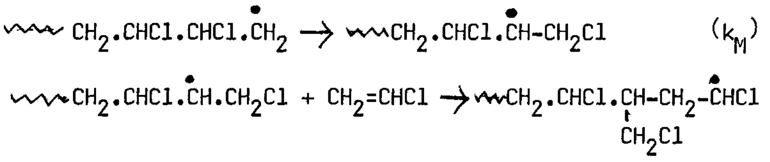


$$\sim CH_2.CHCl.CHCl.\dot{C}H_2 \rightarrow \sim CH_2.CHCl.\dot{C}H\text{-}CH_2Cl \qquad (k_M)$$

$$\sim CH_2.CHCl.\dot{C}H.CH_2Cl + CH_2{=}CHCl \rightarrow \sim CH_2.CHCl.\underset{CH_2Cl}{CH}\text{-}CH_2\text{-}\dot{C}HCl$$

By application of steady state theory this reaction scheme gives

$$k_H\,[P\cdot]\,/\,\,(1/[M] + k_G/k_M)$$

for the rate of production of chloromethyl branches where $[P\cdot]$is the steady state concentration of normal growing polymer radicals and $[M]$ is the monomer concentration. Since the rate of polymerization is given by $k_P[P\cdot][M]$the number of chloromethyl groups, N, per monomer unit in the polymer is

$$N = (k_H/k_P)/(1 + [M]k_G/k_M) \quad . \qquad (1)$$

Here, kp is the propagation rate constant.

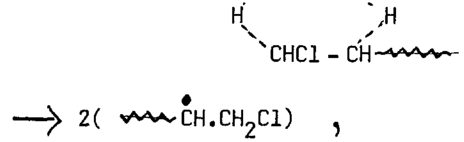
(b) The second mechanism (ABBÅS et al, 1975) simply involves the hydrogen migration:

$$\sim CH_2\dot{C}HCl \rightarrow \sim \dot{C}H.CH_2Cl \quad , \qquad (k_R)$$

followed by the addition of monomer. The rate of production of chlormethyl groups in this scheme is $k_R[P\cdot]$ and so the number, N, per monomer unit is

$$N = k_R/k_P\,[M] \qquad (2)$$

(c) The third mechanism proposed (PARK, 1977) is as follows



$$2(\sim CH_2.\dot{C}HCl) \rightarrow \ldots \rightarrow 2(\sim\dot{C}H.CH_2Cl) \quad , \qquad (k_X)$$

followed by the addition of monomer. Here, the rate of production of chloromethyl groups is $k_X[P\cdot]^2$ and so the number of chloromethyl groups, N, introduced per monomer unit is

$$N = k_X\,[P\cdot]\,/k_P\,[M] \quad . \qquad (3)$$

For an ideal free radical initiated polymerization $[P\cdot]$ can be replaced to give

$$N = (k_X/k_P\,[M])(2k_d\epsilon\,[I]/k_t)^{\frac{1}{2}} \quad , \qquad (4)$$

where $[I]$ is the initiator concentration, ϵ is the efficiency of initiation and k_t is the mutual termination constant. Equations 1, 2 and 4 give different dependences on initiator and monomer concentration and so suggest a method for deciding between the different mechanisms.

EXPERIMENTAL

PVC samples were produced over a range of monomer concentrations by polymerization at 40°C in 1,2-dichloromethane solution with azoisobutyronitrile as initiator at a concentration of

TABLE 1

Polymerization conditions and branching content

PVC					Reduced Polymer		
[M]	10^3[I]	t	%	$10^3\bar{M}_n$	%Cl	10^3N_o	10^3N_c
Bulk	12.2	6	10.6	-	-	4.06	-
Bulk	69.4	1	9.1	-	-	4.34	-
0.5	2.73	26	38.3	8.85	0.58	17.04	14.22
1.0	5.45	20	20.4	11.32	0.64	15.28	13.08
1.5	8.18	20	32.5	14.45	0.56	12.14	10.40
2.0	10.9	20	38.7	18.31	0.58	9.92	8.56
2.5	13.6	21	41.9	15.78	0.64	8.16	6.58
3.0	16.4	20	47.5	21.96	0.40	9.76	8.62
4.0	21.8	18	55.5	23.06	0.43	8.72	7.64
5.0	27.2	18	59.8	26.07	0.39	9.28	8.34

(M) and (I) in mol dm^{-3}*, t is polymerization time in hours, % is percentage conversion to polymer,* $\bar{M}_n$ *is the number average molecular weight,* N_o *is the number of branches per monomer unit from infrared measurements and* N_c *is the value corrected by assuming that each polymer chain has one terminal methyl group with an extinction coefficient only 40% of a methyl side group.*

0.1 moles per litre of monomer. The details are given in Table 1. The polymer was isolated by precipitation into methanol. The effect of changes of initiator concentration was investigated by polymerization at 40°C under heterogeous conditions as shown in the table. All the polymers were purified by reprecipitation from tetrahydrofuran into methanol followed by drying.

The branch contents of the polymers were estimated from the intensities of the 1378 cm^{-1} methyl symmetrical deformation band in polymers that had been reduced to hydrocarbons with tributyl tin hydride (STARNES et al, 1977) in some cases tetrahydrofuran was used instead of the methyltetrahydrofuran recommended by Starnes. The specimens were made into 500 mg KBr disks using 10 mg of hydrocarbon. The double beam compensation method of WILLBOURN (1969) was used to eliminate the CH_2 group absorptions at 1365/1350 cm^{-1} and corrections for the absorption of the methyl group at one end of the polymer chain were made. As in previous work (BAKER et al, 1973) the system was calibrated using polyethylenes containing known numbers of methyl side chains. The molecular weights of the polymers were obtained for us by GPC at the Rubber and Plastics Association.

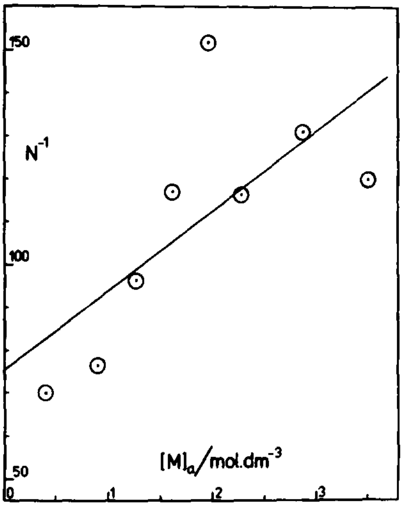


Figure 1. Number of branches per monomer unit, N^{-1}, vs. mean monomer concentration, $(M)_a$, during polymerization.

RESULTS AND DISCUSSION

From the table it will be seen that the degree of branching is almost identical in the two bulk polymers made with widely different initiator concentrations. Molecular weights are not available for these polymers and so no correction for terminal methyl groups is possible. This is not likely to make much difference between the two levels of branching and so the third mechanism is rather improbable (PARK, 1977). The data on the polymers made under homogeneous conditions show a definite increase in branching level as the monomer concentration decreases. All the mechanisms would suggest this. Rearrangement of equation 1 however shows that a plot of 1/N against [M] should give a straight line that does not go through the origin:

$$1/N = k_P/k_H + [M]\; k_G k_P/k_H k_M \qquad (5)$$

The other two mechanisms would give a line going through the origin. Since most of the polymers were made at high conversion (up to 60%) it is necessary to calculate the mean monomer concentration M_a obtaining during the whole of the polymerization instead of using the initial monomer concentration. This has been done and plotted against 1/N in figure 1. Although there is considerable scatter, the data appear to support the mechanism of RIGO et al (1972). The regression line drawn through the points has an intercept of 75 and a slope of 19 dm^{3}mol^{-1}. From equation 5 these would give

$$k_P/k_H = 75 \quad \text{and} \quad k_G/k_M = 0.25\ \mathrm{dm^3 mol^{-1}}$$

This means that there would be about one head-to-head addition for every 75 propagation steps and that in 4 molar monomer about a half of the head-to-head additions would lead to chloromethyl side chains.

The conclusions here are based on the assumption that practically all the branches are only one carbon atom long. C-13 NMR data (ABBÅS et al, 1975) give evidence that about 25% of the branches are longer than this. If the proportion of these change with monomer and initiator concentration our conclusions would need some modification. Further work on this is progressing.

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