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## Physico-Chemical Characterization of Poly(vinyl Chloride). IV. Branching

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### SUMMARY

Degree of branching in PVC as a function of its temperature of polymerization has been determined by the catalytic hydrogenation ( $\text{LiAlH}_4$ ) of the polymer followed by IR measurements. The samples used were prepared at 55, 90, 130, and 160°C. A branching calibration curve ( $\text{ACH}_3/\text{ACH}_2$  vs  $\text{CH}_3/\text{CH}_2$ ) was established for linear hydrocarbons, and was found to follow the relation,  $\text{ACH}_3/\text{ACH}_2 = 20(\text{CH}_3/\text{CH}_2)$ . This equation was used to characterize the branching indices of PVC samples studied. Branching values in units of  $100(\text{CH}_3/\text{CH}_2)$  were as follows: 55°C (1.92), 90°C (1.95), 130°C (2.61), and 160°C (2.96). These results are in agreement with the theoretical prediction that the degree of branching in PVC should decrease with the lowering of its temperature of polymerization because the energy of activation for the propagation step is smaller than that for chain the transfer step.

### INTRODUCTION

This paper deals with the determination of branching index of poly(vinyl chloride) (PVC) as a function of its temperature of polymerization. The technique employed for branching characterization was the same as has been established for polyethylene. The polymer was first catalytically hydrogenated to a structure resembling that of polyethylene by means of  $\text{LiAlH}_4$

catalyst, and then the IR measurement of  $\text{CH}_3$  and  $\text{CH}_2$  groups absorptions [1, 2] was carried out. The  $\text{CH}_3$  groups in the reduced polymer chain are present as a result of 1) head-to-head and tail-to-tail coupling during the propagation step and 2) conversion of  $\text{CHCl}_2$  and  $\text{CH}_2\text{Cl}$  end groups, formed as a result of head-to-tail propagation, into  $\text{CH}_3$  groups during hydrogenation of the polymer.

The  $\text{CH}_2$  groups in the reduced products, on the other hand, are found as a result of the internal units, as well as being due to the conversion of  $\text{CHCl}$  groups into  $\text{CH}_2$  groups.

Some unsaturated end groups may also be found in the polymer chain, and they should be of the  $\text{CH}=\text{CHCl}$  and  $\text{CCl}=\text{CH}_2$  types. These groups are converted to  $\text{CH}_2-\text{CH}_3$  groups upon hydrogenation. It is believed that the amount of such groups as compared to  $\text{CH}_2$  groups is negligible [3].

Finally, one should also consider the end groups  $\text{CH}_2-\text{R}$  or  $\text{CHCl}-\text{R}$ , which are incorporated in the chain as a result of catalyst, additive, or solvent residues (R) during polymerization [3]. It has been shown that the proportion of such end groups when derived from catalyst, additive, and solvent residues is very small and, hence, can be neglected [3, 4].

From what has been said above, it should now be clear that the ratio  $\text{CH}_3/\text{CH}_2$  in the catalytically reduced PVC can be used for the characterization of its branching index [3].

According to the method employed, the branching indices determined for PVC samples used were found to vary directly with their temperature of polymerization.

## EXPERIMENTAL

The following materials and methods were used for this study.

### Materials

**Polymers.** PVC samples were prepared at 55, 90, 130, and 160°C. These products were completely soluble in tetrahydrofuran at room temperature.

**Linear Hydrocarbons.** Cetane ( $\text{C}_{16}\text{H}_{34}$ ), octadecane ( $\text{C}_{18}\text{H}_{38}$ ), tetra-cosane ( $\text{C}_{24}\text{H}_{50}$ ), octacosane ( $\text{C}_{28}\text{H}_{58}$ ), dotriacontane ( $\text{C}_{32}\text{H}_{66}$ ), hexatri-contane ( $\text{C}_{36}\text{H}_{74}$ ), tetracontane ( $\text{C}_{40}\text{H}_{82}$ ), tetratetracontane ( $\text{C}_{44}\text{H}_{90}$ ), and hexacontane ( $\text{C}_{60}\text{H}_{122}$ ), and polymethylene  $[(-\text{CH}_2-)_n]$ , were used as branching calibration standards.

Cetane was obtained from the American Petroleum Co., and octadecane, tetracosane, octacosane, and hexatriacontane were obtained from the Aldrich Chemical Co. Tetracontane, tetratetracontane, hexacontane, and octacontane were prepared by standard methods.

Polymethylene was synthesized by the catalytic decomposition of diazomethane at 0°C in ethereal medium with boron trifluoride etherate as the catalyst [5]. Diazomethane was prepared by N-nitrosomethyl urea [6] obtained from the K. K. Laboratories. Characterization of the polymethylene was by melting point, infrared analysis, and molecular weight. The following results obtained suggested that the product synthesized was a high molecular weight polymethylene (linear polyethylene).

Melting Point: 135°C determined by Perkin-Elmer Differential Scanning Colorimeter at a heating rate of 20°C/min.

Infrared Analysis: No absorptions were found in the regions 3.2, 7.3, and 11.2-11.3 $\mu$ , and for C=C unsaturated groups. A strong doublet was observed at 13.75 and 13.9 $\mu$ . A weak band at 5.9  $\mu$  (C=O) was also observed and is presumed to have been caused by the oxygen-containing catalyst system used in the synthesis of the product [7].

Molecular Weight: Intrinsic viscosity,  $[\eta]$ , of the polymethylene prepared was found to be 8.0 g liter<sup>-1</sup> in mixed xylene at 135°C. The molecular weight calculated from the relation [8],  $[\eta] = 1.35 \times 10^{-4} (\bar{M}_n)^{0.63}$ , was  $3.8 \times 10^7$ .

**Miscellaneous Products.** Lithium aluminum hydride was obtained from the Ventrion Corp., Tetrahydrofuran and Decalin from the E. I. du Pont de Nemours & Co., and xylene from the Fisher Scientific Co. All solvents were distilled prior to use.

## Methods

**Reductive Hydrogenation** [3, 9]. Reductive hydrogenation of the PVC samples was carried out in two stages. In the first stage, a mixture of LiAlH<sub>4</sub> + PVC (9 + 5 g) in THF (300 ml) was charged to a flask (500 ml) equipped with a reflux condenser, a stirrer, and a N<sub>2</sub> inlet and outlet system. The flask was heated to 67  $\pm$  2°C and the reaction was continued for about 360 hr. Then, the reduced mass was poured into an excess of H<sub>2</sub>O to which H<sub>2</sub>SO<sub>4</sub> was added until pH 2 was attained. The precipitated polymer was filtered, dried to a constant weight, and its chlorine content determined by the Schöniger method. The first stage reduced product was then subjected to the second stage (final) of reduction in the

same apparatus under the following conditions:  $\text{LiAlH}_4 + \text{PVC}$ : 7 + 2; THF + Decalin mixture: 95 + 225 ml; temperature:  $96 \pm 2^\circ\text{C}$ ; time: about 150 hr. The isolation of the reduced product and its chlorine analysis was done in the same manner as described above.

**Infrared Analysis.** The absorptions ( $A$ ) of the  $\text{CH}_3$  ( $1378 \text{ cm}^{-1}$ ) and  $\text{CH}_2$  ( $1368 \text{ cm}^{-1}$ ) groups in the linear hydrocarbons and the reduced polymers were recorded on a Perkin-Elmer 521 spectrophotometer. The measurements were carried out on molten samples supported by rock salt plates. The maximum absorbance values were obtained by the well-known base-line method.

**Viscosity Determination.**  $[\eta]$  of the unreduced products were determined in THF at  $30^\circ\text{C}$  and of reduced samples in mixed xylene at  $110^\circ\text{C}$ .

**Computations.** All calculations reported here were carried out by an IBM 1800 computer using a least squares program. The confidence limits reported are at 95% level.

In the equations that follow in the Results and Discussion section, the terms  $Y$  and  $X$  were defined as

$$Y = \text{ACH}_3/\text{ACH}_2 = A_{1378}/A_{1368}$$

and

$$X = \text{CH}_3/\text{CH}_2$$

The statistical indicators,  $R^2$  (correlation coefficient squared),  $F$  (statistical significance fit indicator), and  $\text{STE}$  (standard error), were calculated as shown below.  $Y_o$ ,  $Y_c$ ,  $Y_k$ ,  $X_k$ , and  $X_c$  were  $Y_{\text{observed}}$ ,  $Y_{\text{calculated}}$ ,  $Y_{\text{known}}$ ,  $X_{\text{known}}$ , and  $X_{\text{calculated}}$ , respectively.

$$R^2 = \frac{\Sigma (Y_o - \bar{Y})^2 - \Sigma (Y_o - Y_c)^2}{\Sigma (Y_o - \bar{Y})^2}$$

where

$$\bar{Y} = \frac{\Sigma Y_o}{\text{Number of data points}}$$

$$F = \frac{\text{Number of data points} - \text{Number of constants}}{\text{Number of constants}} \left( \frac{R^2}{1 - R^2} \right)$$

$$\text{STE} = \sqrt{\frac{\sum (Y_0 - Y_c)^2}{\text{Number of data points} - \text{Number of constants}}}$$

## RESULTS AND DISCUSSION

In Table 1 data are given for the  $\text{ACH}_3/\text{ACH}_2$  and  $\text{CH}_3/\text{CH}_2$  ratios for the linear hydrocarbons used in the establishment of the branching calibration curve. Since polymethylene did not show any absorption in the  $1378 \text{ cm}^{-1}$  region, its  $\text{ACH}_3/\text{ACH}_2$  ratio was zero, and, being a very high molecular weight hydrocarbon, its  $\text{CH}_3/\text{CH}_2$  ratio was also regarded as zero.

The hydrocarbon data was fitted to the following equations:

$$Y = (19.94 \pm 0.28)X \quad (1a)$$

$$R^2 = 0.999 \quad F = 684 \quad \text{STE} = 0.032$$

$$Y = 20X \quad (1b)$$

$$R^2 = 0.999 \quad F = 669 \quad \text{STE} = 0.032$$

Both Eq. (1a) and (1b) showed equally good statistical fit, but the latter model was selected because of its simplicity. A graph of Eq. (1b) and the plotted data are shown in Fig. 1.

Recently Boccato et al. [3] published their results for PVC branching. Their calibration curve has been reconstructed and is shown in Fig. 2 [10]. Notice that there are two distinct regions in the reconstructed calibration curve. One, covering the linear hydrocarbon data, is shown by the extrapolated broken line (- -), and the other, fitting the mixtures (higher hydrocarbons made up of polymethylene and lower hydrocarbons) data, is shown as a solid line (—). The reconstructed calibration curve was analyzed empirically. The following equations were found to fit the data:

$$Y = (20.19 \pm 0.42)X \quad (2a)$$

$$R^2 = 0.998 \quad F = 224 \quad \text{STE} = 0.028$$

$$Y = 20X \quad (2b)$$

$$R^2 = 0.999 \quad F = 160 \quad \text{STE} = 0.033$$

Table 1. A Test of the Various Calibration Equations

Linear hydrocarbon	Y <sub>0</sub>	X <sub>k</sub>	Eq. (1b)		Eq. (3)		Eq. (4)		Eq. (5)	
			X <sub>c</sub>	X <sub>k</sub> - X <sub>c</sub>	X <sub>c</sub>	X <sub>k</sub> - X <sub>c</sub>	X <sub>c</sub>	X <sub>k</sub> - X <sub>c</sub>	X <sub>c</sub>	X <sub>k</sub> - X <sub>c</sub>
16	2.8517	0.1430	0.1426	0.0004	0.1683	-0.0253	0.1426	0.0004	0.1426	0.0004
18	2.5190	0.1250	0.1259	-0.0009	0.1474	-0.0224	0.1259	-0.0009	0.1259	-0.0009
24	1.7876	0.0909	0.0889	0.0020	0.1007	-0.0098	0.0889	0.0020	0.0889	0.0020
28	1.5270	0.0769	0.0764	0.0005	0.0850	-0.0081	0.0763	0.0006	0.0763	0.0006
32	1.3468	0.0667	0.0763	-0.0006	0.0736	-0.0069	0.0671	-0.0004	0.0671	-0.0004
36	1.1591	0.0588	0.0580	0.0008	0.0618	-0.0030	0.0577	0.0011	0.0577	0.0011
40	1.0493	0.0526	0.0525	0.0001	0.0549	-0.0023	0.0520	0.0006	0.0520	0.0006
44	0.9143	0.0476	0.0457	0.0019	0.0464	0.0012	0.0449	0.0027	0.0449	0.0027
60	0.6753	0.0345	0.0338	0.0007	0.0314	0.0031	0.0320	0.0025	0.0320	0.0025
80	0.5905	0.0256	0.0295	-0.0039	0.0261	0.0005	0.0270	-0.0014	0.0270	-0.0014
Poly-methylene	0	0	.	.	.	.	.	.	.	.
Maximum difference:				-0.004		0.0253		0.003		0.003
Per cent uncertainty in 100 (CH <sub>3</sub> /CH <sub>2</sub> ):				±0.4		±2.5		±0.3		±0.3

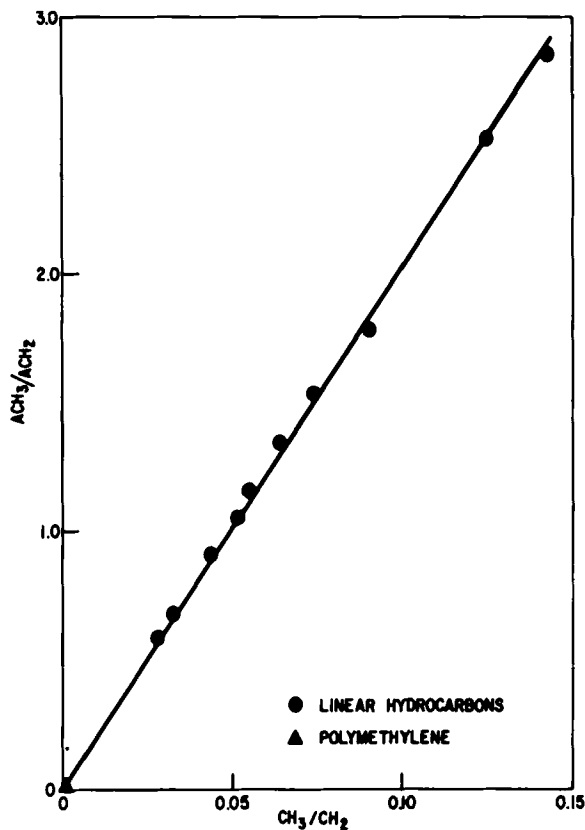


Fig. 1. Branching calibration curve based on pure linear hydrocarbons.

Equations (2a) and (2b) were found to fit the linear hydrocarbon data, but the latter model was selected because of its simplicity.

$$Y = (0.176 \pm 0.057) + (15.90 \pm 1.67)X \quad (3)$$

$$R^2 = 0.997 \quad F = 925 \quad \text{STE} = 0.021$$

Equation (3) was found to fit the mixtures data.

$$Y = 20X + 0.298 \exp(-66.07 \pm 36.27)X \quad (4)$$



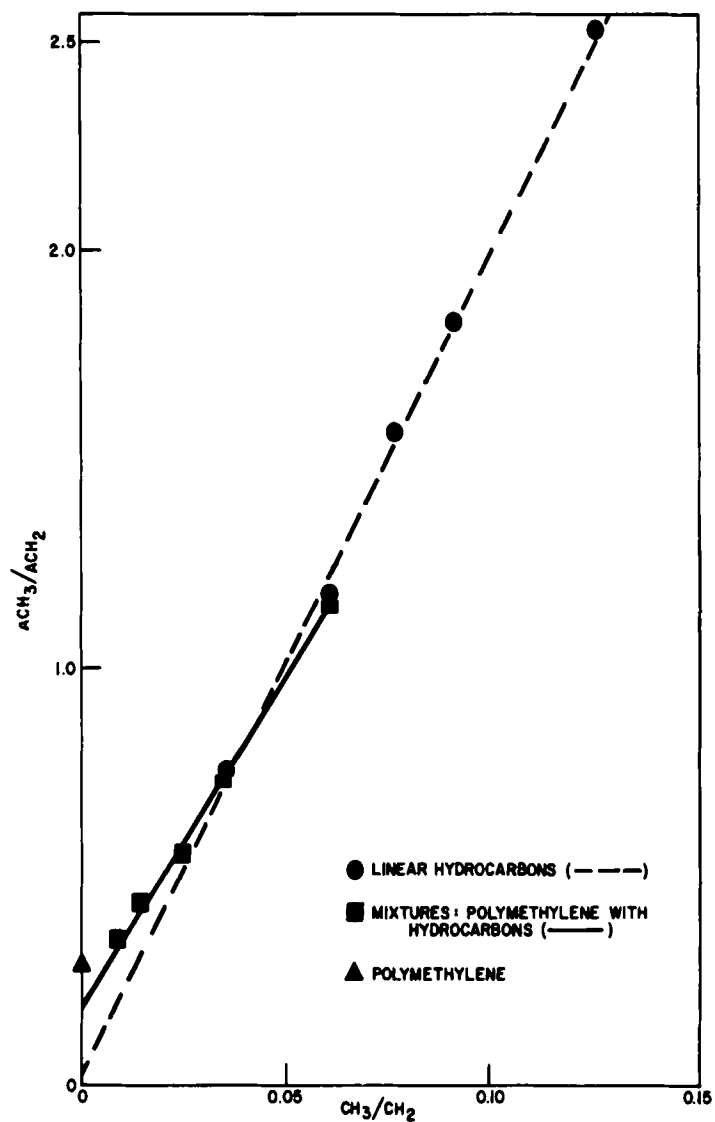


Fig. 2. Branching calibration curve based on pure and mixed linear hydrocarbons.

Confidence limits on the preexponential factor varied from 0.113 to 0.786.

$$R^2 = 0.918 \quad F = 33 \quad STE = 0.267$$

Equation (4) was fitted to all the data points excluding polymethylene.

$$Y = 20X + 0.289 \exp(-65.15 \pm 19.80)X \quad (5)$$

Confidence limits on the preexponential factor varied from 0.179 to 0.420.

$$R^2 = 0.954 \quad F = 83 \quad STE = 0.231$$

Equation (5) was fitted to all the data points.

The models available for the calculation of branching indices were then (1a) or (2b), (3), (4), and (5). But before getting into the calculation of polymer branching, it is important to first point out the reasons which motivated our reexamination of the branching calibration published by Boccato et al. [3]. The reasons were 1) that the nonlinear portion of this calibration curve deserved further examination, and 2) that  $ACH_3/ACH_2 = 0.284$  reported for polymethylene deserved further scrutiny. This is because of the fact that polymethylene has only two  $CH_3$  groups attached as chain ends, and their absorption is so weak that it cannot be recorded. Recall here that polymethylene prepared for this investigation did not show any absorption for  $CH_3$  groups.

A test of the various calibration equations is shown in Table 1. The per cent uncertainty in X as calculated through Eq. (1b), (4), and (5) is essentially the same, but Eq. (3) shows higher uncertainty. A further test of these equations is in the branching index results, and this should become evident when the data of Table 2 are discussed.

Table 2. Branching Indices,  $100(CH_3/CH_2)$ , of the Polymers Studied

Temperature of preparation of PVC samples t (°C)	$Y_0$	Eq. (1b)	Eq. (3)	Eq. (4)	Eq. (5)
55	0.3835	1.92	1.31	1.28	1.29
90	0.3902	1.95	1.35	1.33	1.35
130	0.5218	2.61	2.17	2.28	2.28
160	0.5907	2.96	2.61	2.70	2.70

The IR spectra of the reduced polymers were found to be essentially the same as for typical polyethylene spectrum, and no absorption corresponding to  $\text{CH}=\text{CH}_2$  groups at  $910\text{ cm}^{-1}$  was observed. A part of a spectrum of a reduced polymer, in the region of interest, is reproduced in Fig. 3.

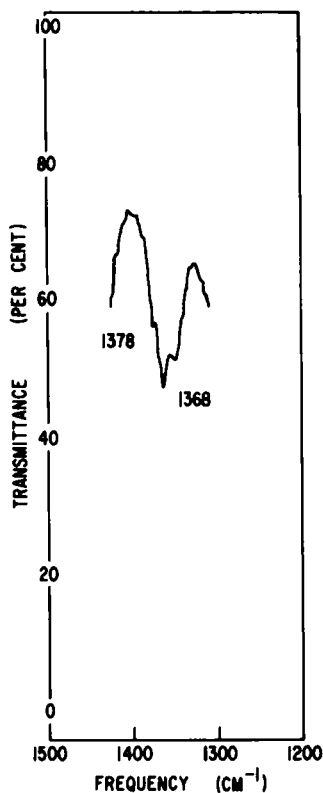


Fig. 3. An infrared spectrum of a reduced PVC sample.

Branching indices of the polymers studied were calculated on the basis of such typical spectrum. These results are summarized in Table 2. Equations (4) and (5), as expected, calculated essentially the same branching indices, while Eq. (3) shows slightly lower values for high temperature PVC samples, and all these equations give lower branching results than those calculated by Eq. (1b). These differences in the branching indices and also those reported in Table 1 may be rationalized in terms of  $Y_0$  values of reduced polymers and of hydrocarbons as reported by Boccatto et al. [3].

Branching indices calculated according to Eq. (1b) were preferred because of the following considerations: 1) Eq. (1b) is based on pure hydrocarbons and polymethylene data 2) Eq. (3) is not a valid model because it is based on insufficient experimental evidence and also because it shows a higher uncertainty in the predicted values of X and 3) Eqs. (4) and (5) are not suitable models because they are based on two different types of hydrocarbons.

$Y = 20X$  is then suggested as the branching calibration equation for PVC. The usefulness of this correlation lies in the fact that it should enable one to determine the branching index of an unknown polymer with only one measurement, e.g.,  $ACH_3/ACH_2$  ratio.

In order to make sure that the branching results presented here represented true values, the status of the reduced polymer was checked. During the hydrogenation process the polymer chains may degrade, resulting in erroneous branching results. This complication, as a first approximation, did not occur in the experiments carried out because  $[\eta]$  data of the polymers in the unreduced and reduced states were not significantly different. These results are shown in Table 3. A more sensitive test

Table 3. Status of the Reduced Polymer

Temperature of preparation of PVC sample $t$ ( $^{\circ}\text{C}$ )	$[\eta]$ unreduced ( $\text{dl g}^{-1}$ )	$[\eta]$ reduced ( $\text{dl g}^{-1}$ )	$\frac{[\eta] \text{ unreduced}}{[\eta] \text{ reduced}}$	Residual chlorine (%)
55	0.235	0.215	1.09	1.4
90	0.348	0.362	0.96	1.4
130	0.152	0.139	1.09	0.7
160	0.156	0.163	0.96	1.4

for checking molecular scission would, of course, be the measurement of dilute solution properties of the polymer in the unreduced and reduced states in the same solvent and at the same temperature. This is not possible in PVC because upon reduction the physical properties of the polymer are changed and a drastic change in its dilute solution behavior is thus brought about. As far as the residual chlorine in the finally reduced polymer is concerned, it varied from 0.7 to 1.4%. These results are also given in Table 3.

Several other groups of workers [1, 2, 4, 9, 11-16] have also carried out PVC branching studies, but their results cannot be compared with those given here because of the differences involved in the calibration curves.

As far as the quality of branches is concerned, it is expected that  $\text{CH}_3$  and  $\text{CH}_2\text{Cl}$  (and  $\text{CHCl}_2$ ) ended side chains should be of unequal length because of the different mechanisms involved in their formation.

On the basis of this study, two conclusions can be drawn: 1) that  $\text{ACH}_3/\text{ACH}_2$  varies linearly with  $\text{CH}_3/\text{CH}_2$  and 2) that there is a 10% upward change in branching as the temperature of polymerization increases from 55 to 160°C.

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