Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

High-Field ^{1}H-NMR Study of Poly(Vinyl Chloride) Defects

M. F. Darricades-llauro[a]; A. Michel[a]; A. Guyot[a]; H. Waton[b]; R. Petiaud[b]; Q. T. Pham[b]
[a] C.N.R.S. Laboratoire des Matériaux Organiques, France [b] C.N.R.S. Service Central d'Analyse, France

To cite this Article Darricades-llauro, M. F. , Michel, A. , Guyot, A. , Waton, H. , Petiaud, R. and Pham, Q. T.(1986) 'High-Field ^{1}H-NMR Study of Poly(Vinyl Chloride) Defects', Journal of Macromolecular Science, Part A, 23: 2, 221 — 269
To link to this Article: DOI: 10.1080/00222338608063389
URL: http://dx.doi.org/10.1080/00222338608063389

J. MACROMOL. SCI.–CHEM., A23(2), pp. 221-269 (1986)

High-Field ^{1}H-NMR Study of Poly(Vinyl Chloride) Defects

M. F. DARRICADES-LLAURO, A. MICHEL, and A. GUYOT

C.N.R.S. Laboratoire des Matériaux Organiques
BP 24-69390 Vernaison, France

H. WATON, R. PETIAUD, and Q. T. PHAM

C.N.R.S. Service Central d'Analyse
BP 22-69390 Vernaison, France

ABSTRACT

Radical poly(vinyl chlorides), (PVC), obtained in bulk and in suspension polymerizations, and their low molecular weight extracts have been thoroughly studied by high-field NMR to obtain better qualitative and quantitative analyses of their structural defects. Assignments have been achieved by ^{1}H-^{1}H decoupling experiments and hyperfine spectral structure analysis of model compounds and low molecular weight extracts. Strong effects of the nature of the solvents used in ^{1}H-NMR analysis were observed. Most of the defects of these radical PVC's have been quantitatively estimated in terms of average number values in correlation with their $\overline{M}_n$. End-groups of type [I] (= $-CH_2-CH=CH-CH_2Cl$) are about 0.5 per chain; internal double bonds can only be estimated by difference, and their amount increases with increasing conversion. A very low quantity of vinyl chain end [I'] (= $-CHCl-CH=CH_2$) has been found only in low molecular weight extracts. For the three probable saturated chloromethyl ends [II] (= $-CHCl-CH_2Cl$), [III] (= $-CH_2-CH_2Cl$),

0022-233X/86/2302-0221$3.50/0

and [IV] (= >CH–CH_2Cl), only [II] and [III] were definitely identified. Finally, in taking into account all the endgroups, it has been concluded that branches would be grafted throughout the process. On the average, 4 to 5 branches have been found per chain of high molecular weight PVC.

INTRODUCTION

Structural defects are generally believed to be the cause of the thermal instability of poly(vinyl chloride) (PVC). Thus, a number of studies have been devoted to the identification of these defects by both chemical and spectroscopic methods. Recently, a IUPAC group has been working on this problem, and the results were summarized in a report [1]. This paper is a detailed report on our contribution.

The mechanisms responsible for some of these defects are still disputed. It has long been accepted that the molecular weight of the polymer is governed by a transfer process to the monomer having a very large transfer constant (10^{-3} at 50°C). However, no evidence had been given for the expected endgroups generated by this transfer mechanism, as discussed thoroughly by Caraculacu et al. [2-5].

From a study of low molecular weight extracts by ^{1}H-NMR at 60 MHz, Petiaud and Pham [6] showed that the main unsaturated chain end corresponds to –CH_2–CH=CH–CH_2Cl [I] while the main saturated chain end is –CHCl–CH_2Cl [II]. More recent studies [7-9] confirmed these results. The branch structures have been studied by ^{13}C-NMR using hydrogenated and deuterated PVC's. The initial work of Abbas et al. [10] first proved that most of the branches are one-carbon-atom branches. Later on, the same authors proved that these are chloromethyl branches (>CH–CH_2Cl [IV]) and showed conclusively that they were formed after head-to-head addition followed by an internal transfer mechanism [11-15]. As initially suggested by Rigo et al. [16], this result should explain the absence of head-to-head structures in PVC, in contrast with poly(vinyl acetate)–a polymer produced by growing radicals of similar reactivity–that contains about 1-2% of head-to-head additions. Branches such as butyl (actually 2,4-dichlorobutyl) branches [9, 15a, 17] were detected and their presence explained by internal transfer to the polymer (back-biting). Other short branches have also been mentioned [9], but their existence is more disputed.

A small amount of long branches involving the presence of tertiary chlorine atoms should exist. They can be explained by a transfer mechanism to the polymer, which is more frequent when polymerization is carried out under monomer subsaturation conditions [18]. These transfer reactions are thought to be responsible for the second main saturated chain end structure, viz., –CH_2–CH_2Cl [III]. All these

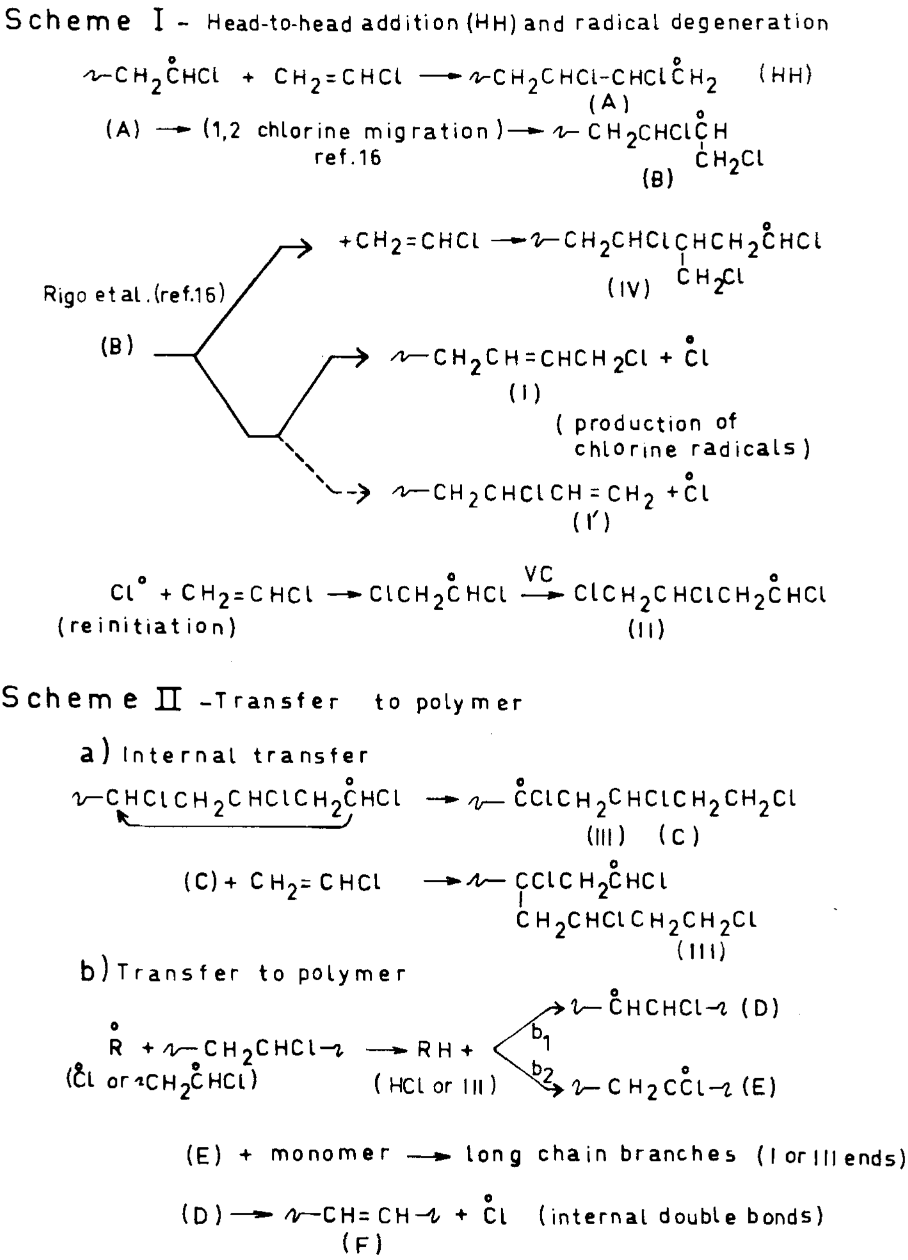


FIG. 1. Reaction mechanisms for the generation of structural defects in poly(vinyl chloride).

structures can be explained by the mechanisms given in the qualitative schemes described in Fig. 1, which also gives a possible route for the formation of internal unsaturation sites. This type of unsaturation has mostly been detected through chain breaking by ozonolysis [19]; however, its exact nature remains unknown. Hjertberg and Sörvik [8] have shown that at 200 MHz the ^{1}H-NMR spectrum of a sample prepared under very low monomer pressures ($P/P_0 = 0.59$, P_0 being the saturation pressure of vinyl chloride at 55°C) is very complex and poorly resolved.

This work deals with a ^{1}H-NMR study at 350 MHz of some of the PVC samples prepared and examined in the framework of the IUPAC working Party. Complementary information was obtained by ^{13}C-NMR at 88 MHz. Attempts are made to give more quantitative estimations of the different types of chain ends, branches, and unsaturated structures.

EXPERIMENTAL

Polymers

Three of the PVC samples examined in this study are those of the IUPAC Working Party. Their characteristics are reported in Table 1. Samples A, B, and C correspond to Samples XIII, XII and X, respectively, in the IUPAC reports. The four others are commercial polymers.

Vapor Pressure Osmometry (VPO)

The number-average molecular weights ($\overline{M}_n$) of the extracts (A_e, B_e, and C_e) were measured in toluene at 40°C using an A.I.S. vapor pressure osmometer.

NMR Spectrometry

Low molecular weight extracts (A_e, B_e, and C_e) were studied by ^{1}H-NMR in the following solvents: $CDCl_3$, CD_3COCD_3, a mixture of CD_3COCD_3/CS_2 (5:3 by volume) at room temperature, C_6D_6 at 60°C, and $C_6D_5NO_2$ at 140°C. Complementary information was obtained by studying sample B_e by ^{13}C-NMR in CD_3COCD_3 at room temperature.

TABLE 1. Characteristics of the PVC Samples

		Sample[a]		
		A	B[b]	C[c]
Supplier		Chloé-Ch.	Chloé-Ch.	BF Goodrich
Process		Bulk	Bulk	Suspension subsaturation
Temperature (°C)		56	56	60
Initiator		Cyclohexyl peroxydicarbonate	Cyclohexyl peroxydicarbonate	Azobisiso-butyronitrile
Conversion		54.7	83.5	85
Crude PVC:	$\overline{M}_n \times 10^{-3}$	43.3	37.5	40.6
	$\overline{M}_w \times 10^{-3}$	94.2	91.8	91.2
Extracts[d]	Amount (%)	0.5	1.3	0.6
	$\overline{M}_n$	2 980 ± 150	2 400 ± 120	3 950 ± 200

[a] Correspondence with the IUPAC Working Party: A = XIII, B = XII, C = X.

[b] Spontaneous final overheating at 8.3 kg/cm^2 because the pressure had been kept as constant as possible. Elimination of traces of monomer by degassing at 80°C.

[c] Sample C was prepared under saturation conditions up to 20% conversion. After vacuum evaporation of 52% of the monomer into a second reactor, the pressure was decreased by 0.35 kg/cm^2 while the evaporated monomer was slowly reintroduced into the reactor. The pressure drop at the end of the process was 1.4 kg/cm^2.

[d] Extraction by a tenfold volume of hexane (75) + acetone (25) over a period of 20 h at 20°C, evaporation at 30°C under vacuum (0.1 torr).

We used a Caméca 350 (350 MHz and 88 MHz for ^1H and ^{13}C, respectively) spectrometer. The internal reference used was tetramethylsilane (TMS). All the relative intensities of ^1H resonances were measured by planimetry.

RESULTS AND DISCUSSION

According to the reaction mechanisms given schematically in Fig. 1, the structural defects investigated in this study are:

(a) $-CH_2-CH=CH-CH_2Cl$ [I] and $-CHCl-CH=CH_2$ [I'] (part of the polymer chain ends and part of the long branch ends)

(b) $-CHCl-CH_2Cl$ [II]

(c) $-CH_2-CH_2Cl$ [III] (complementary part of the polymer chain ends + complementary part of the long branch ends + all the butyl branches)

(d) $>CH-CH_2Cl$ [IV] (chloromethyl branches)

I. Olefinic Structures. Pseudo-Terminal [I], Terminal [I'], and Internal Double Bonds

$$\overset{4}{-CH_2}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_2}Cl \quad [I]$$

Because of the complexity of ^1H spectra—even at high field—examination of low molecular weight extracts in different solvents gives complementary qualitative and quantitative information.

I.1. PVC Extracts

I.1.1. ^1H Spectra of the Extracts in $CDCl_3$ at Room Temperature. The ^1H spectrum of C-extract (C_e) is shown in Fig. 2. The olefinic proton resonances lie between 5.7 and 6 ppm (a_2, Fig. 2). Their shape is nearly symmetrical, except for the presence of small peaks in the 5.7-5.5 ppm region that are more intense in the B-extract (B_e) than in the A-extract (A_e) (Fig. 3). The pattern of these olefinic resonances corresponds to the two protons ($H_2 + H_3$) of the pseudo-terminal double bond of [I]. In $CDCl_3$, the H_2 and H_3 resonances (a_3, Fig. 2; Fig. 4, bottom) are very close together, and they are coupled, with both of the doublets centered at 4.06

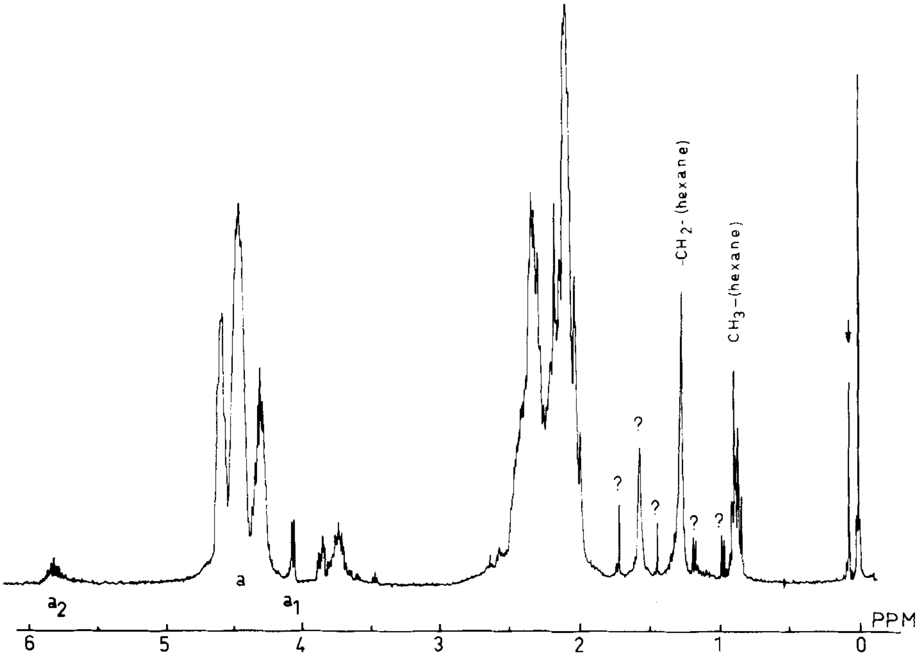


FIG. 2. General ^{1}H spectrum of low molecular weight PVC. Extract of C studied in $CDCl_3$ at room temperature. (↓): Methylsiloxane resonance from traces of silicone grease. (?): Unidentified impurities.

and 4.10 ppm (a_1, Fig. 2) belonging to H_1 of [I]. The first doublet originates from the trans isomer and the second one from the cis isomer.

The (H_2 + H_3) olefinic resonances of [I] decoupled from H_1 (4.1 ppm) and H_4 (2.56 ppm) are shown in Fig. 4 (middle and top). Irradiating (H_2 + H_3) centered at 5.8 ppm (a_2, Fig. 2) causes effects on the resonances of H_1 and H_4 (Fig. 5). The two doublets of H_1 become two singlets (Fig. 5a) (Structure [I] is mainly trans) and the triplet of H_4 (Fig. 5b, b') gives a doublet (Fig. 5b") because of its remaining coupling with the adjacent –CHCl– group.

[I] has 2 olefinic and 2 chloromethylic protons. In terms of relative intensities, one expects theoretically (a_2) = (a_1). Actually (a_2) is found to be much greater than (a_1); the excess of olefinic resonances

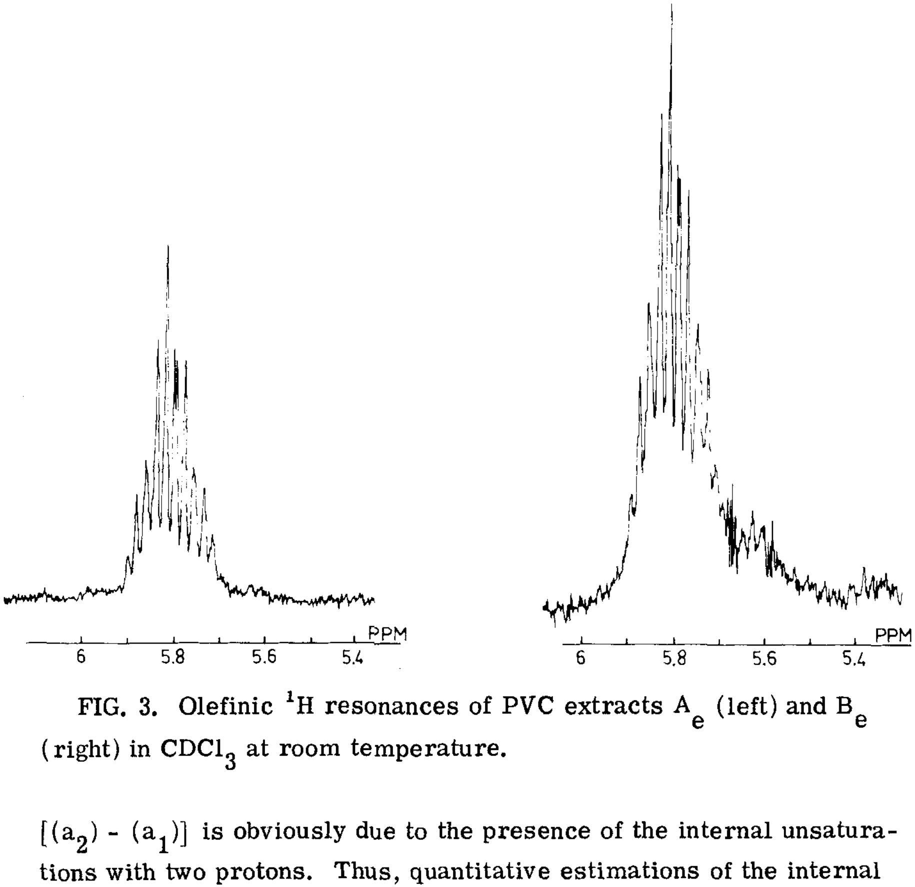


FIG. 3. Olefinic ^{1}H resonances of PVC extracts A_e (left) and B_e (right) in $CDCl_3$ at room temperature.

$[(a_2) - (a_1)]$ is obviously due to the presence of the internal unsaturations with two protons. Thus, quantitative estimations of the internal double bonds are possible from the difference $[(a_2) - (a_1)]$ by taking into account the intensity of –CHCl– (4.1-5 ppm; a, Fig. 2). If N_T is the average number of total double bonds and N_t is the average number of pseudo-terminal double bonds per 1000 vinyl chloride (VC) monomer units, the difference $(N_T - N_t)$ represents the average number of internal double bonds per 1000 vinyl chloride units (N_i):

$$N_t = \frac{(a_2)}{2(a)} \times 10^3 \quad \text{and} \quad N_t = \frac{(a_1)}{2(a)} \times 10^3. \qquad (1)$$

The values of N_T, N_t, and N_i, as well as the corresponding values

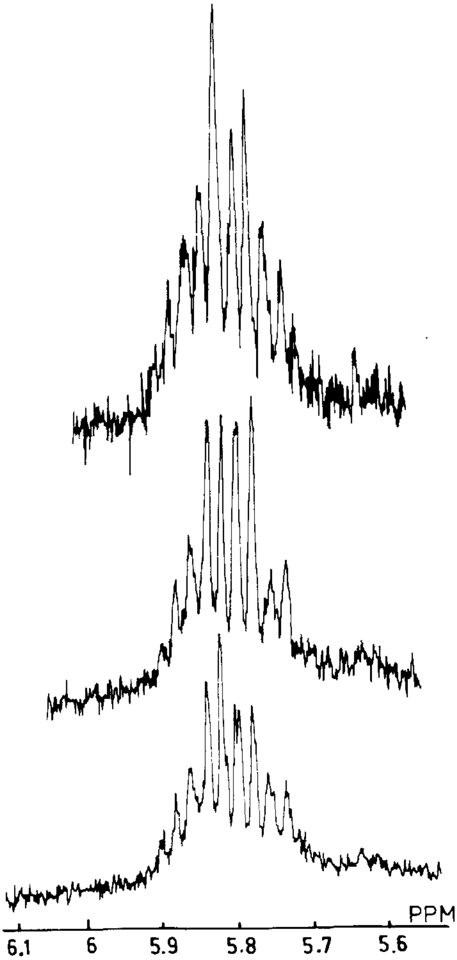


FIG. 4. Olefinic ^{1}H resonances of PVC extract C_e in $CDCl_3$ at room temperature. Bottom: Normal spectrum. Middle: Under irradiation of protons H_1 of the trans isomer of structure [I] at 4.06 ppm. Top: Under irradiation of protons H_4 of structure [I] at 2.56 ppm.

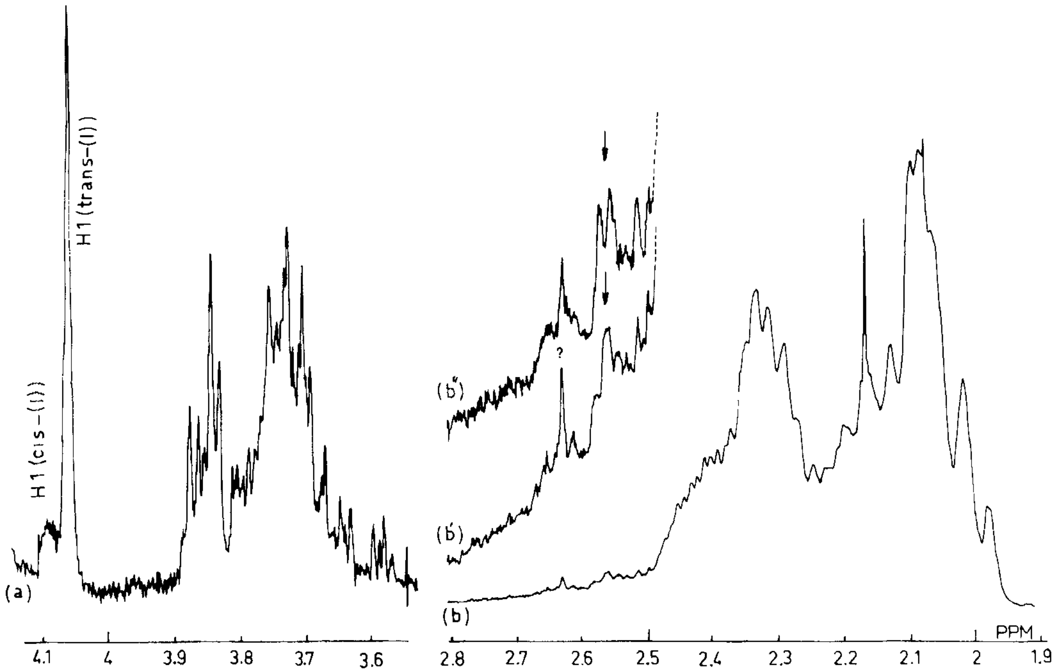


FIG. 5. ^1H resonances in the 3.6-4.1 ppm and 1.9-2.8 ppm regions of PVC extract C_e in $CDCl_3$ at room temperature. H_1 (left) and H_4 (right) resonances of structure [I]. (a): $-CH_2Cl-$ resonances decoupled from H_2 and H_3 resonances centered at 5.82 ppm. (b): $-CH_2-$ resonances (H_4). (b'): Enhanced $-CH_2$ resonances (H_4) in the 2.5-2.80 ppm region. (b"): Modified H_4 resonances obtained by irradiation of the olefinic resonances centered at 5.82 ppm

TABLE 2. Quantitative Determinations of the Average Number of Total Double Bonds per 1 000 Monomer Units (N_T) and per Chain (N_T') of Three PVC Extracts from NMR Analysis in Various Solvents

(Solvent) $\overline{M}_n$:	A_e 2 980 ± 150	B_e 2 400 ± 120	C_e 3 950 ± 200
N_T ($CDCl_3$)	16.5	22.5	15.4
N_T (CD_3COCD_3)	18.1	20.8	14.4
N_T (CD_3COCD_3/ CS_2)	20.8	22.2	14.4
N_T (C_6D_6)	16.5	21	nd[a]
N_T ($C_6D_5NO_2$)	nd[a]	nd[a]	14.3
$\langle N_T \rangle$ (mean value)	18 ± 1.5	21.6 ± 0.7	14.6 ± 0.4
$\langle N_T' \rangle$ (mean value)	0.86 ± 0.1	0.83 ± 0.07	0.92 ± 0.07

[a] nd = not determined.

of the average numbers of double bonds per chain (N_T', N_t', N_i'), calculated by taking into account the $\overline{M}_n$ of the three extracts A_e, B_e, and C_e, are reported in Tables 2 and 3.

$$N_T' = \frac{N_T}{1000} \times \overline{DP}_n, \qquad N_t' = \frac{N_T}{1000} \times \overline{DP}_n, \qquad N_i' = N_T' - N_t'. \tag{2}$$

In the A_e and B_e spectra recorded in $CDCl_3$, another very weak pair of doublets was observed at 5.21 and 5.36 ppm (Fig. 6, top). These should be assigned to the two H_a and H_b protons of a vinyl terminal double bond with the two cis and trans coupling constants J_{ac}(cis) = 10.3 Hz and J_{bc}(trans) = 16.8 Hz.

TABLE 3. Quantitative Determinations of the Average Number of Pseudo-Terminal Double Bonds (t) ($-CH_2-CH=CH-CH_2Cl$) [I] and Internal Double Bonds (i) per 1 000 Monomer Units (N_t, N_i) and per Chain (N_t', N_i') for the Three PVC Extracts from NMR Analysis in Various Solvents

	A_e	B_e	C_e
(Solvent) $\overline{M}_n$:	2 980 ± 150	2 400 ± 120	3 950 ± 200
N_t ($CDCl_3$)	13.2	12.2	11.6
N_t (CD_3COCD_3)	12.5	12	10.1
N_t (CD_3COCD_3/CS_2)	12.6	10.2	8.8
N_t (C_6D_6)	14.4	12.2	nd
N_t ($C_6D_5NO_2$)	nd	nd	11.5
Mean values per 1000 VC: $\langle N_t \rangle$	13.2 ± 0.8	11.6 ± 0.7	10.5 ± 1
$\langle N_i \rangle$	4.8 ± 2.1	10 ± 1.2	4.1 ± 0.8
Mean values per chain: $\langle N_t' \rangle$	0.63 ± 0.07	0.45 ± 0.05	0.66 ± 0.08
$\langle N_i' \rangle$	0.23 ± 0.1	0.38 ± 0.06	0.26 ± 0.06

$-CHCl-CH=CH_2$: [I'], vinyl chain end
(c) (a,b)

The model compound 3-chloro-1-butene, examined under the same conditions, gives (H_a) = 5.10 ppm, (H_b) = 5.25 ppm, J_{ac}(cis) = 10.3 Hz, and J_{bc}(trans) = 16.8 Hz (Fig. 6, bottom). The vinyl chain ends are only about 2% of the whole olefinic resonances.

I.1.2. ^{1}H Spectra of Extracts in CD_3COCD_3 at Room Temperature. The olefinic proton resonances of these three extracts in deuterated acetone, lying between 5.6 and 6.1 ppm,

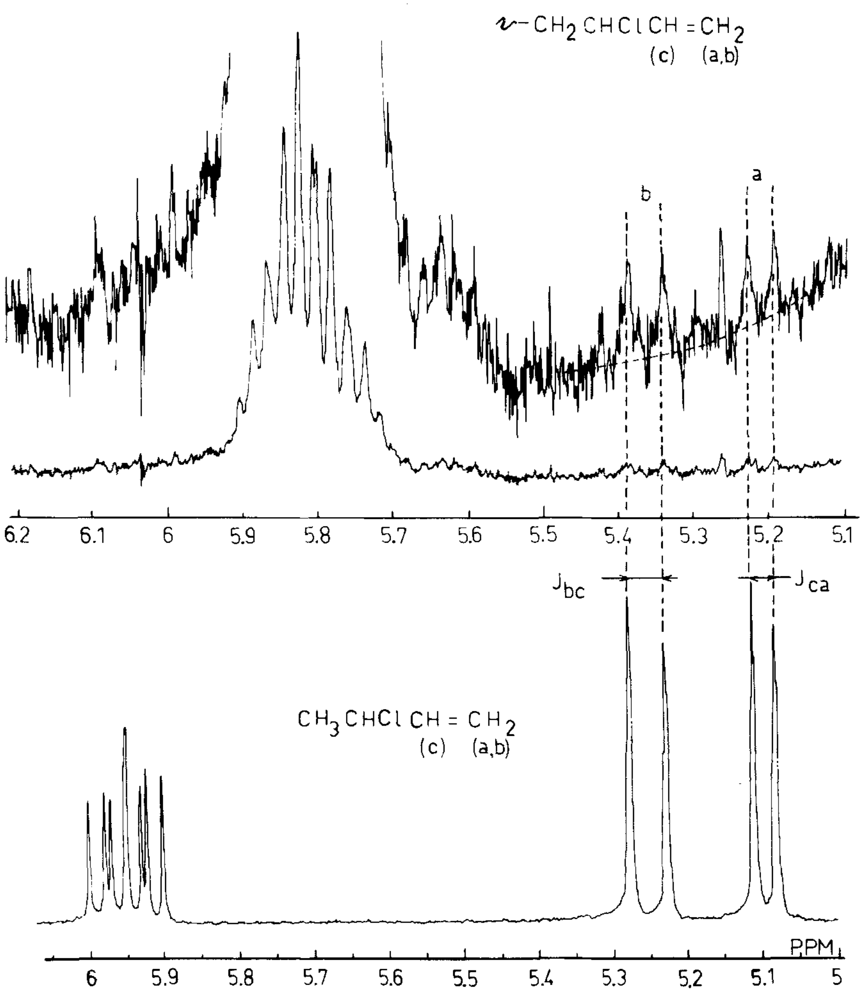


FIG. 6. Identification of the minor methylene ^{1}H resonances of the vinyl endgroup [I'] in $CDCl_3$ at room temperature. Bottom: Olefinic resonances of 3-chloro-1-butene. Top: Olefinic resonances of extract C_e.

are divided into two groups, well separated and fairly symmetrical (Fig. 7). The two H_1 doublets at 4.16 and 4.23 ppm (J(trans) = J(cis) = 7 Hz) are resolved (Fig. 8) better than in $CDCl_3$. Thus, more precise values of cis and trans isomers of [I] can be calcu-

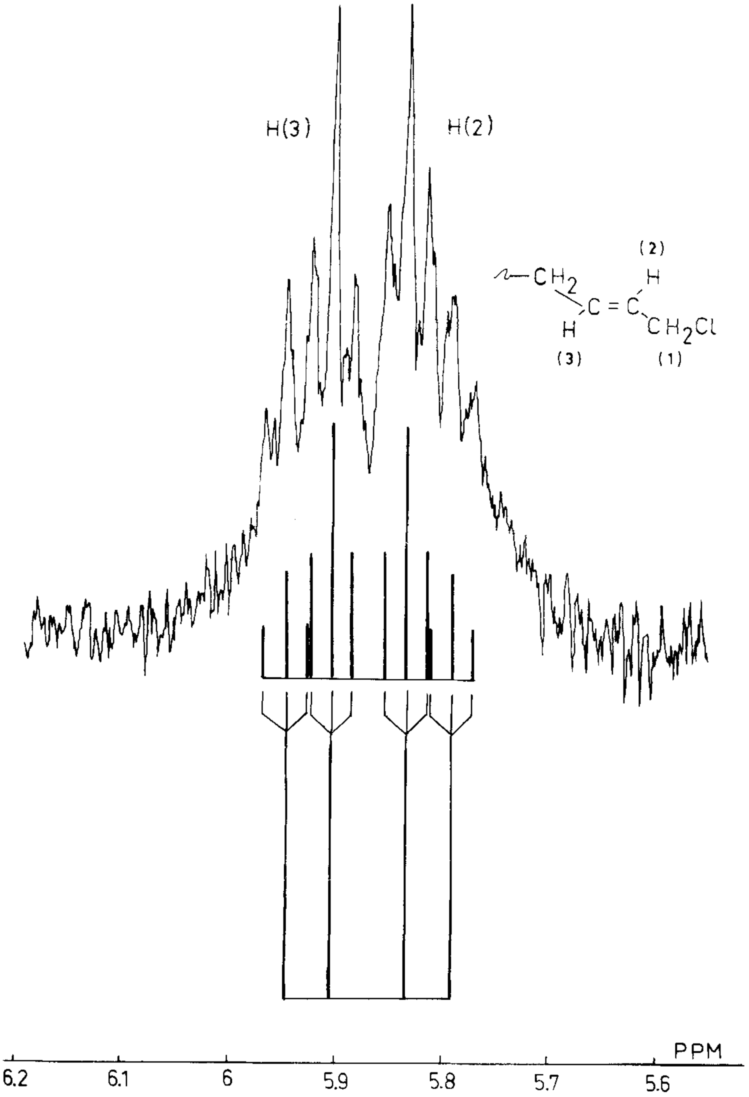


FIG. 7. ^{1}H olefinic resonances of extract C_e in CD_3COCD_3 at room temperature. Stick spectrum: Theoretical pattern of the AB part of an ABX system.

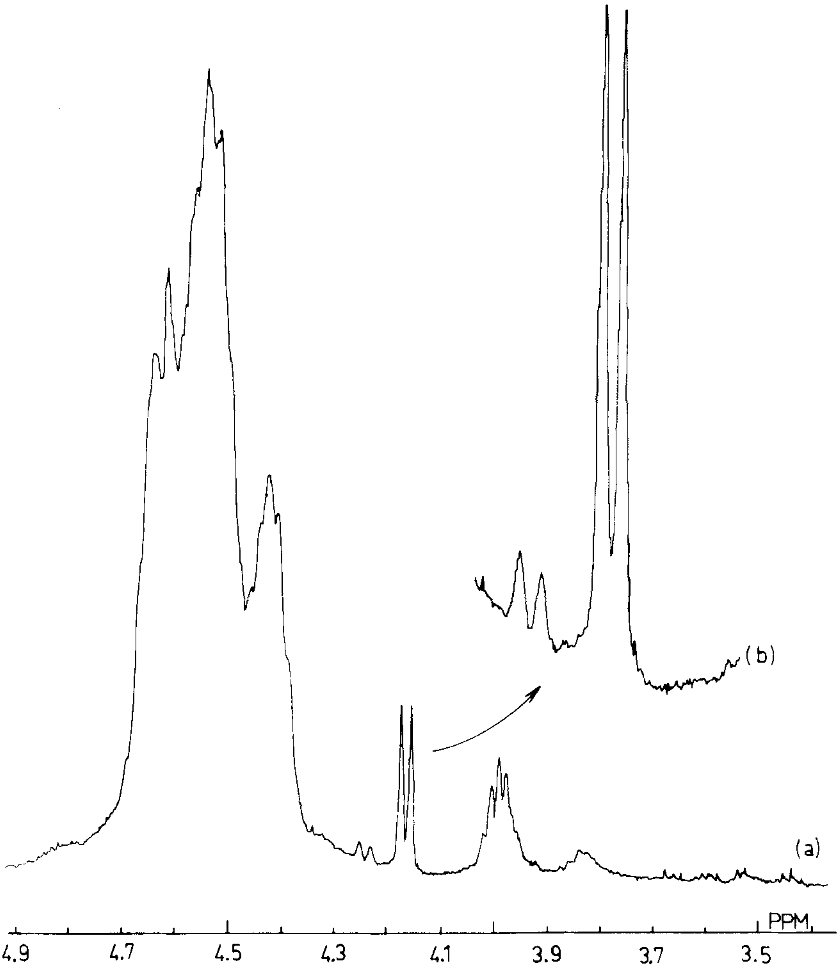


FIG. 8. –CHCl– and –CH_2Cl resonances of extract A_e in CD_3COCD_3 at room temperature (a) and enlarged spectrum of H_1 of pseudo-terminal double bonds (b).

culated from acetone-d_6 solution measurements. All three samples A_e, B_e, and C_e have 87% of chain end [I] in the trans configuration.

By irradiating H_1 of the trans isomer (4.16 ppm) and H_4 (2.6 ppm), respectively, the olefinic resonance patterns shown in Fig. 9 are ob-

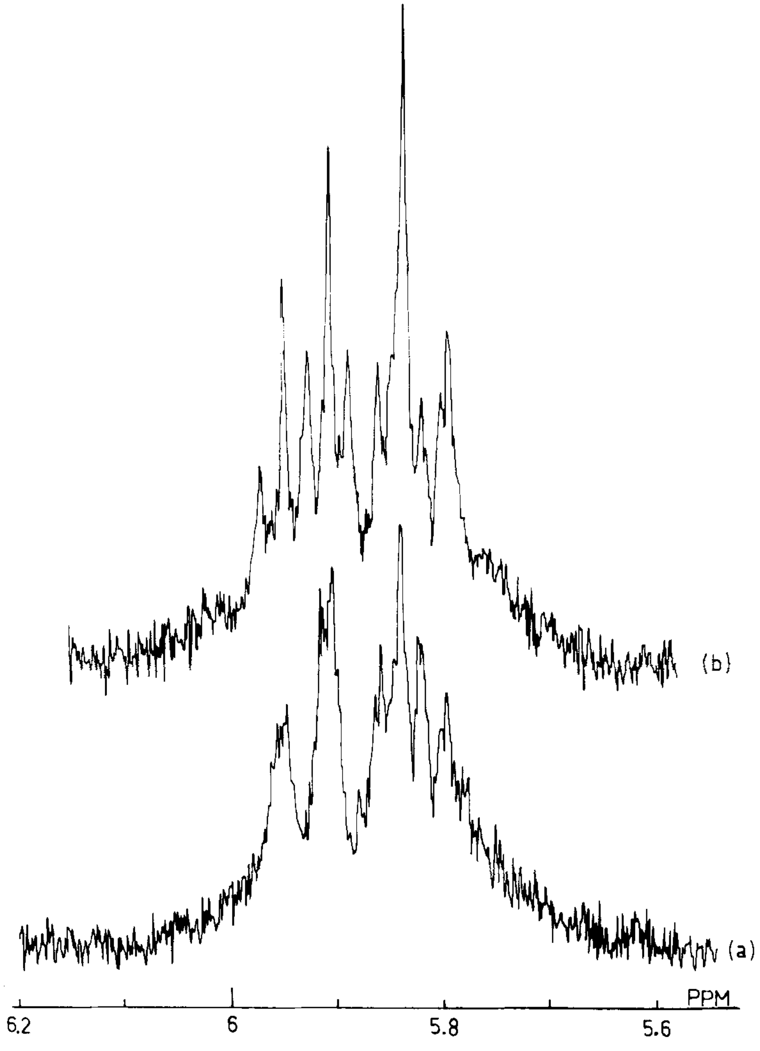


FIG. 9. Decoupled ^1H olefinic resonances of extract C_e in CD_3COCD_3 at room temperature with (a) irradiation of H_4 (at 2.6 ppm) and (b) irradiation of H_1 (at 4.16 ppm).

tained. Obviously, H_3 of the predominant trans isomer of [I] is resonating at lower field. The precise values of the chemical shifts and coupling constants are:

$(H_2) = 5.82$ ppm $J(1,2) = 6.5$ Hz

$(H_3) = 5.925$ ppm $J(2,3) = 15.5$ Hz

$J(3,4) = 6.5\text{-}7$ Hz.

The data concerning the average values of pseudo-terminal (N_t) and internal (N_i) double bonds are reported in tables 2 and 3. The results are in good agreement with those obtained in $CDCl_3$ for B_e and C_e, while some discrepancies are observed for A_e.

I. 1. 3. ^{1}H Spectra of Extracts in CD_3COCD_3/CS_2 Mixture (5:3 by volume) at Room Temperature. This solvent mixture is of particular interest because it can dissolve low molecular weight (extracts) as well as high molecular weight (crude) PVC.

The spectra of A_e, B_e, and C_e are very similar to those observed in acetone-d_6 solution with a slight shift (+0.07 ppm) of the resonances of H_1 (cis and trans) and of H_2 and H_3.

Planimetric measurements of pseudo-terminal (N_t) and internal (N_i) double bonds reported in Tables 2 and 3 are in good agreement with those of the other two solvents. Thus, the CD_3COCD_3/CS_2 solvent mixture can be used for examination of both extracted and crude samples of the same PVC.

The calculated average values of N_t, N_t' ($\langle N_t \rangle$, $\langle N_t' \rangle$) and N_i, N_i' ($\langle N_i \rangle$, $\langle N_i' \rangle$) from the different solvents are also reported in Tables 2 and 3.

For the extracts A_e, B_e and C_e, N_T increase with decreasing $\overline{M}_n$ (Table 2), while N_t (Table 3) is nearly constant and equal to 12 pseudo-terminal double bonds [I] per 1 000 monomer units. $N_i = (N_T - N_t)$, obtained with very poor accuracy for A_e, increases from approximately 4 (C_e) to 10 (B_e) internal double bonds per 1 000 monomer units when $\overline{M}_n$ decreases from 4×10^3 (C_e) to 2.4×10^3 (B_e) (Table 3). However, if the $\overline{M}_n$ values are taken into account, there are approximately 0.9

total double bond (N_T') per chain with about 0.45-0.65 pseudo-terminal double bond (N_t') and 0.3 internal double bond (N_i') per chain, regardless of the $\overline{M}_n$.

I.1.4. ^1H Spectra of Extracts in C_6D_6 (at 60°C) and $C_6D_5NO_2$ (at 140°C) (Tables 2 and 3). In C_6D_6 solution, all the olefinic proton resonances are between 5.4 and 5.8 ppm, but, compared with $CDCl_3$, no hyperfine structure is obtained. Even the H_1 resonances that appear in the 3.55-3.75 ppm region are poorly resolved and do not allow any determination of either the trans/cis ratio or the different coupling constants.

The same lack of resolution is observed in $C_6D_5NO_2$ solution, in which the olefinic resonances have been observed between 5.70 and 6.10 ppm. For the H_1 resonances, there are at least three doublets in the 3.98-4.30 ppm region due to the aromatic effect of the solvent that might distinguish differences in the spatial orientations of the end structure [I] relative to the penultimate unit. As in C_6D_6, there is no hyperfine structure.

The chemical shifts measured in the five solvents are reported in Table 4.

I.1.5. ^{13}C Resonances (88 MHz) of Olefinic Carbons of the Extracts in $CDCl_3$ and CD_3COCD_3. ^{13}C resonances of the olefinic carbons of B_e recorded in $CDCl_3$ solution (Fig. 10) do not allow more precise assignments, even if organic compounds (cis and trans-1-chloro-2-butene, 4-chloro-2-hexene, 2-chloro-3-hexene) are used and their chemical shifts measured in $CDCl_3$ (Table 5) for comparison purposes.

Acetone was selected for ^{13}C-NMR study of the extracts owing to the good ^1H spectral resolution of the olefinic protons; efficient (^1H-^{13}C) selective decoupling experiments can be carried out. ^{13}C resonances in the 120-150 ppm region of B_e and the enlargement of the same spectrum around 130 ppm are presented in Figs. 11 and 12, respectively. The analytical conditions were chosen to allow quantitative determinations (repetition time = 3 s, flip angle = 60°). Owing to the ^1H-NMR results, the bigger set of peaks centered at 130.8 ppm (1, Fig. 12) should be assigned to the olefinic carbons of the trans configuration and the smaller one at 129.4 ppm (2, Fig. 12) to the cis configuration of [I]. Planimetric determination of the trans/cis ratio gives 81/19, which is close to the ratio (87/13) obtained by ^1H-NMR in acetone solution. Moreover, by ^1H selective decoupling experiments, irradiation at 5.82 (H_2) and 5.925 (trans H_3) ppm showed that C_2 and C_3 resonate at 130.7 and 130.9, respectively. The difference

TABLE 4. Effect of the Structure of the Solvent on the Proton Chemical Shifts of Structure [I] of the Three PVC Extracts.

$$[I]:\ -\underset{4}{CH_2}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{CH_2}Cl$$

		Solvent				
		$CDCl_3$	CD_3COCD_3	CD_3COCD_3/CS_2	C_6D_6	$C_6D_5NO_2$
T, °C		20	20	20	60	140
Spectral resolution		Medium	Good	Good	Poor	Poor
$\delta(H_1)$, ppm	cis	4.086	4.23	4.16	3.55-	4.0-
	trans	4.06	4.16	4.09	3.75	4.3
$\delta(H_2)$, ppm		5.6-	5.82 and	5.6-	5.3-	5.7-
$\delta(H_3)$, ppm		6.0	5.925	6.10	5.8	6.1
$\delta(H_4)$, ppm		2.56	2.6		Hidden	Hidden
J, Hz		J(1,2) = 6.5, J(2,3) = 15.5, J(3,4) = 6.5-7				

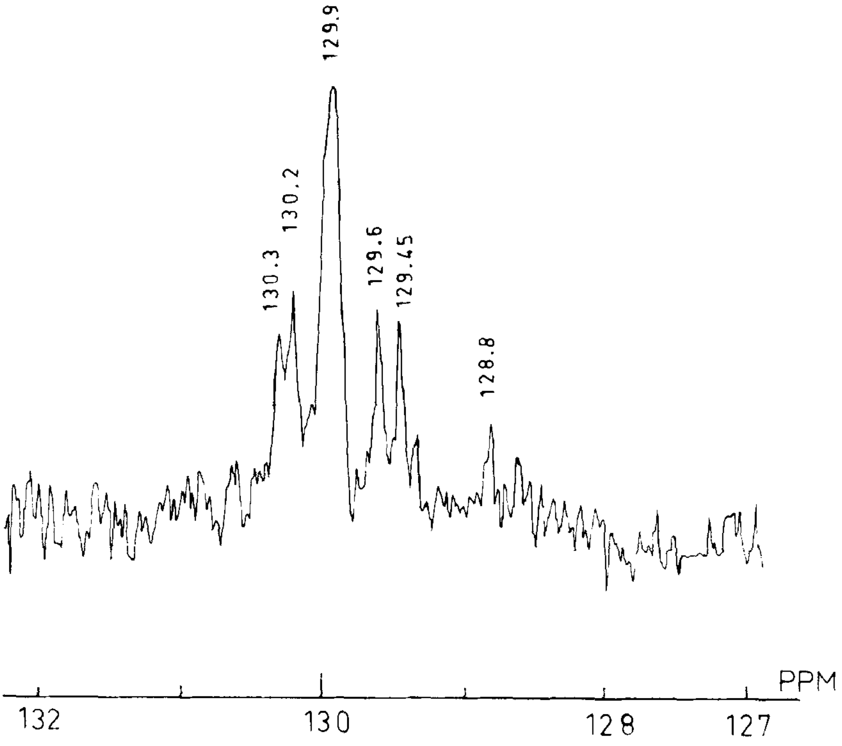
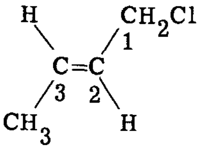
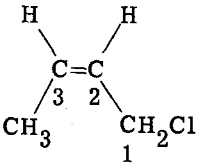
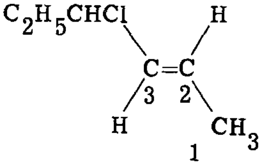
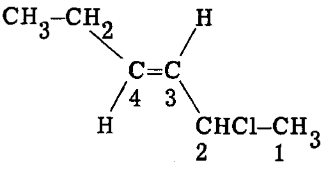


FIG. 10. ^{13}C resonances (88 MHz) of the olefinic carbons of extract B_e in $CDCl_3$ at room temperature.

in chemical shifts between these carbons is only 0.2 ppm (0.3 ppm in $CDCl_3$) instead of the 3 ppm observed with similar short organic compounds (Table 5).

As shown with the model compounds 4-chloro-2-hexene and 2-chloro-3-hexene (Table 5), the carbons of the internal double bonds resonate at lower field. For the extracts, the carbon resonances of their internal double bonds should spread between 125 and 140 ppm, and only two small maxima were observed at 134.4 and 135.8 ppm (Fig. 11). If this assumption is correct, a pseudo-terminal/internal double bonds ratio of 56/44 is found for B_e by planimetry, in very good agreement with the ^{1}H-NMR results (Table 3) for the same extract (0.45/0.38 = 1.18 = 54/46).

TABLE 5. ^{13}C Chemical Shifts of the Model Compounds for Olefinic Structures of PVC

		δ, ppm	
Model compounds	C_i	Calculated[a]	Observed
trans-1-Chloro-2-butene			
	C_2	125	127.65
	C_3	128	130.58
cis-1-Chloro-2-butene			
	C_2	124	126.55
	C_3	127	129.49
trans-4-Chloro-2-hexene			
	C_2	128	128.15
	C_3	131	132.31
trans-2-Chloro-3-hexene			
	C_3	130.5	131.51
	C_4	133.5	133.91

[a] Calculated according to Dorman et al. [20].

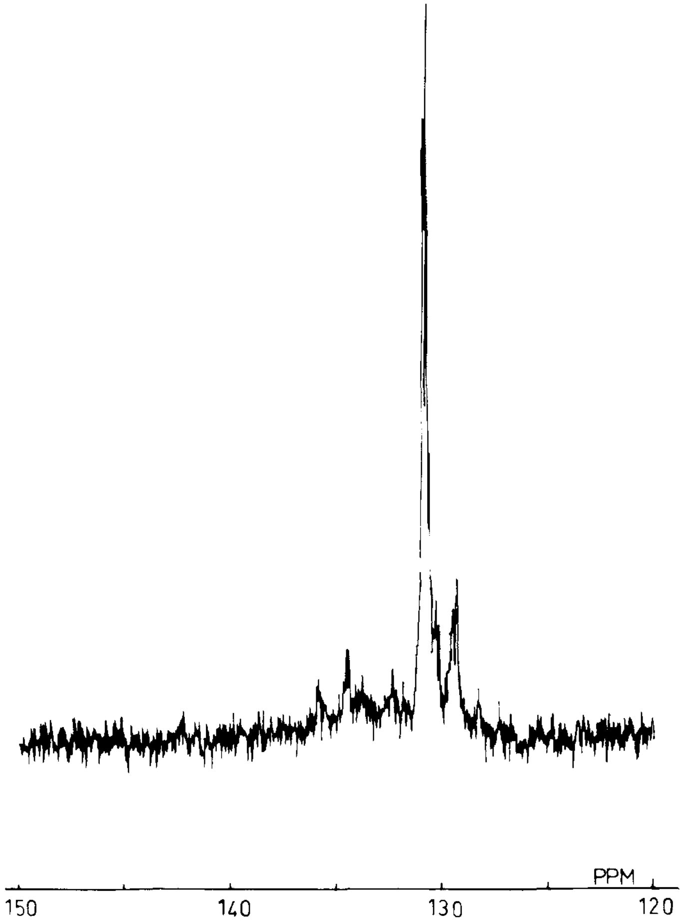


FIG. 11. ^{13}C resonances of the olefinic carbons of extract B_e in CD_3COCD_3 at room temperature (flip angle, 60°; repetition time, 3 s).

I.2. ^1H Analysis of High Molecular Weight PVC's in CD_3COCD_3/CS_2 (5:3 by volume) at Room Temperature

With a good understanding of the olefinic resonances of the PVC extracts, the study of the unsaturation of the crude PVC's becomes easier. Except for an unidentified impurity at 5.63 ppm (singlet, Fig. 13), the olefinic resonances of crude PVC-A obtained at low conversion (54.7%) are not very different from the ones of extracts A_e or B_e and C_e.

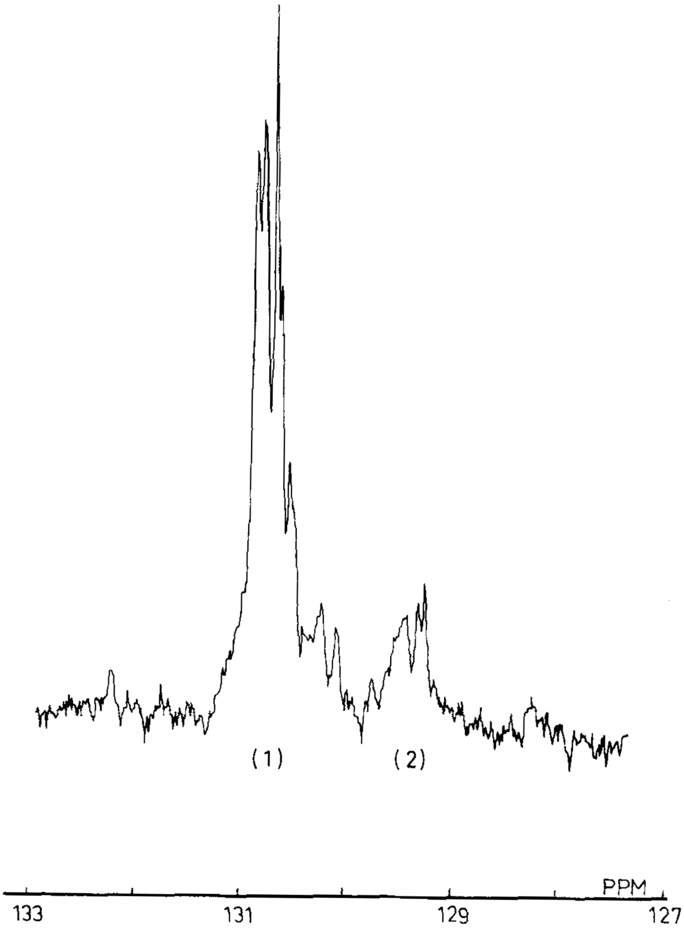


FIG. 12. ^{13}C resonances of the olefinic carbons of extract B_e in CD_3COCD_3 at room temperature. Enlargement of the 127.5-133 ppm region.

On the contrary, crude B and C prepared at high conversion (83-85%) have new unresolved resonances that spread out between 5.20 and 5.65 ppm. Moreover, resonances between 5.65 and 5.85 ppm become stronger (Fig. 13B, C). Quantitatively, A (Table 6) as well as A_e, B_e, and C_e (Table 3) contain nearly 0.9 total double bond per chain, whereas B and C have, respectively, 2.8 and 2.0 total double bonds per chain (Table 6).

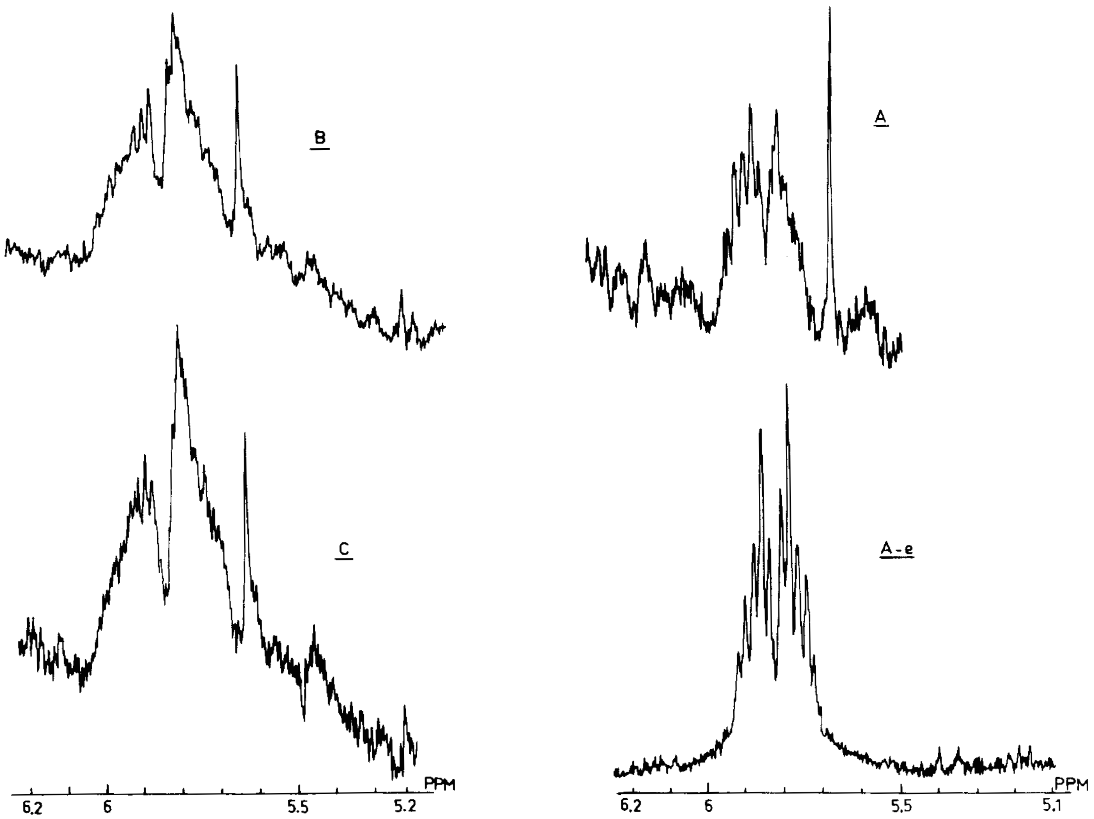


FIG. 13. ^1H resonances of the olefinic proton of extract A_e, crude PVC's A, B, and C.

TABLE 6. Quantitative Determinations by ^{1}H-NMR of the Average Numbers of Total, Pseudo-Terminal, and Internal Double Bonds of Three Crude PVC's. (solvent = CD_3COCD_3/CS_2, mixture 5:3 by volume)

	Sample		
	A	B	C
$\overline{M}_n \times 10^{-3}$:	43.3	37.5	40.6
Double bonds/1 000 units:			
Total (N_T)	1.2	4.6	3.1
Pseudo-terminal (N_t)	0.75	0.8	0.6
Internal (N_i)	0.45	3.8	2.5
Double bonds/chain:			
Total (N_T')	0.8	2.8	2
Pseudo-terminal (N_t')	0.5	0.5	0.4
Internal (N_i')	0.3	2.3	1.6

But in all these six samples, the average number of structure [I] is about 0.5 per chain (Tables 3 and 6).

The high concentration of internal double bonds of crude B and C should be due to their higher conversions. The exact structures of the new types of internal double bonds obviously present in B and C remain unknown.

In order to check the capacity of ^{1}H-NMR for quantitative determination, four other high molecular weight PVC's (D-G) were examined in acetone/CS_2. If the $\overline{M}_n$ values are taken into account, all 10 of these polymers–high molecular weights and extracts–have 0.5 structure [I] per chain (Table 7).

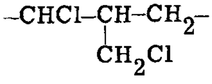
II. ^{1}H-NMR Study of Model Compounds and Saturated Chloromethyl Groups [II], [III], and [IV] of PVC in $CDCl_3$ and CD_3COCD_3

$-CHCl-CH_2Cl$

[II]

$-CH_2-CH_2Cl$

[III]


$-CHCl-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-CH_2-$

[IV]

TABLE 7. Quantitative Determinations of the Average Numbers of Pseudo-Terminal Double Bonds [I] in Various PVC's ([I] = $-CH_2-CH=CH-CH_2Cl$, D-G = commercial PVC's)

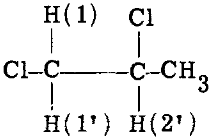
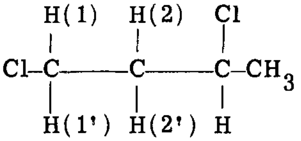
		Average number of [I]	
Sample	$M_n \times 10^{-3}$	Per 1000 VC (N_t)	Per chain (N_T')
A_e	2.98	13.2	0.65
B_e	2.4	11.6	0.45
C_e	3.95	10.5	0.65
A	43.3	0.75	0.5
B	37.5	0.8	0.5
C	40.6	0.6	0.4
D	37	0.9	0.55
E	46	0.7	0.5
F	50	0.6	0.5
G	62	0.65	0.65

II.1. Model Compounds

1,2-Dichloropropane (DCP) and 1,3-dichlorobutane (DCB) have been studied in $CDCl_3$ and CD_3COCD_3 in order to select the best NMR solvent for allowing one to distinguish between [II] and [III]. In both compounds the magnetic nonequivalence of the H1 and H1' protons is to be expected since they contain an asymmetric carbon. The values of the chemical shifts and coupling constants are reported in Table 8.

In $CDCl_3$ solution the two pairs of doublets (ABX type) of the two H1 protons of DCP are fairly well separated with a difference in chemical shifts ($\Delta\delta$) of 0.18 ppm (Fig. 14, bottom). On the other hand, the resonances of the two H1 protons of DCB (Fig. 14, top), overlapping each other with $\Delta\delta = 0.04$ ppm, are between those of the two DCP-H_1 protons. The situation is quite different in CD_3COCD_3 solution (Fig. 15); the DCP-H1 resonances are close together ($\Delta\delta = 0.06$ ppm) and appear at lower field than the two DCB-H1 resonances. By using both $CDCl_3$ and CD_3COCD_3, some modifications of the chloromethyl proton resonance patterns would be expected, allowing the detection of both [II] and [III] chloromethyl groups.

TABLE 8. Chemical Shifts and Coupling Constants to 1,2-Dichloropropane and 1,3-Dichlorobutane (models of structures [II] and [III]) in $CDCl_3$ and CD_3COCD_3 at Room Temperature

		δ, ppm	
Model	Proton	$CDCl_3$	CD_3COCD_3
1,2-Dichloropropane:			
 $Cl{-}\overset{H(1)}{\underset{H(1')}{C}}{-}\overset{Cl}{\underset{H(2')}{C}}{-}CH_3$	H1	3.76	3.82
	H1'	3.58	3.76
J, Hz: J(1,1') = 11.2, J(1,2') = 5.2, J(1',2') = 7.7			
1,3-Dichlorobutane:			
 $Cl{-}\overset{H(1)}{\underset{H(1')}{C}}{-}\overset{H(2)}{\underset{H(2')}{C}}{-}\overset{Cl}{\underset{H}{C}}{-}CH_3$	H1	3.72	3.76
	H1'	3.68	3.72
J, Hz: J(1,1') = 11.2, J(1,2') = 6, J(1,2) = 8.6, J(1',2) = 5.6, J(1',2') = 6			

In addition to the two model compounds (DCP and DCB) mentioned, another low molecular weight PVC (PVC-Z) prepared with a modified Ziegler catalyst [21] was used as a model. PVC-Z has only one type of chloromethyl group, $-CH_2-CH_2Cl$ [III]. Thus, in the chloromethyl proton resonance region (3.4-4.0 ppm), PVC-Z should facilitate the identification of [III] among the whole chloromethyl resonances of [II] + [III] + [IV].

In $CDCl_3$, the chloromethyl group [III] resonances spread between 3.5 and 3.9 ppm, with two peaks centered at 3.745 and 3.757 ppm (Fig. 16, bottom). Two irradiations centered at 2.20 and 2.09 ppm enhance the two peaks at 3.757 (Fig. 16, middle) and 3.745 ppm (Fig. 16, top), respectively. In acetone solution these chloromethyl groups resonate at lower field (3.825 ppm). The effect of the nature of the solvent is then not negligible.

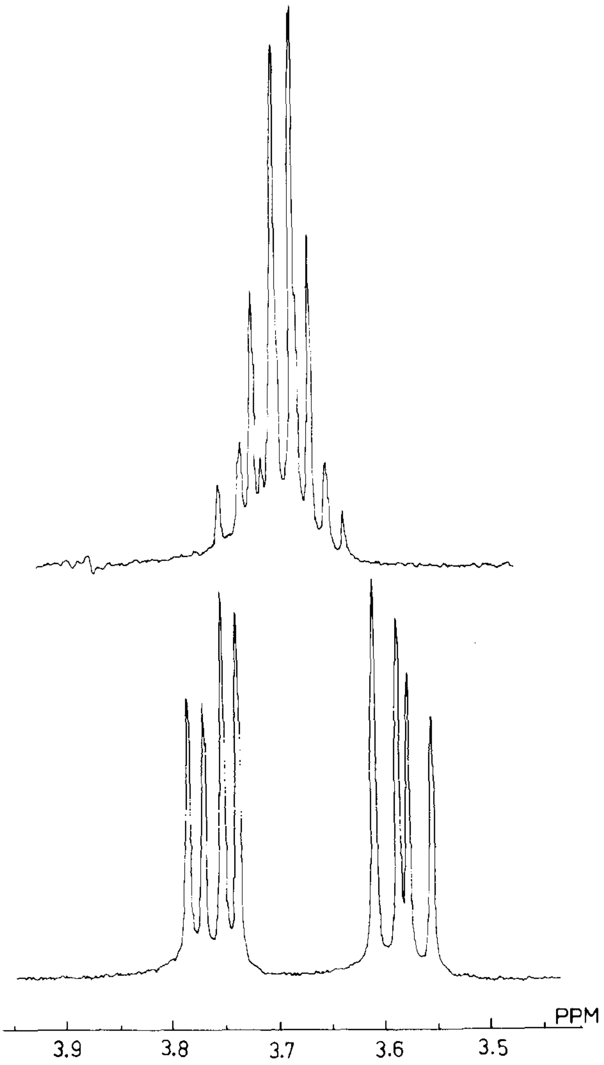


FIG. 14. ^{1}H resonances of the chloromethyl group of the two model compounds in $CDCl_3$ at room temperature. Bottom: 1,2-Dichloropropane, a model of Structure [II]. Top: 1,3-Dichlorobutane, a model of Structure [III].

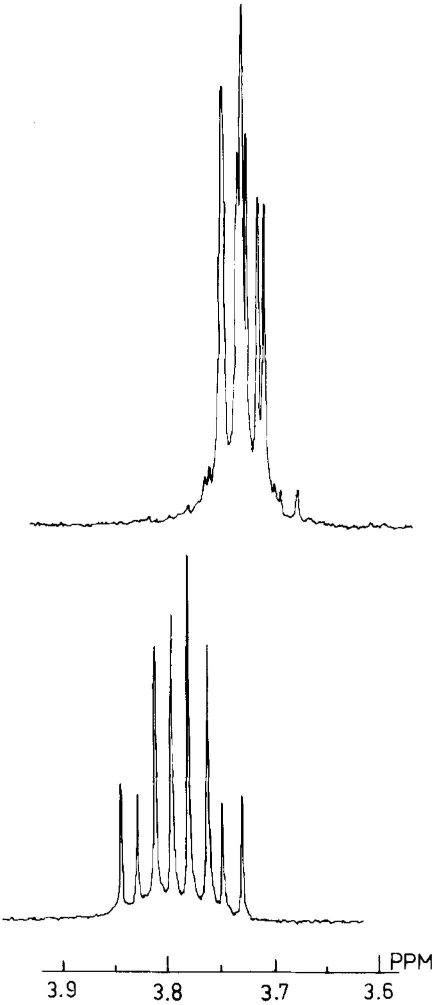


FIG. 15. ^{1}H resonances of the chloromethyl group of the two model compounds in CD_3COCD_3 at room temperature. Bottom: 1,2-Dichloropropane, a model of Structure [II]. Top: 1,3-Dichlorobutane, a model of Structure [III].

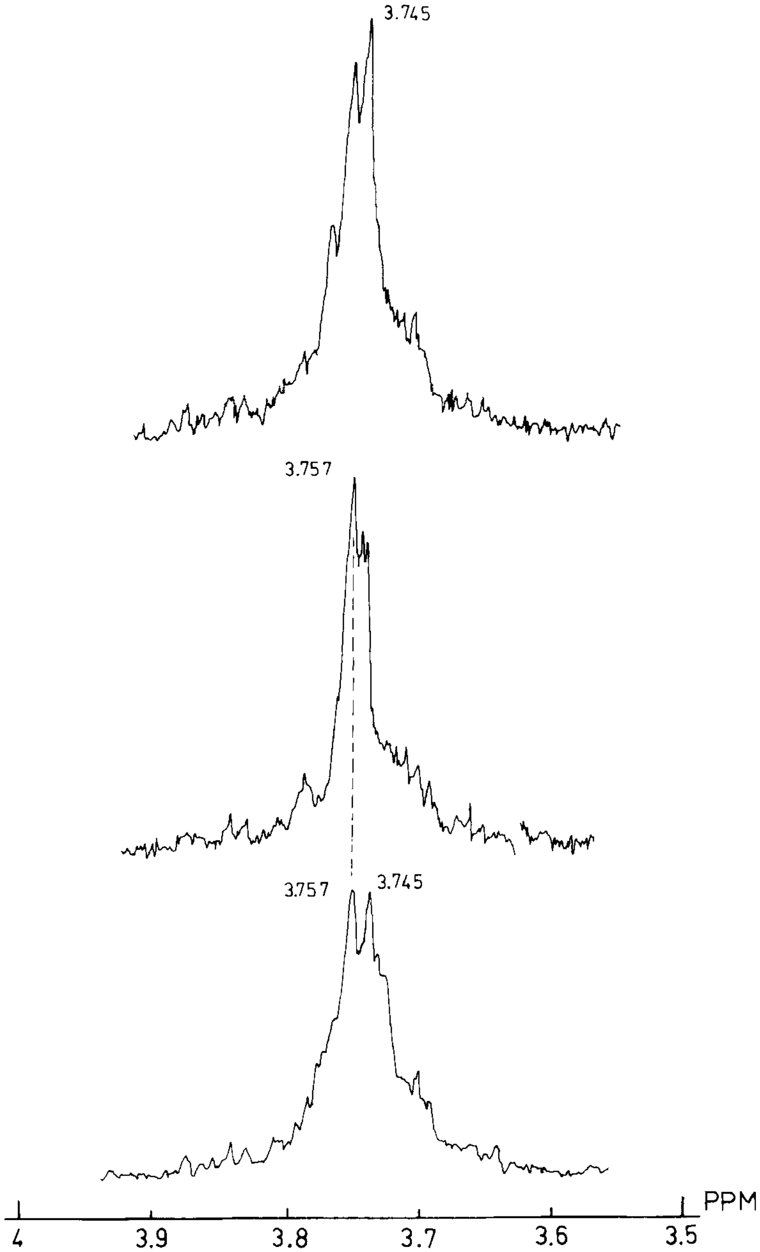


FIG. 16. ^1H resonances of the chloromethyl group of $-CHCl-CH_2-CH_2Cl$ [III] in a model PVC in $CDCl_3$ at room temperature. Normal spectrum (bottom) and spectra obtained with irradiation at 2.2 ppm (middle) and 2.09 ppm (top).

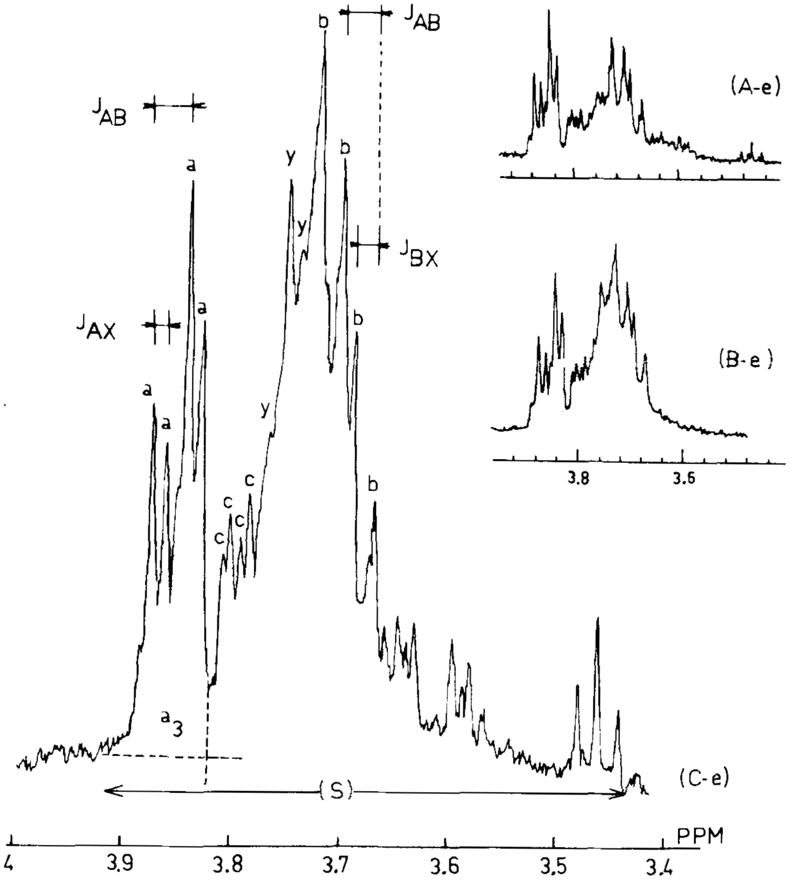


FIG. 17. ^{1}H resonances of the chloromethyl groups of extracts C_e (bottom), B_e (middle), and A_e (top) in $CDCl_3$ at room temperature.

II.2. Study of the Extracts in $CDCl_3$ at Room Temperature

As mentioned previously, the three chloromethyl groups of [II], [III], and [IV] are expected to show resonances in the 3.4-4.0 ppm region. The general feature (Fig. 17) of the three extracts A_e, B_e, and C_e are as follows:

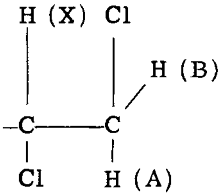
Two pairs of strong doublets (a) and (b) (the AB part of an ABX system, X being –CHCl–), (b) being partially overlapped by unresolved resonances.

A set of four peaks (c).

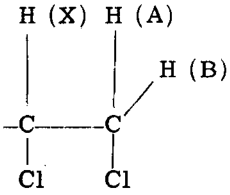
A poorly resolved set of three peaks (y), the relative intensities of which are different in the three different extracts.

In addition, some minor differences are observed: in the 3.4-3.65 ppm region, a triplet and two pairs of doublets are observed only in A_e and C_e, but not in B_e.

In the –CHCl– resonance region (4.2-4.8 ppm), an irradiation centered at 4.46 ppm (H_X resonances of the ABX system: $-CH_XCl-CH_AH_BCl$ [II]) does change (a) + (b) into a pair of doublets (Fig. 18, bottom) while (c) becomes a wide singlet (Fig. 18, top) if another irradiation is applied at 4.3 ppm. Although no other modification is observed in this 3.4-4 ppm region when the –CHCl– group is irradiated, one cannot be sure that (a) + (b) + (c) represent all the chloromethyl resonances of structure [II]. Indeed, (c) is strongly affected by an irradiation centered at 3.69 ppm (Fig. 19). Thus it is reasonable to assume that (a) + (b) should belong to the richer stereoisomer (racemic) and (c) to the visible half of the poorer one (meso).



racemic-II



meso-II

For the racemic configuration, one has $\delta(H_A) = 3.85$, $\delta(H_B) = 3.70$, $\delta(H_X) = 4.46$ ppm, and J_{AB} (gem) = 11.4, $J_{AX} = 4.5$, and $J_{BX} = 7.5$. These values are in good agreement with those reported in Table 9 for the spectrum of 1,2-dichloropropane in $CDCl_3$ (Fig. 14, bottom). In $CDCl_3$, the protons of structure [II] in PVC are at a lower field than in the 1,2-DCP model ($\Delta\delta = +0.1$ ppm).

The last set of resonances in the 3.4-4 ppm region consists of three peaks at 3.745, 3.757, and 3.772 ppm (y, Fig. 17). The first two–at a higher field–can be assigned to the chloromethyl group of [III], as shown by the PVC-Z model (Fig. 16). The relative intensities of these two peaks are modified by two irradiations centered, respectively, at 2.08 (Fig. 20, bottom, at asterisks) and 2.31. (Fig. 20, top, at asterisks). The chemical shifts and spin-spin decoupling results are in very good agreement with those observed in the spectrum of PVC-Z (Fig. 16). Compared with those in the 1,3-DCB model, the protons of structure [III] in PVC are at a slightly lower field ($\Delta\delta = 0.05$ ppm).

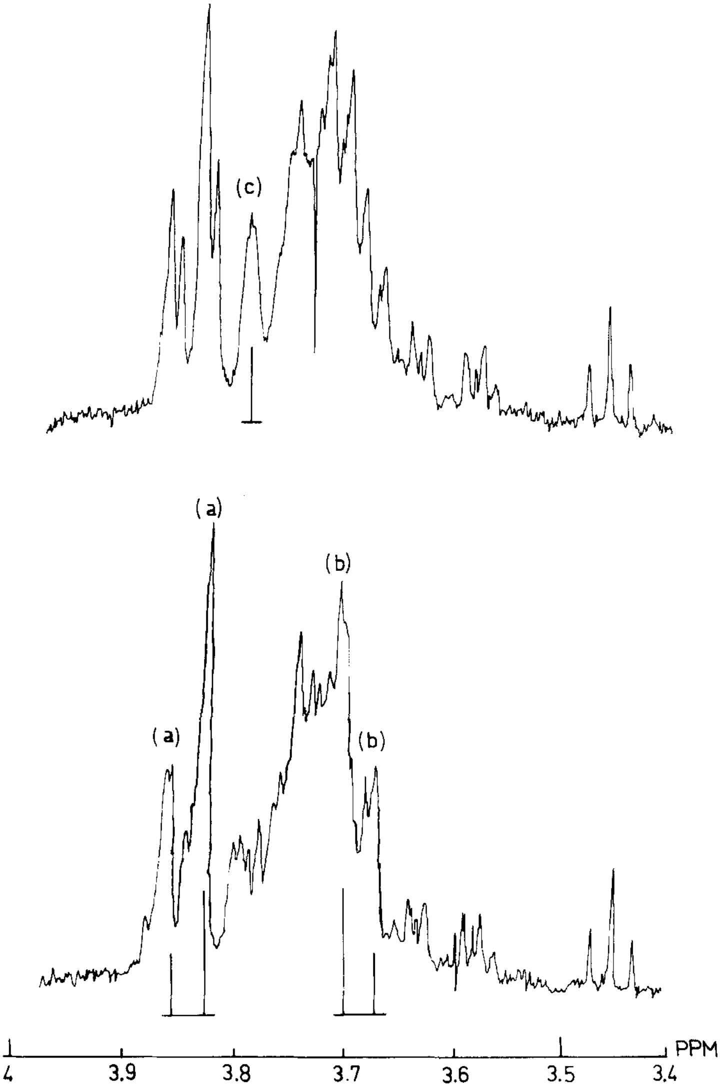


FIG. 18. ^{1}H resonances of the chloromethyl groups of extract C_e in $CDCl_3$ at room temperature with irradiation at 4.46 ppm (bottom) and 4.3 ppm (top).

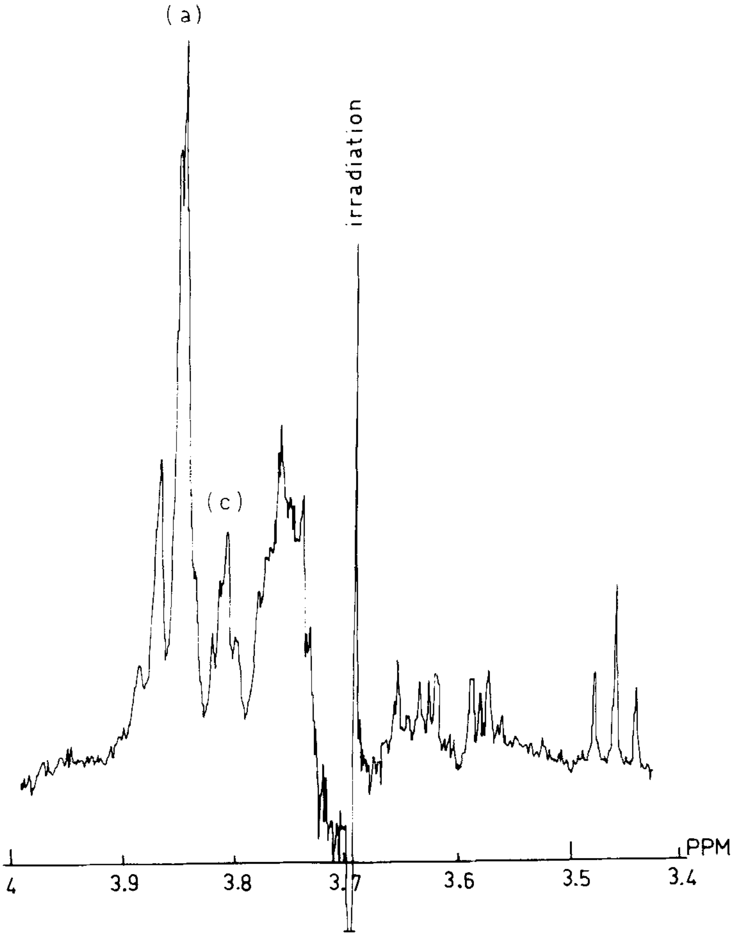


FIG. 19. ^{1}H resonances of the chloromethyl groups of extract C_e in $CDCl_3$ at room temperature with irradiation at 3.69 ppm

In spite of all the step-by-step irradiations in the 1.75-2.75 ppm region (nonchlorinated methine and methylene proton resonances), no modifications suggesting the presence of the chloromethyl groups of [IV] were observed in the 3.4-4 ppm region. It is important to note here that the ^{13}C-NMR analysis of hydrogenated high molecular weight PVC showed that there are about four short chloromethyl branches per 1 000 monomer units [10]. In the present case of a low molecular weight extract, it is possible that structure [IV] cannot be

TABLE 9. Differences in Chemical Shifts and Coupling Constants of H_A and H_B (of the ABX spectrum) between 1,2-Dichloropropane (1,2-DCP) and Chain End Structure [II] of PVC Extracts Examined in $CDCl_3$ (1,2-DCP = $ClH_AH_BC–CH_XCl–CH_3$, [II] = $ClH_AH_BC–CH_XCl–CH_2–$)

	1,2-DCP, δ, ppm	[II], δ, ppm	Δδ, ppm
H_A	3.76	3.85	0.09
H_B	3.58	3.70	0.12
$\delta(H_A) - \delta(H_B)$	0.18	0.15	
$\frac{1}{2}[\delta(H_A) + \delta(H_B)]$	3.67	3.77	0.10
J_{AB} (gem)	11.2	11.4	
J_{AX} (trans)	5.2	4.5	
J_{BX} (cis)	7.7	7.5	

detected because of (i) the complex AB part of the ABX (X = CH) resonance pattern and (ii) its too small contribution in this resonance region accounts for 30-60 chloromethyl groups (II + III + IV) per 1 000 VC units (Table 10).

Quantitative determinations of the whole saturated $-CH_2Cl$ chain ends/1 000 VC units have been achieved by planimetric measurements of the whole area (S) lying between 3.4 and 4 ppm (Fig. 17) and the one (a) of –CHCl– resonances (Fig. 2). The average number of saturated $-CH_2Cl$ (N_S) of ([II] + [III] + [IV]) is given by

$$N_S = \frac{S}{2a} \times 10^3. \qquad (3)$$

The data are reported in Table 10.

Along the same lines, a rough estimation of the average number of structure [II] (N_{II}) can be calculated by using the area of the pair of doublets (a) (a_3, Fig. 17) (the pair of doublets (c) (Fig. 17) are not

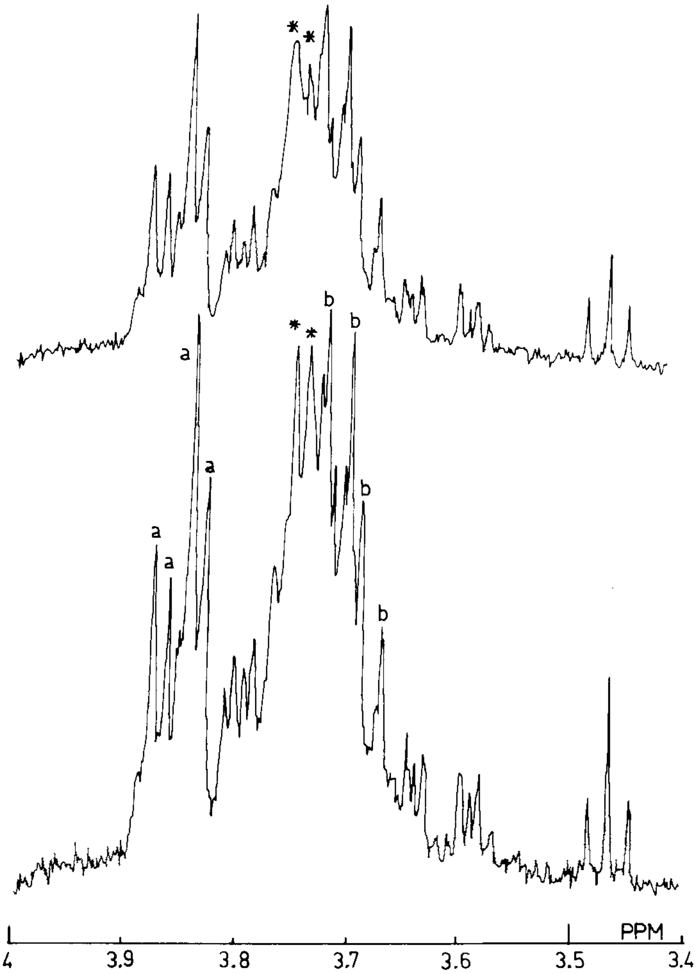


FIG. 20. ^1H resonances of the chloromethyl groups of extract C_e in $CDCl_3$ at room temperature with irradiation at 2.08 ppm (bottom) and 2.31 ppm (top). Asterisks indicate resonances modified by irradiation.

taken into account, and the chloromethyl resonances of [IV] might be hidden in this region).

$$N_{II} = \frac{a_3}{a} \times 10^3. \qquad (4)$$

TABLE 10. Quantitative Determinations of the Average Total Numbers of Saturated Chloromethyl Groups ([II] + [III] + [IV]) per 1 000 Monomer Units (N_S) and per Chain (N_S') of the Three PVC Extracts in Different Solvents

		N_S		
Solvent (T, °C)	Region, ppm	A_e	B_e	C_e
$CDCl_2$ (20)	3.4-4	32.6	56.2	44.2
CD_3COCD_3 (20)	3.5-4.1	27.8	57.8	44.1
CD_3COCD_3/CS_2 (20)	3.5-4	31.9	55.9	38.9
C_6D_6 (60)	3.1-3.55	35.5	61.3	nd
$C_6D_5NO_2$ (140)	3.65-4	nd	nd	43.1
Mean values:				
Per 1 000 VC (N_S)		32	57.8	42.6
Per chain (N_S')		1.5	2.2	2.7

The results are reported in Table 11.

The total average numbers of saturated $-CH_2Cl$ (N_S') per chain are 1.5, 2.2, and 2.7 for A_e, B_e, and C_e, respectively (Table 10), while the average numbers of pseudo-terminal double bonds (structure [I]) per chain (N_t') are 0.63, 0.45, and 0.66 (Table 3). By taking into account the two chain ends of each polymer chain, the average number of branches per chain (N_b') may be estimated as follows:

$$N_b' = N_S' + N_t' - 2. \tag{5}$$

Chloromethyl, butyl, and long branches are included in N_b'.

In Eq. (5) it is assumed that the polymer chains are mainly initiated by a chlorine radical and that all the chain ends are chloromethyl groups resonating in the 3.4-4.10 ppm region. Thus extract A_e (conversion = 54.7%) has 0.15 branch/chain and B_e and C_e (conversion = 85%) 0.65 and 1.35 branch/chain respectively. If their $\overline{DP}_n$

TABLE 11. Semiquantitative Determinations of Chain Ends [II] $-CH_2-CHCl-CH_2Cl$ in $CDCl_3$ (a_3, Fig. 17) in Comparison with Resonances (1) in CD_3COCD_3 (Fig. 21) and Resonances (1') in CD_3COCD_3/CS_2 (Fig. 22)

		Per 1000 units (N_{II})		
Solvent	Region, ppm	A_e	B_e	C_e
$CDCl_3$ (Fig. 17)	(a_3): 3.82-3.92	16.5	27	21
CD_3COCD_3 (Fig. 21)	(1): 3.90-4.1	21.2	30	24.4
(CD_3COCD_3/CS_2) (Fig. 22)	(1'): 3.80-4	23.7	30.4	22
Mean values:				
Per 1 000 VC (N_{II})		20.5	29.1	22.5
Per chain (N_{II}')		1	1.1	1.4

(Table 1) is taken into account, 17 and 21 branches/1 000 VC units are found for B_e and C_e, but A_e has only 3 branches/1 000 units (Table 13). So, it seems that (for the three extracts) statistically the number of branches (N_b) increases with increasing conversion. At approximately the same high conversion (85%), C_e, when obtained under subsaturation conditions, has more branches than B_e. One can see further (Table 13) that the same phenomenon is also observed in crude PVC.

II.3. Study of Extracts in CD_3COCD_3 at Room Temperature

In view of the results of the model compounds (Table 8) in CD_3COCD_3 (Fig. 15), the second-order resonances of the chloromethyl groups of structure [II] are expected to be at slightly lower field than the ones of structure [III]. In the same solvent, the chloromethyl group [III] of the model PVC-Z resonates at 3.825 ppm. From the difference between the resonances [III] of PVC-Z and of the 1,2-DCB model in this solvent ($\Delta\delta = +0.08$ ppm) and the observation, made in $CDCl_3$, that the difference between the PVC [II] groups and the 1,2-DCP is twice as large, it is estimated that the [II] groups of PVC resonate at about 3.95 ppm (3.79 + 0.16 ppm) in CD_3COCD_3.

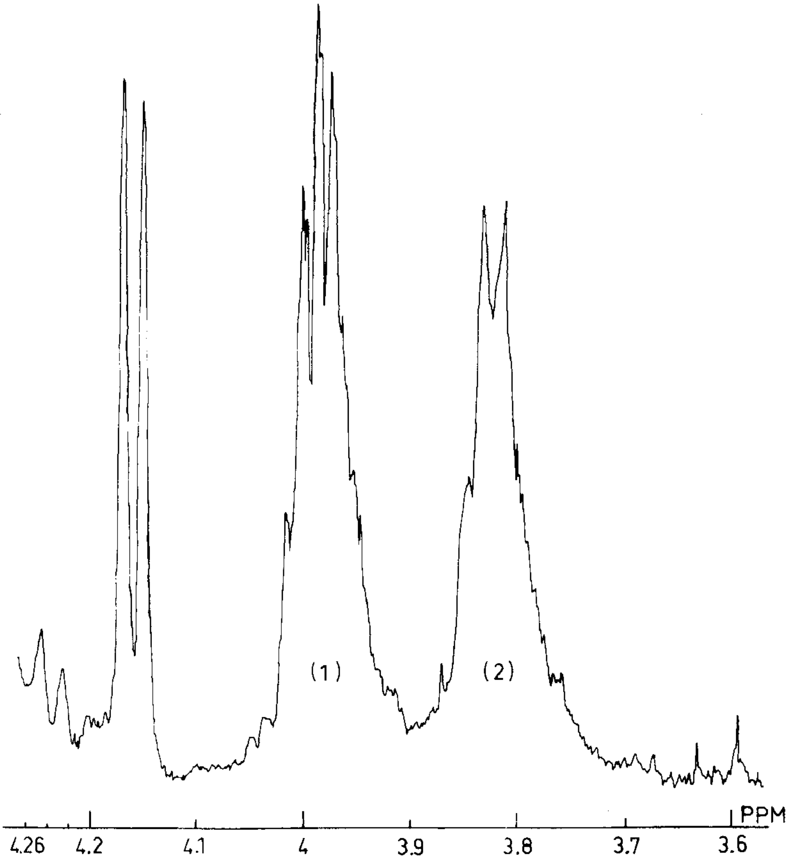


FIG. 21. ^{1}H resonances of the chloromethyl groups of extract B_e in CD_3COCD_3 at room temperature.

For A_e, B_e, and C_e, the chloromethyl proton resonances of saturated $-CH_2Cl$ show two unresolved multiplets centered at 3.983 (1) and 3.818 ppm (2) (Fig. 21), respectively. Multiplet (1) is affected by irradiation of –CHCl– (4.53 ppm) and multiplet (2) by irradiation of $-CH_2-$ (2.25 ppm). The agreement with the values expected from model compounds is very good.

As in $CDCl_3$, the chloromethyl resonances of [IV] cannot be localized by decoupling experiments, probably again because of its very low concentration compared to [II] and [III]. The quantitative determinations of the whole saturated $-CH_2Cl$ (N_S) (multiplets (1) + (2), Fig. 21) are reported in Table 10. The values of N_{II} (multiplet (1), Fig. 21) corresponding to a rough estimation of [II] are reported in Table 11. In the present case, (1) is found to be bigger than $2a_3$ (measured in $CDCl_3$, Fig. 17) and sometimes bigger than one per chain. Obviously, (1) should include resonances other than the ones of structure [II].

II.4. Study of the Extracts in CD_3COCD_3/CS_2 (5:3 by volume) at Room Temperature

In the 3.6-4 ppm region, the spectra (Fig. 22) are of poorer resolution than the ones recorded in pure CD_3COCD_3. Two sets of resonances are observed between 3.8 and 4.0 ppm (1', Fig. 22), the higher field of which appears to have approximately the same relative intensity in the three extracts. All these resonances are affected by irradiation of the $-CHCl-$ region. The second part of the saturated $-CH_2Cl$ resonances is spread from 3.63 to 3.8 ppm (2', Fig. 22). This part is affected only by irradiation of the $-CH_2-$ and CH– region.

Similar calculated values of N_S and N_{II} are reported in Tables 10 and 11. As previously observed in CD_3COCD_3. Resonances (1') (Fig. 22) are found again to be bigger than $2a_3$ of Fig. 17. The average numbers of structure [II] are approximately 1 per chain for A_e and B_e, and 1.4 per chain for C_e. This difference should be correlated to the increase of the average numbers of branches from A_e to B_e and C_e (Table 13).

II.5. Study of Crude PVC's in $CD_3COCD_3-CS_2$ (5:3 by volume) at Room Temperature

High molecular weight PVC's are expected to have more branches/chain than the extracts. The spectral resolution is unfortunately very poor for the assignment of the different abnormal resonances. The identification of the chloromethyl resonances of structures [II] and [III] could only be achieved thanks to the previous study of extracts in the same solvent mixture. Here again, the assignment of the saturated $-CH_2Cl$ group of structure [IV] by decoupling experiments remains unsuccessful.

As observed for extracts, all the saturated $-CH_2Cl$ resonances are in the 3.6-4 ppm region, which can be divided grossly into two parts: 3.8-4 ppm (1', Fig. 23) and 3.8-3.6 ppm (2', Fig. 23). Quantitative determinations for the seven PVC's, including the three IUPAC sam-

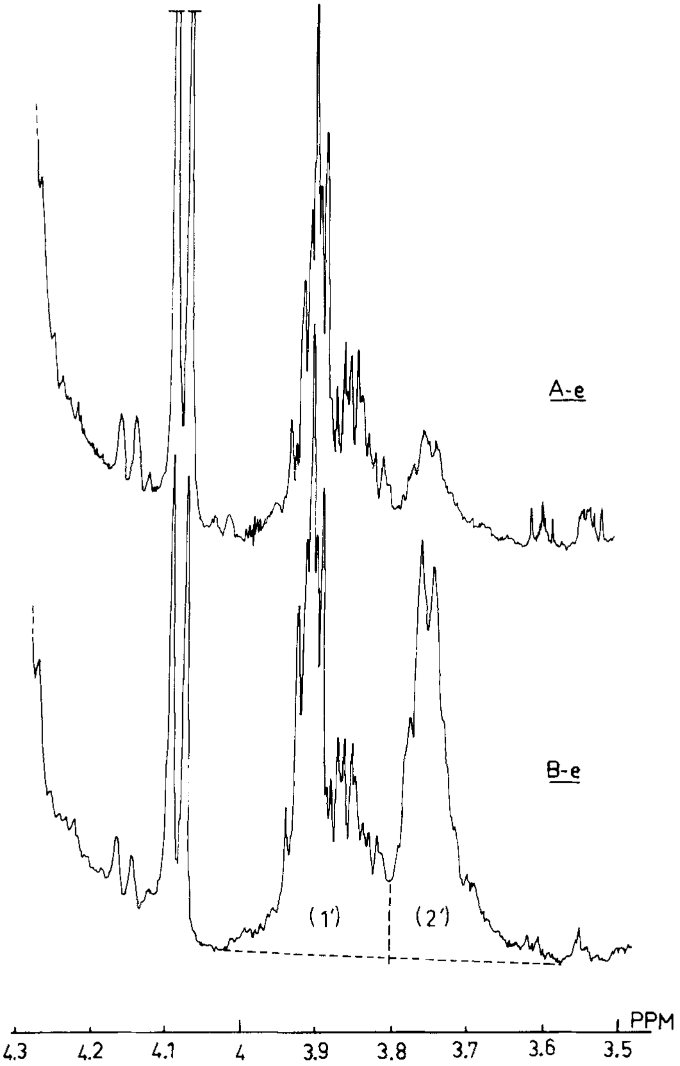


FIG. 22. ^{1}H resonances of the chloromethyl groups of extract B_e (bottom) and A_e (top) in (CD_3COCD_3–CS_2) at room temperature.

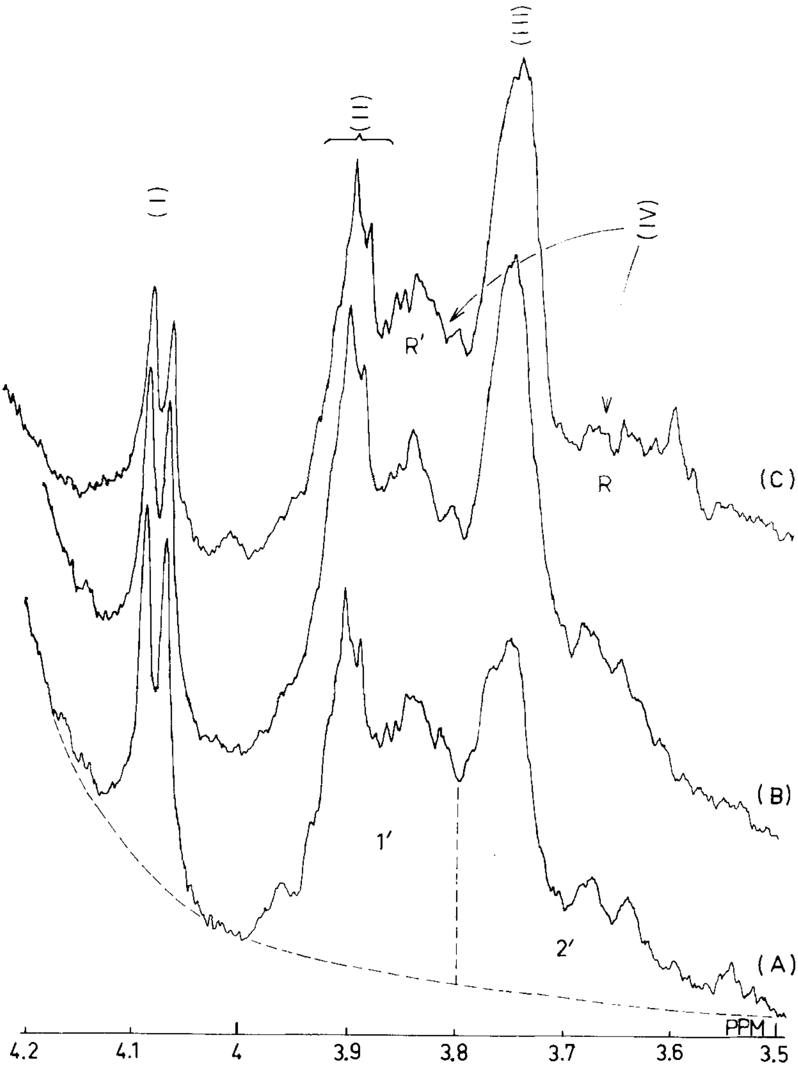


FIG. 23. ^{1}H resonances of the chloromethyl groups of crude PVC's A (bottom), B (middle) and C (top) in CD_3COCD_3–CS_2 at room temperature.

TABLE 12. Quantitative Determinations of the Average Total Numbers of Saturated Chloromethyl Groups ([II] + [III] + [IV]) (1' + 2', Fig. 23) and Separate Estimations of Resonances (1') and (2') (Fig. 23)

	Total 1' + 2'				1'		2'	
Sample	N_S per 1 000 VC	N_S' per chain	N_b per 1 000 VC	N_b' per chain	Per 1 000 VC	Per chain	Per 1 000 VC	Per chain
A	6.2	4.2	4	2.7	3.5	2.4	2.7	1.8
B	8.6	5.2	6.1	3.7	4.2	2.5	4.4	2.7
C	9.1	6	6.7	4.4	4	2.6	5.1	3.4
D	8.3	4.9	5.8	3.4	4.5	2.7	3.8	2.2
E	8.2	6.0	6.1	4.5	3.7	2.7	4.5	3.3
F	5.9	4.7	4	3.2	2.9	2.3	3	2.4
G	6.6	6.5	5.2	5.1	3.6	3.5	3	3

TABLE 13. Average Numbers of Pseudo-Terminal ([I], N_t and N_t') and Internal (N_i, N_i') Double Bonds, Saturated Chloromethyl Ends ([II] + [III] + [IV]) (N_s and N_s') and Branches (N_b and N_b') of the Three Samples (A, B, and C) and Their Extracts (A_e, B_e, and C_e)[a]

Sample	$\overline{M}_n \times 10^{-3}$ (%) (a)	N_t per 1 000 VC	N_t' per chain	N_i per 1 000 VC	N_i' per chain	N_s per 1 000 VC	N_s' per chain	N_b per 1 000 VC	N_b' per chain
A	43.3	0.75	0.5	0.45	0.3	6.2	4.2	4	2.7
A_e	3 (0.5)	13.2	0.63	4.8	0.23	32	1.5	3.1	0.15
B	37.5	0.8	0.5	3.8	2.3	8.6	5.2	6.1	3.7
B_e	2.4 (1.3)	11.6	0.45	10	0.38	57.8	2.2	16.9	0.65
C	40.6	0.6	0.4	2.5	1.6	9.1	6	6.7	4.4
C_e	3.9 (0.6)	10.5	0.66	4.1	0.26	42.6	2.7	21.4	1.35

[a] [I] = $-CH{=}CH-CH_2Cl$, [II] = $-CH_2-CHCl-CH_2Cl$, [III] = $-CHCl-CH_2-CH_2Cl$, [IV] = $>CH-CH_2Cl$. (a) = percentages by weight - see text for the calculations of the different N values.

ples, are reported in Table 12. Calculated N_S' values ([II] + [III] + [IV]) (4.2-6.5/chain) are greater than those found for low molecular weight extracts (1.5-2.7/chain, Table 10). But if the N_S values are considered, obviously the concentration of saturated $-CH_2Cl$ is far greater in the extracts (32-58/1 000 monomer units) than in the crude PVC's (6-9/1 000 monomer units).

The calculated values of N_b = 4-6.7/1 000 monomer units (Table 12) are of the same order of magnitude as those estimated by ^{13}C-NMR for hydrogenated PVC's [7, 9]. Besides, owing to the known ^{13}C NMR studies [7, 9-15], these branches are mostly chloromethyl short branches [IV]. Unfortunately, in the present case, direct examination of PVC's by ^{1}H-NMR does not allow the identification of structure [IV]. However, careful inspection of the crude PVC's whole chloromethyl resonances (Fig. 23) reveals that their patterns are very different from the ones of low molecular weight extracts (Fig. 22). Clearly, the resonances in the 3.50-3.7 ppm and 3.8-3.9 ppm regions (Fig. 23) have their relative intensities strongly enhanced compared to those of extracts (Fig. 22). These resonances should belong to the chloromethyl group of [IV].

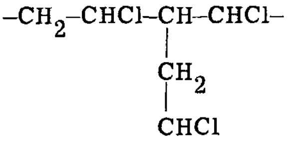
CONCLUSIONS

The study of model compounds and low molecular weight extracts by ^{1}H-NMR at high field in different solvents allows most of the proton resonances of the olefinic and chloromethylic structures to be assigned. Unfortunately, the chloromethyl short branches (Structure IV), considered as the main branches according to the ^{13}C-NMR studies of hydrogenated PVC's, could not be identified by ^{1}H-NMR. However, reliable quantitative measurements have been achieved on high molecular weight crude PVC's using the selected (CD_3COCD_3/CS_2) solvent mixture. Thus the average numbers of double bonds and branches have been quantitatively estimated, allowing some instructive comments about the relative contributions of the different mechanisms that govern the radical polymerizations of vinyl chloride in bulk and in suspension.

The pseudo-terminal olefinic structure [I] ($-CH_2-CH=CH-CH_2Cl$) reported by Petiaud and Pham [6] is again confirmed. Surprisingly, a quasi-constant value of 0.5 [I] per chain has been found in the crude PVC's studied, regardless of the conversion and the polymerization conditions, though until now, the most accepted value has been 0.7-0.8 [I] per chain [18]. Besides, we found that the main configuration of the double bond of [I] is trans (87%). This mainly trans configuration should be due to the less sterically hindered racemic head-to-head irregular addition, the two adjacent chlorine atoms of Structure A (Fig. 1) being more likely in the trans position. If, as suggested by Starnes

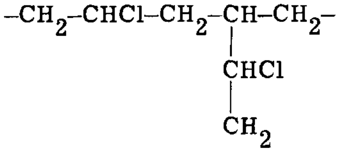
[9], the 1-2 chlorine migration is fast, the trans configuration should be preserved after abstraction of the second chlorine atom, thus giving a trans double bond [I]. Molecular models show that the less sterically hindered configuration for [I] is trans.

Only small amounts (~2%) of vinyl endgroups with an allylic chlorine ($-CHCl-CH=CH_2$ [I']) have been detected in the extracts. They probably came from the abstraction of primary chlorine from Radical B (Scheme I, Fig. 1). A possible radical polymerization of [I'] may explain their very low concentration, yet allyl chloride is known to polymerize badly. However, if this polymerization does occur, the resulting long branches should be similar (^{13}C-NMR analysis of hydrogenated PVC's) to those suggested by Hjertberg and Sörvik [7], having a methine group with at least one –CHCl– group in the α-position.



$-CH_2-CHCl-\underset{\substack{|\\ CH_2\\ |\\ CHCl}}{CH}-CHCl-$

or



$-CH_2-CHCl-CH_2-\underset{\substack{|\\ CHCl\\ |\\ CH_2}}{CH}-CH_2-$

Branch resulting from reinitiation after radical transfer to a $-CH_2-$ group

Branch resulting from copolymerization with [I']

Quantitative estimations for the internal double bond (i)–achieved by difference–can only be attempted if each (i) is assumed to bear two protons. Under these conditions, about 0.3 (i) per chain is found in all three extracts. At the present time, the exact structures of these internal double bonds are not known. There probably is more than one type of internal double bond, because some accidental dehydrochlorinations may occur on the normal chain (2 protons per olefinic structure) as well as from branch points with tertiary hydrogens or chlorine atoms (1 proton per olefinic structure). Differences in the resonance patterns are actually observed in the spectra of crude samples B and C compared to A and to all the extracts (Fig. 13).

On the basis of 2 protons per double bond, it is interesting to note that, at limited conversion (54.7%, Sample A), the crude bulk PVC should only have N_i = 0.45 internal double bond/1 000 VC, while N_i should be eight times higher at a conversion of 83.5% (Sample B). In bulk polymerization, internal double bonds are mainly formed in the last steps of the polymerization process. At the same conversion, approximately (85%), the suspension polymer obtained under subsaturation conditions appeared to be significantly less unsaturated (N_i = 2.5/1 000 VC). The important difference between A (low conversion) and B or C (high conversion) suggests that the concentration of internal double bonds increases with decreasing monomer pressure. The mechanisms giving branches or double bonds should compete with the propagation as proposed in Scheme II (Fig. 1). But the difference between B and C is probably caused more by a final step at higher polymerization temperature for Sample B (spontaneous final overheating, see Table 1).

Finally, higher unsaturation is found in the present study compared to other data of the IUPAC Working Party. The differences may be due to several causes:

(a) The bromination carried out in the IUPAC group for estimation of the total unsaturation might not have been complete.

(b) In ozonolysis (used for selective estimation of internal double bonds) the drop of the molecular weight depends only on those isolated internal double bonds that are significantly far from each other and far from the chain ends. Thus pseudo-terminal double bonds and internal double bonds close to extremities, as well as neighboring internal double bonds, cannot be determined by ozonolysis.

(c) Direct quantitative determination by ^{1}H-NMR at high field should give more reliable values because of its better sensitivity and spectral resolution.

Of the three saturated ends, $-CH_2-CHCl-CH_2Cl$ [II], $-CHCl-CH_2-CH_2Cl$ [III], $>CH-CH_2Cl$ [IV], only the two former structures were definitely identified by ^{1}H-NMR. Careful inspection of the chloromethyl resonances of extracted (Fig. 22) and crude (Fig. 23) samples shows that the $-CH_2Cl$ groups of Structure [IV] have resonances in the two regions 3.5-3.7 ppm (R) and 3.8-3.9 ppm (R'). The relative intensities of these resonances increase strongly in high molecular weight PVC in which the contribution of saturated $-CH_2Cl$ chain ends [II and III] decreases.

In the crude samples A, B, and C, the relative intensities of R + R' and those of the resonances beyond 3.9 ppm (belonging mostly to Structure [II] with one Structure [II] per chain) remain quasi-constant on the one hand, and on the other hand the average number of pseudo-terminal double bonds ($N_t' \approx 0.5$ per chain) also remains constant. These two experimental observations suggest that:

(a) The two Rigo mechanisms giving either [I] or [IV] (Scheme I, Fig. 1) should not be greatly affected by the decrease of the monomer concentration in bulk as well as in suspension. This suggests that the increase of N_b' should mostly be due to an increase of transfer to polymer (Scheme II, Fig. 1). Starnes et al. (15b) have shown that for polymers prepared in solution under strictly homogeneous conditions, the chloromethyl branch concentration was essentially independent of the concentration of vinyl chloride.

(b) The decrease in monomer concentration increases the relative intensity of the 3.7-3.8 ppm resonance region (Structure [III]) compared to [II] (1 per chain). For the macroradicals, in the competition between propagation and intra- or intermolecular radical transfer, the relative importance of the second mechanism increases and it gives more branches longer than 2 carbon atoms as well as internal double bonds. Unfortunately, the relative possibilities of these different routes of Scheme II (Fig. 1) cannot be discussed adequately because the actual concentration of internal double bonds is not known.

If all the chloromethyl resonances in the 3.6-4.0 ppm region are taken into account, the average numbers of branches (N_b and N_b') can be calculated. For bulk polymerization (Samples A and B), small chains should be formed throughout the polymerization process. According to the percentages and $\overline{M}_n$ values of the extracts A_e (0.5% at conversion = 54.7%) and B_e (1.3% at conversion = 83.5%), the calculated $\overline{M}_n$ values of the corresponding residues are 46.4×10^3 and 45.6×10^3, respectively. Thus the apparent decrease of $\overline{M}_n$ for the crude Sample B (37.5×10^3) is due to a higher percentage of low molecular weight. Likewise, grafting mechanisms should occur throughout the polymerization process, but branches are more frequently grafted in the latter steps of the bulk polymerization.

At the similar conversion of 85%, suspension polymerization under subsaturation conditions seems to favor branching mechanisms (N_b = 6.7 and 6.1/1 000 VC for C and B, respectively), and final degassing in bulk polymerization should increase dehydrochlorination mechanisms that contribute–in addition to transfer reactions–to the increase of internal double bonds (N_i = 3.8 and 2.5/1 000 VC for B and C, respectively). Curiously, $N_i' + N_b'$ equals 6 for B as well as for C. Thus the total numbers of structural defects should remain constant, B being richer in internal double bonds and C more branched.

Finally, it is of interest to observe that at a conversion of 54.7%, bulk polymerization gives the best PVC with highest $\overline{M}_n$ (43.3×10^3) and lowest concentration of internal double bonds (N_i' = 0.3/chain) and branches (N_b' = 2.7/chain). Thus it is believed that all the structural defects–internal double bonds and branches–increase with decreasing monomer concentration.

More detailed discussion would require the identification and quantitative determination of the chloromethyl short branches and different types of internal double bonds by NMR studies of model compounds in different solvents. A better quantitative account of the mechanisms involved should be achievable provided that proper and adequate polymer samples should be available. Work is in progress in our laboratory to solve these problems.

REFERENCES

[1] IUPAC Working Party on Defects in the Molecular Structure of Polyvinyl Chloride and their Relation to Thermal Stability: Reports, To Be Published.

[2] A. Caraculacu and E. C. Bezdadea, Rev. Roum. Chim., 14, 1171 (1969).

[3] E. C. Bezdadea, E. C. Buruiana, and A. Caraculacu, Eur. Polym. J., 7, 1649 (1971).

[4] E. C. Bezdadea, E. C. Buruiana, G. Istrate-Robila, and A. Caraculacu, Ibid., 9, 445 (1973).

[5] A. Caraculacu and E. Bezdadea, J. Polym. Sci., Polym. Chem. Ed., 15, 611 (1977).

[6] R. Pétiaud and Q. T. Pham, Makromol. Chem., 178, 741 (1977).

[7] T. Hjertberg and E. M. Sörvik, Polymer, 24, 673 (1983).

[8] T. Hjertberg and E. M. Sörvik, Ibid., 24, 685 (1983).

[9] W. H. Starnes Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, D. J. Freed, R. L. Hartless, and F. A. Bovey, Macromolecules, 16, 790 (1983).

[10] K. B. Abbas, F. A. Bovey, and F. C. Schilling, Makromol. Chem., Suppl., 1, 227 (1975).

[11] F. A. Bovey, K. B. Abbas, F. C. Schilling, and W. H. Starnes, Macromolecules, 8, 437 (1975).

[12] W. H. Starnes, Jr., F. C. Schilling, K. B. Abbas, I. M. Plitz, R. L. Hartless, and F. A. Bovey, Ibid., 12, 13 (1979).

[13] W. H. Starnes Jr., F. C. Schilling, K. B. Abbas, R. E. Cais, and F. A. Bovey, Ibid., 12, 556 (1979).

[14] W. H. Starnes Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, D. J. Freed, and F. A. Bovey, Paper Presented at Third International Symposium on PVC, Cleveland, August 1980.

[15] (a) W. H. Starnes Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, and F. A. Bovey, Polym. Bull., 4, 555 (1981). (b) W. H. Starnes Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, F. A. Bovey, G. S. Park, and A. H. Saremi, Abstracts, 23rd Rocky Mountain Conference, Denver, Colorado, August 2-6, 1981.

[16] A. Rigo, G. Palma, and G. Talamini, Makromol. Chem., 153, 219 (1972).

[17] T. Hjertberg and E. Sörvik, J. Polym. Sci., Polym. Lett. Ed., 19, 363 (1981).

[18] T. Hjertberg and E. M. Sörvik, J. Macromol. Sci.–Chem., A17, 983 (1982).

[19] A. Michel, G. Schmidt, E. Castaneda, and A. Guyot, Angew. Makromol. Chem., 47, 61 (1975).

[20] D. E. Dorman, J. Jautelat, and J. D. Roberts, J. Org. Chem., 36, 2757 (1971).

[21] Q. T. Pham, P. Rocaniere, and A. Guyot, J. Appl. Polym. Sci., 14, 1291 (1970).

Received December 7, 1984