

NMR Analysis of Chlorinated Poly(vinyl Chloride)

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Synopsis

The chlorination of poly(vinyl chloride) takes place preferentially at the methylenic carbon, leading to 1,2-dichloroethylene units, and to a lower extent at the methynic, leading to 1,1-dichloroethylene units. The ratio between 1,2- and 1,1-dichloroethylene units tends to decrease with increasing degree of chlorination, and it seems to depend also on the chlorination conditions. The number-average sequence length of 1,2-dichloroethylene units does not differ significantly from 1 during a great part of the process, substantially in agreement with a random distribution of these units along the chain. The 1,1-dichloroethylene units can be found either between two unchlorinated units or at one end of a sequence of chlorinated units. Since among the unchlorinated units more racemic units are present than expected for a completely random chlorination, it can be suggested either that chlorination is affected by stereoregularity or that it does not take place in the crystalline regions of the polymer.

INTRODUCTION

The technological properties of poly(vinyl chloride) (PVC) undergo considerable changes on chlorination. Such changes depend on the degree of chlorination but cannot be completely explained on this basis. Polymers with the same chlorine content can differ greatly in their properties.

The first problem studied in the past has been to determine whether the chlorine is introduced in the PVC molecule mainly at the methylenic carbon or at the methynic carbon.

According to Seipold,¹ chlorination takes place at the methynic carbon, giving a product of the same composition as poly(vinylidene chloride) (PVDC). The differences between completely chlorinated PVC and PVDC are explained by assuming a helical structure for chlorinated PVC and a planar one for PVDC. The same results have been obtained by Ohé² on the basis of characteristic chemical reactions of chlorinated PVC.

On the basis of infrared measurements, Fuchs and Louis³ stated, on the contrary, that chlorination takes place at the methylenic and not at the methynic carbon; Nambu,⁴ in analogous research on chlorinated polyethylene, rules out the possibility of the presence of two chlorine atoms on the same carbon. According to Oswald and Kubu,⁵ formation of CCl_2 groups can occur in chlorination of polyethylene when the condition is approached of one chlorine atom for each carbon of the polymeric chain.

They predict also with fair approximation the glass transition temperature of chlorinated polyethylene considering it as a terpolymer of ethylene, vinyl chloride, and 1,2-dichloroethylene.

More recent studies support the prevailing substitution at the methylenic carbon of PVC, leading to the formation of 1,2-dichloro-ethylenic units, and the interest is focused on the influence of the experimental conditions on the orientation of the substitution. Two fundamental PVC chlorination processes are considered: the solution process that leads to highly soluble products used in paints, fibers, and adhesives, and the suspension process that improves the thermal stability and the mechanical properties at high temperatures.

Germar⁶ determined by infrared analysis, the fractions of unchlorinated, 1,2-, and 1,1-dichloroethylenic units in products obtained with either chlorination process. An inspection of his data leads to the result that the ratio between 1,2- and 1,1-dichloroethylenic units is independent of the chlorination process. Fredriksen and Crowo,⁷ in an infrared study of the suspension chlorination process, found that the distribution of chlorine atoms is independent of experimental conditions and statistically determined by the number of exchangeable hydrogens on the two carbon atoms. The probability of chlorination at the methylenic and methynic carbon is therefore in the ratio 2:1.

Petersen and Rånby,⁸ in an NMR study of a PVC chlorinated in suspension by the Goodrich process,⁹ found that, in the first stages of reaction, chlorination takes place almost completely at the methylenic carbon and only later at the methynic, up to a value of 34% of 1,1-dichloroethylenic units corresponding to a degree of chlorination of 94.5%. A lower content in 1,1-dichloroethylenic units was found by Sobajima et al.¹⁰ at the same degree of chlorination.

Trautvetter,¹¹ studying products obtained by both chlorination processes, comes to the conclusion that, for the same degree of chlorination degree, the amount of 1,2- and 1,1-dichloroethylenic units is the same, independent of the process, and that there is evidence that the process induces neither breakdown nor crosslinking of the polymeric chain. The results of the molecular weight fractionation experiments show that the degree of chlorination of the product obtained from the solution process is independent of the molecular weight, while the degree of chlorination of the product from the suspension process does depend on it, the chlorine content being higher for the high molecular weight fractions. As these data do not explain the very different solubilities of the two products, Trautvetter advances the hypothesis that, in the suspension process, chlorination takes place preferentially on the chain segments of the region where the concentration of the swelling agent is higher.

Kaltwasser and Klose¹² concluded, on the basis of infrared measurements, that chlorination of PVC takes place only at the methylenic carbon in both processes. On this basis they stated¹³ that, in the suspension process, sequences of adjacent CHCl groups form more easily.

We studied the structure of PVC chlorinated according to different suspension techniques, some of them patented.¹⁴ We tried to establish the influence of the process on the distribution of chlorine at the methylenic and methynic carbons, by determination of the fractions of 1,2- and 1,1-dichloroethylene units. We tried also to determine the average sequence lengths of chlorinated and unchlorinated units to get information about the distribution of chlorine atoms along the chain.

EXPERIMENTAL

We studied samples of chlorinated PVC obtained with four different processes: (A) PVC swollen with CHCl_3 , suspended in aqueous HCl , with chlorination with gaseous chlorine activated by ultraviolet radiation; (B) PVC swollen with CHCl_3 , anhydrous environment, with chlorination by gaseous chlorine activated by ultraviolet radiation; (C) PVC suspended in CCl_2F_2 containing small amounts of CHCl_3 with chlorination by gaseous chlorine activated by ultraviolet radiation; (D) Dynamit-Nobel commercial products (trade name Rhenoflex).

The purified resins were analyzed by high-resolution NMR in different solvents, mainly monochlorobenzene and *o*-dichlorobenzene in the range of 60–160°C.

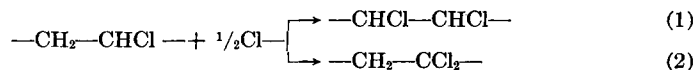
The instrument used was a Varian A 56/60.

RESULTS AND DISCUSSION

Distribution of Chlorine on the Methylenic and Methynic Carbons of the PVC Chain

The NMR spectrum of PVC consists of: (1) methylenic protons absorption at 7.87 τ , early interpreted by Johnsen¹⁵ as composed of two overlapping triplets due to methylenes in isotactic and syndiotactic diads and more recently in terms of tetrad configurational sequences of monomeric units^{16,17} and (2) of the methynic protons absorption at 5.55 τ composed of three overlapping quintuplets corresponding to syndiotactic, heterotactic, and isotactic triads.¹⁸

In the usual chlorination processes of PVC it is not possible to introduce more than one chlorine atom for each monomeric unit.^{1,3,6–8} A further chlorine atom can be introduced only in very special conditions,³ and it is very easily accompanied by breaking of the chain.¹² The introduction of a chlorine atom in the monomeric unit of PVC leads therefore to a 1,2-dichloroethylene unit if the substitution takes place at the methylenic carbon or to a 1,1-dichloroethylene unit if the substitution takes place at the methynic carbon:



In case (1) a methylenic group disappears and a CHCl group is formed; in case (2) the number of methylenic groups does not undergo any variation

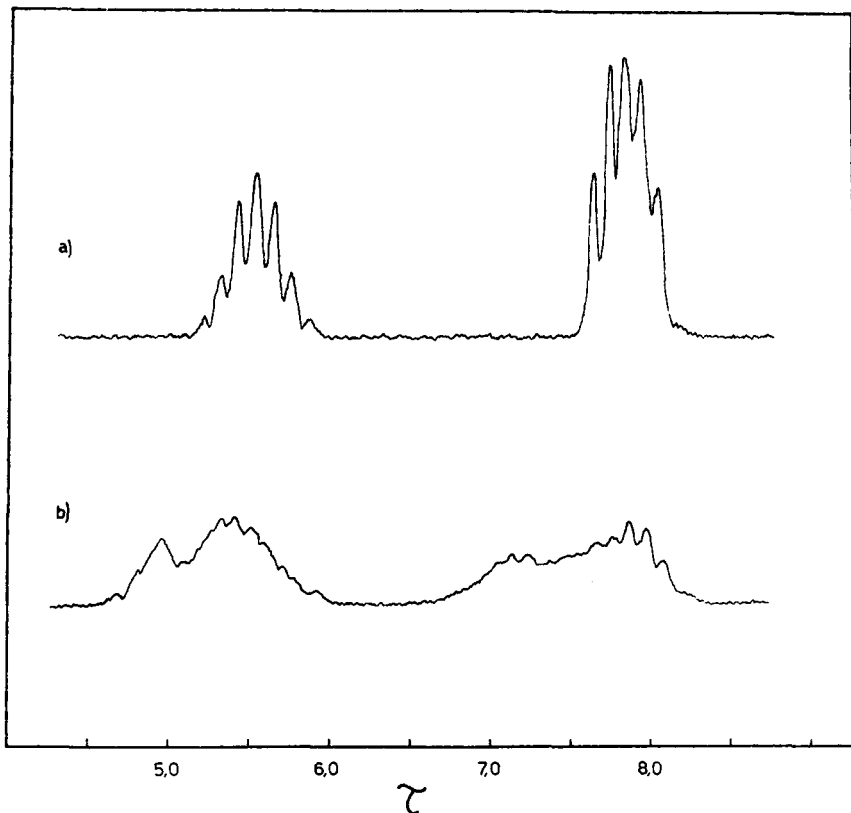


Fig. 1. NMR spectra of: (a) PVC and (b) chlorinated PVC, Cl = 66.7%, degree of chlorination 0.5, in monochlorobenzene at 130°C.

but a CHCl group disappears. These variations on the number of CH_2 and CHCl groups can be seen in the NMR spectrum as variations in the area of the bands of methylenic and methynic protons (Fig. 1). We determine, by chlorine elemental analysis, the degree of chlorination, i.e., the fraction of monomeric chlorinated units, X :

$$X = (62.46 C - 3544)/(3544 - 34.34 C) \quad (3)$$

where C is the weight percentage chlorine. The fraction of 1,2- and 1,1-dichloroethylene units can be determined from the NMR spectrum by measuring the areas of methylenic and methynic protons bands:

$$A_{\text{CH}_2}/A_{\text{CH}} = (X_{\text{VC}} + X_{11})/(1/2 X_{\text{VC}} + X_{12}) \quad (4)$$

$$X_{11} + X_{12} = X \quad (5)$$

where A_{CH_2} and A_{CH} are the areas of methylenic and methynic protons, respectively, X_{VC} is the fraction of unchlorinated units, and X_{12} and X_{11} the fraction of 1,2- and 1,1-dichloroethylene units, respectively.

TABLE I
Concentration of the Different Structural Units in Chlorinated PVC

Chlorination process	Sample number	Cl, %	Degree of chlorination, \bar{X}	$[\text{CH}_2-\text{CHCl}]$ X_{VC}	$[\text{CHCl}-\text{CHCl}]$ X_{12}	$[\text{CH}_2\text{CCl}_2]$ X_{11}	$\frac{[\text{CHCl}-\text{CHCl}]}{[\text{CH}_2-\text{CCl}_2]}$
A	1	60.5	0.16	0.84	0.14	0.02	7.0
	2	65.0	0.39	0.61	0.31	0.08	3.9
	3	67.1	0.52	0.48	0.38	0.14	2.7
	4	70.0	0.73	0.27	0.49	0.24	2.0
B	1	65.0	0.39	0.61	0.35	0.04	8.7
	2	67.0	0.52	0.48	0.45	0.07	6.5
	3	68.2	0.59	0.41	0.50	0.09	5.5
C	1	60.6	0.16	0.84	0.12	0.04	3.0
	2	63.1	0.29	0.71	0.21	0.08	2.7
	3	63.2	0.30	0.70	0.22	0.08	2.7
D	1	62.2	0.24	0.76	0.20	0.04	5.0
	2	62.7	0.27	0.73	0.23	0.04	5.7

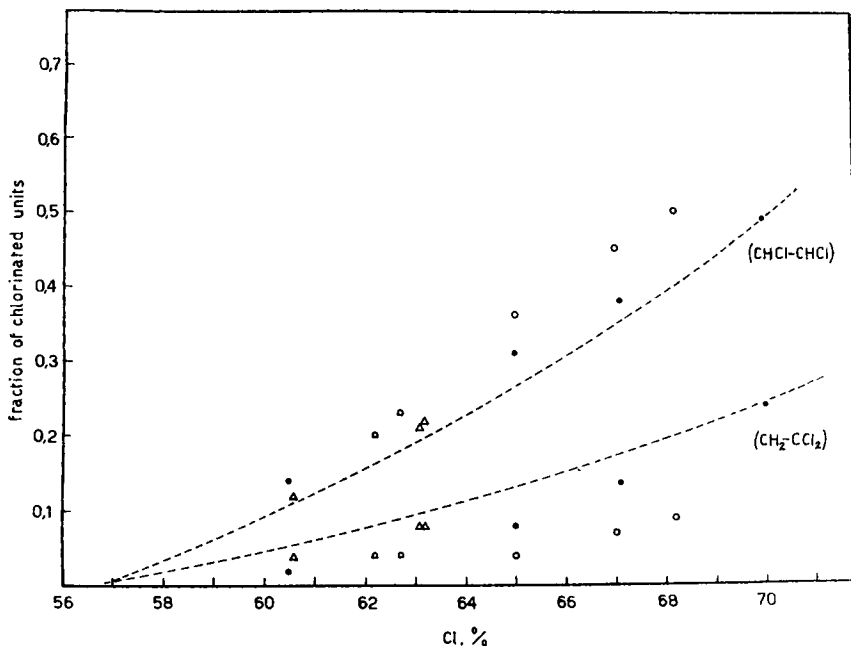


Fig. 2. Fraction of 1,2- and 1,1-dichloroethylenic units in PVC chlorinated according to different procedures.

Our experimental data are presented in Table I and plotted in Figure 2, where the two dotted lines represent the statistical distribution of chlorine atoms on methylenic and methynic carbon as proposed by Fredriksen and Crowo.⁷

We see that the chlorination process has some orientating influence. The ratio between 1,2- and 1,1-dichloroethylenic units decreases, as can be seen particularly from the process A data, as degree of chlorination increases; this means that substitution at the methylenic carbon is the preferred reaction in the early stages and that only later does substitution at the methynic carbon become significant. This is in agreement with Petersen and Rånby's results.⁸

Analysis of the Absorption Bands of Methylenic and Methynic Protons

Now we want to determine the distribution of chlorinated units along the polymeric chain, that is, to determine whether the chlorination concentrates on preferred segments of the chain or whether it takes place completely at random. This can be achieved through a more complete interpretation of the complex absorption related to methylenic and methynic protons. Chlorinated PVC can be considered, from what we have seen, as a terpolymer of vinyl chloride, 1,2-dichloroethylene, and 1,1-dichloroethylene. Our analysis rules out the presence of other structures, except in

TABLE II
 Chemical Shifts of Methylenic Protons in Chlorinated PVC

			τ
$\text{CH}_2\text{—CHCl—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CHCl}$	racemic	7.96	} 7.87
	meso	7.78	
$\text{CHCl—CHCl—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CHCl}$			7.87
{	$\text{CHCl—CHCl—CHCl—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CHCl}$		} 7.67
	$\text{CHCl—CHCl—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CHCl—CHCl}$		
$\text{CHCl—CHCl—CHCl—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CHCl—CHCl}$			7.47
$\text{CH}_2\text{—CCl}_2\text{—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CHCl}$	racemic	7.77	} 7.69 ^a
	meso	7.61	
{	$\text{CH}_2\text{—CCl}_2\text{—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CHCl—CHCl}$		} 7.49
	$\text{CHCl—CHCl—CHCl—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CCl}_2$		
$\text{CH}_2\text{—CCl}_2\text{—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CCl}_2$	racemic	7.67	} 7.59 ^a
	meso	7.51	
{	$\text{CH}_2\text{—CHCl—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CCl}_2\text{—CH}_2\text{—CHCl}$		} 7.18 ^a
	$\text{CH}_2\text{—CHCl—CH}_2\text{—CCl}_2\text{—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CHCl}$		
{	$\text{CHCl—CHCl—CH}_2\text{—CCl}_2\text{—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CHCl}$		} 7.18
	$\text{CHCl—CHCl—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CCl}_2\text{—CH}_2\text{—CHCl}$		
{	$\text{CH}_2\text{—CHCl—CHCl—CHCl—}\underline{\text{CH}_2}\text{—CCl}_2\text{—CH}_2\text{—CHCl}$		} 6.98
	$\text{CH}_2\text{—CHCl—CH}_2\text{—CCl}_2\text{—}\underline{\text{CH}_2}\text{—CHCl—CHCl—CHCl}$		
{	$\text{CH}_2\text{—CCl}_2\text{—CH}_2\text{—CHCl—}\underline{\text{CH}_2}\text{—CCl}_2\text{—CH}_2\text{—CHCl}$		} 7.02 ^a
	$\text{CH}_2\text{—CHCl—CH}_2\text{—CCl}_2\text{—}\underline{\text{CH}_2}\text{—CHCl—CH}_2\text{—CCl}_2$		

^a Data of Enomoto and Satoh.²²

very small amounts. There is therefore a wide range of possible combinations of these units, and this leads to the existence of the methylenic and methynic protons in many different molecular environments, each of which generates a peculiar chemical shift for the methylenic and methynic protons. We must furthermore take into account the effect of spin coupling and the possibility of different configurations for the same structure, as the monomeric unit of PVC has an asymmetric carbon atom and the prevailing chlorination on the methylene generates a second asymmetric carbon. The chemical shifts of the different structural groups originating by chlorination of PVC have been tentatively attributed by taking into account the chemical shifts of related compounds, as low molecular weight halocompounds, copolymers of vinyl chloride with vinylidene chloride,^{19,20} ethylene,²¹ and 1,2-dichloroethylene. In Table II we list the chemical shifts of the central methylene of a tetrad of monomeric units being progressively chlorinated on the methylenic and methynic carbon. We take into account four monomeric units, as the absorption of methylenic protons is influenced by the chlorination of methynic carbon in γ position; four monomeric units are thus needed. Further chlorination does not influence the absorption of methylenic protons.

The structures listed in Table II are present in PVC for a degree of chlorination < 0.6 ; we can rule out, from the inspection of the spectrum,

TABLE III
Chemical Shifts of Methynic Protons in Chlorinated PVC

	τ
$(\text{CH}_2\text{—CHCl})_n$	5.55
$\text{CH}_2\text{—CHCl—CHCl—CHCl—CH}_2\text{—CHCl}$	5.43
$\text{CH}_2\text{—CHCl—CH}_2\text{—CHCl—CH}_2\text{—CCl}_2$	5.32
$\text{CH}_2\text{—CHCl—CHCl—CHCl—CH}_2\text{—CCl}_2$	5.20
$\text{CH}_2\text{—CCl}_2\text{—CH}_2\text{—CHCl—CH}_2\text{—CCl}_2$	5.09 ^a
$(\text{CHCl—CHCl})_n$	4.95

^a Data of McClanahan and Previtera.²³

sequences of 1,1-dichloroethylene units which absorb in the range 6.13–6.52 τ ^{8,20} and structures of adjacent CCl_2 and CHCl groups ($\text{CH}_2\text{—CCl}_2\text{—CHClCHCl}$). This means that every 1,1-dichloroethylene unit must be followed by an unchlorinated unit which would be difficult to chlorinate. This could explain the experimental difficulty of obtaining, with the usual chlorination processes, completely chlorinated products having two chlorine atoms for each monomeric unit. The absorption of methynic protons (Table III) goes from 5.55 τ (CHCl groups in PVC) to 4.95 τ (internal CHCl in sequences $(\text{CHCl})_n$); the absorption of endgroups of $(\text{CHCl})_n$ sequences and the CHCl groups of PVC bound to 1,1-dichloroethylene units takes place in the middle. With increasing degree of chlorination the complex absorption band shows two maxima at 5.40 and 4.95 τ .

Distribution of Chlorinated Units along the Polymeric Chain

We will now introduce a model of chlorinated PVC where completely random chlorination has taken place. This has been done by attributing the same probability of chlorination for each monomeric unit in the chain, excluding any orientating effect due to stereoregularity or to neighboring chlorinated units. In such a model the distribution of chlorinated units along the chain can be calculated after the treatment of Bernoulli trial statistics. We will compare now the calculated with the experimental data.

1,2-Dichloroethylene Units. The methynic protons of (CHCl—CHCl) units absorb in the low field band (Fig. 3), together with the methynic

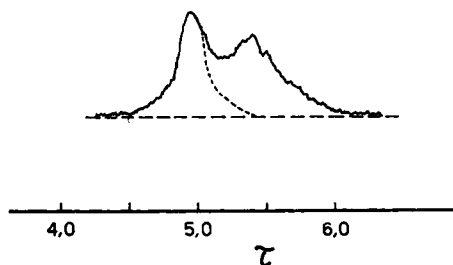


Fig. 3. Absorption of methynic protons: area of internal CHCl groups in $(\text{CHCl})_n$ sequences.

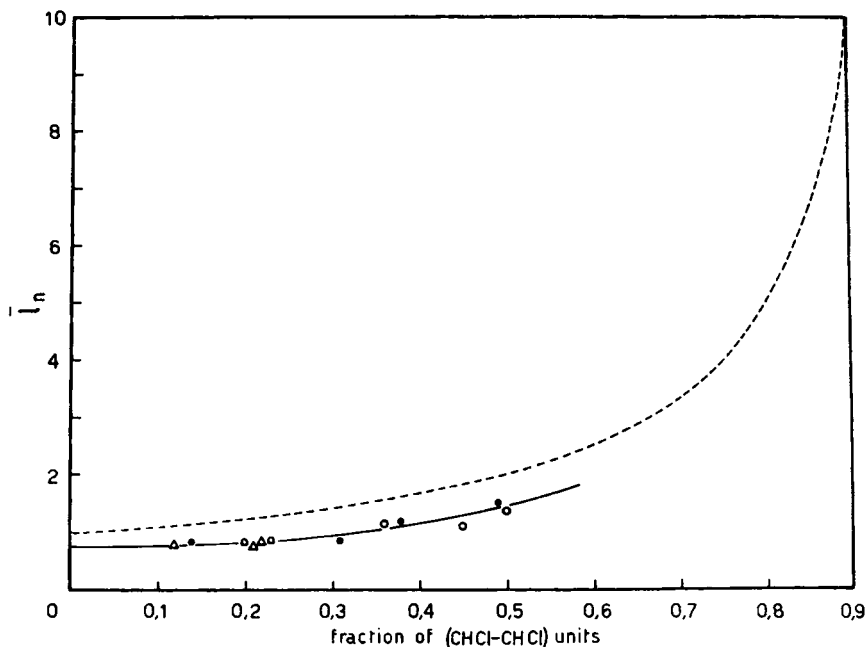


Fig. 4. Number-average sequence length of 1,2-dichloroethylene units: (---) calculated according to a completely random distribution; (—) experimental data.

protons of unchlorinated units. This band has two maxima at 4.95 and 5.40 τ . From the analysis of the spectrum it has been possible to establish that the largest part of the intensity related to internal CHCl groups in a (CHCl) $_n$ sequence lies within the dashed area at 4.95, in Figure 3. From this, the number-average sequence lengths, \bar{l}_n , of 1,2-dichloroethylene units can be calculated.

The procedure is as follows. First we calculate the area related to the protons of 1,2-dichloroethylene units, A_{12} :

$$A_{12} = A_{\text{CH}} [X_{12}/(X_{12} + 1/2 X_{\text{VC}})] \quad (6)$$

From this area we subtract the area related to the internal methynic protons in the (CHCl) $_n$ sequences, $A_{12 \text{ int}}$, and obtain the area related to the protons of the CHCl endgroups, $A_{12 \text{ term}}$:

$$A_{12} - A_{12 \text{ int}} = A_{12 \text{ term}} \quad (7)$$

The number-average sequence length is:

$$\bar{l}_n = A_{12}/2A_{12 \text{ term}} \quad (8)$$

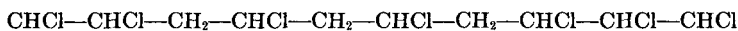
The number-average sequence length of entirely random distributed 1,2-dichloroethylene units along an infinite succession of monomeric units is:

$$\bar{l}_{\text{nr}} = 1/(1 - X_{12}) \quad (9)$$

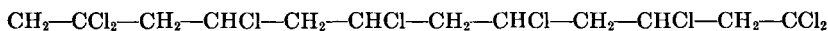
We plot in Figure 4 the experimental and calculated data versus the fraction of 1,2-dichloroethylene units (X_{12}). The number-average sequence length, that reaches 1.5 for a fraction of 1,2-dichloroethylene units of 0.5, has been found to be 0.8 in the early stages of chlorination; this value is evidently too low, as the minimum possible value of \bar{l}_n is 1. It must be considered that these data are obtained from rather poorly resolved spectra, where it is practically impossible to determine the pure contribution of CHCl groups internal in sequences (CHCl) $_n$. However, even if we should admit a constant 25% systematic error along the experimental curve, we would never have the experimental data lying above the \bar{l}_n calculated according to Bernoulli's distribution, and we can note that in any case the slopes of the two curves are almost parallel. If this cannot be taken as conclusive proof that the distribution of 1,2-dichloroethylene units along the polymeric chain obeys the Bernoulli distribution, it allows us on the other hand to conclude that there is no evidence that chlorination at methylene is more likely at a monomeric unit near one already chlorinated at the methylene, as this would give sequences of 1,2-dichloroethylene units longer than expected from a Bernoulli distribution.

1,1-Dichloroethylene Units. As previously stated the (CH₂—CCl₂) units cannot appear as sequences and cannot be followed by 1,2-dichloroethylene units when the total chlorination degree is < 0.6. This means that every 1,1-dichloroethylene unit necessarily interrupts a sequence of chlorinated units, as it is always followed by at least one unchlorinated unit.

Unchlorinated Units. The resonance of the methylenic protons of a (CH₂—CHCl) unit does not undergo any shift with respect to that in the homopolymer when the chlorination occurs at a carbon which is farther than the γ position (see Table II). Therefore, in the case of chlorination at the methylenic carbon, a unit, to be unshifted, must be flanked on both sides by two unchlorinated units, only the successive ones being able to undergo chlorination at the methylenes:



In the case of chlorination at the methylenic carbon, a unit, to be unshifted, must have two unchlorinated units on the left side and only one unchlorinated unit on the right side, as in the preceding case:



Thus, in order to have an unshifted unit, we have to consider in the first case a triad and in the second case a tetrad of unchlorinated units, the choice depending on the chlorinated unit being on the left side of the unshifted unit, as on the right side we need in both cases only one unchlorinated unit, independent of whether the sequence ends with a 1,2- or a 1,1-dichloroethylene unit. Thus it follows that, in an entirely random chlorinated polymer, the concentration of unshifted units is related to the concentration of unchlorinated triads and tetrads, the ratio between triads and tetrads being determined by the ratio of 1,2- to 1,1-dichloroethylene units.

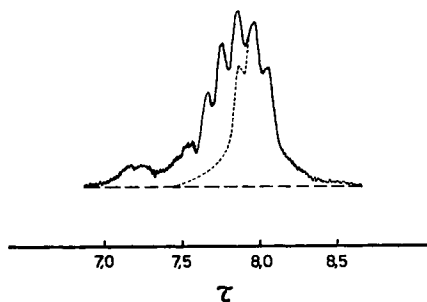


Fig. 5. Absorption of methylenic protons: area of unshifted racemic methylenes.

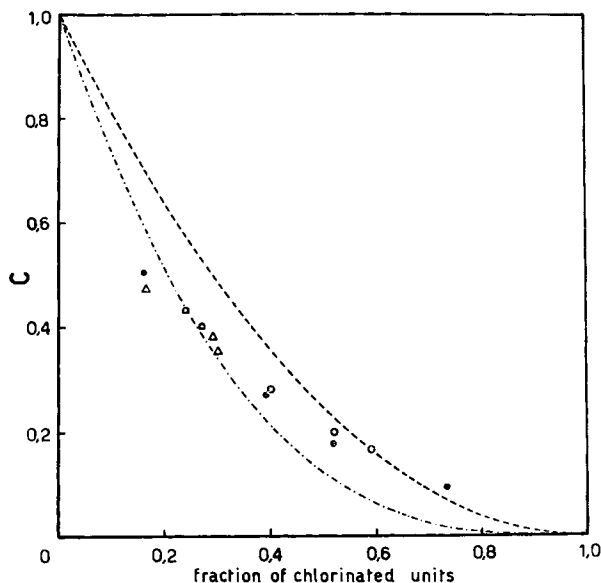


Fig. 6. Concentration of unshifted racemic units vs. fraction of chlorinated units. The lines give the calculated concentration of triads and tetrads of unchlorinated units in a completely random chlorination process.

It is impossible to determine from the spectrum the concentration of all unshifted units, as the absorption of the meso methylenes overlaps that of the methylenes belonging to chlorinated units. We can however calculate the concentration, F_{re} , of unshifted racemic units according to Johnsen's procedure:¹⁵

$$F_{re} = (A_r/A_{CH_2}) (X_{VC} + X_{11}) \quad (10)$$

where A_{CH_2} is the total area of methylenic protons, A_r is the area under the dashed curve of Figure 5 related to the racemic methylenes, X_{VC} and X_{11} are the fractions of unchlorinated and 1,1-dichloroethylene units. F_{re} is plotted in Figure 6 together with the concentration of unchlorinated triads and tetrads, calculated according to the ideal random process of chlorination

TABLE IV
 Concentration (Calculated According to a Random Distribution) of All, F , and Racemic,
 F_r , Unchlorinated Unshifted Units in Comparison with the Experimental Values of Racemic Unshifted Units, F_{re}

Chlori- nation process	Sample number	X	α	β	$(1 - X)^2$	$(1 - X)^3$	F	F_r	F_{re}
A	1	0.16	0.87	0.13	0.71	0.59	0.69	0.40	0.50
	2	0.39	0.79	0.21	0.37	0.23	0.34	0.20	0.27
	3	0.52	0.73	0.27	0.23	0.11	0.20	0.11	0.18
	4	0.73	0.67	0.33	0.07	0.02	0.06	0.03	0.09
B	1	0.40	0.90	0.10	0.36	0.22	0.35	0.20	0.28
	2	0.52	0.86	0.14	0.23	0.11	0.21	0.12	0.20
C	3	0.59	0.85	0.15	0.17	0.07	0.15	0.09	0.17
	1	0.16	0.75	0.25	0.71	0.59	0.68	0.39	0.47
	2	0.29	0.72	0.28	0.50	0.36	0.46	0.27	0.38
D	3	0.30	0.73	0.27	0.49	0.34	0.45	0.26	0.35
	1	0.24	0.83	0.17	0.58	0.44	0.55	0.32	0.43
	2	0.27	0.85	0.15	0.53	0.39	0.51	0.30	0.40

by means of the relations: $(1 - X)^2$ and $(1 - X)^3$, where X is the fraction of chlorinated units. The experimental concentrations of unshifted racemic units are rather high, lying between the curves of unchlorinated triads and tetrads among which are of course included those which have a meso central methylene. For a better understanding of this phenomenon we have calculated the concentration of unshifted racemic units according to the ideal random process.

To derive this quantity we have determined first the concentration of all unshifted units F , which, for a certain degree of chlorination, is given by the sum of the concentration of unchlorinated triads and tetrads, each multiplied by the parameters α and β , respectively, which represent the contribution of triads and tetrads in determining the concentration of all unshifted units:

$$F = \alpha(1 - X)^2 + \beta(1 - X)^3 \quad (11)$$

where $\alpha + \beta = 1$. These parameters are related to the fraction of 1,2- and 1,1-dichloroethylenic units in this way:

$$\alpha = X_{12}/X \quad (12)$$

$$\beta = X_{11}/X \quad (13)$$

The dependence of α and β on the chlorination process does not have a great influence on the concentration of all unshifted units, as can be seen from the data of Table IV where we list the fraction of chlorinated units X , the corresponding α and β , the triad and tetrad concentrations, and the concentration of all unshifted units F for the various samples analyzed.

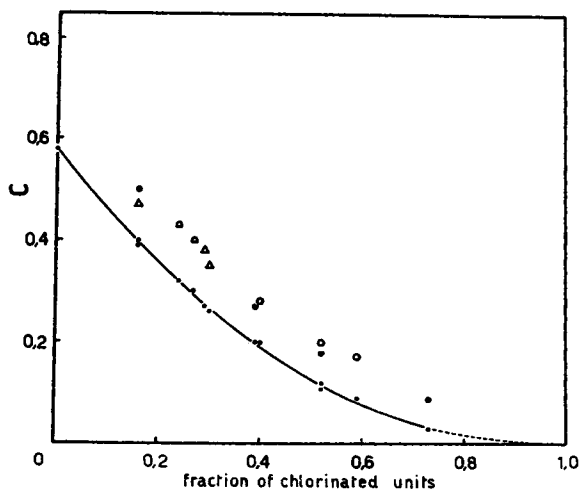
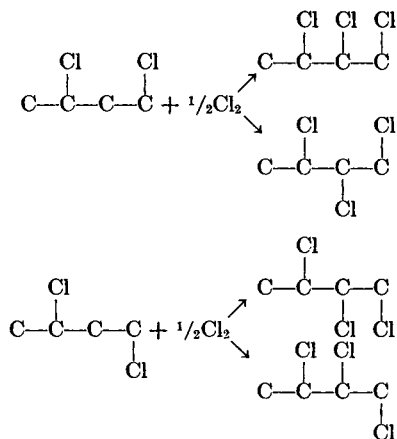


Fig. 7. Concentration of unshifted racemic units vs. fraction of chlorinated units. The line gives the concentration of unshifted racemic units calculated for a completely random chlorination process.

Now we have to consider that, in the random model of chlorination, we have assumed the same probability of chlorination for each monomeric unit; therefore the meso and racemic unchlorinated units will be in the same ratio as in the original PVC, namely 58% racemic. The probability of the methylene of the central unit of a triad being racemic is still 0.58 and the same is true for the central methylene of a tetrad. The concentration of unshifted racemic units is thus given by the product of the concentration of all unshifted units by 0.58. We collected in Table IV the concentration of racemic unshifted units, F_r , together with the corresponding experimental values, F_{re} . These values are also plotted in Figure 7. The fact that the experimental values are higher than the calculated ones in the whole range considered could be explained by a block chlorination in which rather long sequences of chlorinated units are followed by rather long sequences of unchlorinated units. In this case we should have experimental data higher than the calculated ones also for the meso units. Unfortunately we cannot check this, as the unshifted meso units are experimentally undeterminable. In any case the hypothesis of a block polymer is not supported by the experimental results of the distribution along the chain of 1,2- and 1,1-dichloroethylene units. As the chlorinated units do not form a block structure, the unchlorinated ones cannot form it either. Therefore we advance the hypothesis that the chlorination can be influenced by the steric configuration of the PVC chain and that it takes place preferentially on the meso units. This could be supported by electrostatic and steric considerations: the chlorination at the methylenic carbon, that we have seen to be prevailing, gives a *trans* configuration of adjacent chlorine atoms only if it takes place on isotactic units.



In the case of suspension chlorination, a second hypothesis cannot be ruled out according to which chlorination would take place at the amorphous regions of the PVC chain swollen by the organic solvent and not in the crystalline regions. In fact, in this polymer, only the racemic sequences are crystallizable, and the minimum sequence length necessary to allow crystal-

lization has been found to be of the order of 5 units.²⁴ According to this, the fraction of crystallizable units may be determined by the relation:²⁵

$$f_{NR} = (1 - \sigma)^{N+1}(1 + \sigma N)$$

which gives the mole fraction of racemic units in the sequences longer than N units. Taking $N = 5$ and $\sigma = 0.42$, which represents the fraction of meso units in the original PVC, we obtain a fraction of crystallizable units of 0.12.

The hypothesis that PVC does not undergo chlorination in the crystalline regions, which concerns on the other hand only 12% of the total units, does not rule out the possibility that chlorination proceeds in the amorphous regions, giving a non-block structure of chlorinated units according to our experimental results.

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