Table V
Sequence Fractions in the I-DB Copolymer[a]

	triads exptl	triads calcd		tetrads exptl	tetrads calcd
III	0.726	0.352	IIII	0.234	0.124
IID + DII	0.221	0.482	DIII	0.079	0.085
DID	0.053	0.166	IIID	0.063	0.085
IDI	0.210	0.352	DIID	0.024	0.058
DDI	0.235	0.241	IID<	0.113	0.143
IDD	0.267	0.241	DID<	0.091	0.098
DDD	0.288	0.166	>DII	0.102	0.143
			>DID	0.080	0.098
			>DD<	0.214	0.166

[a] Sample no. 5 of Table I.

evident in the case of the triad IDI. Therefore the I–DB copolymer displays a distribution of the monomeric units which is indicative of a tendency toward blockiness.

Conclusions

The spectroscopic analyses (IR and NMR) of cationic I–DB copolymers have shown that the enchainment of the diene is essentially trans-1,4. Signals attributable to other possible structural units of DB are not evident. The quantitative evaluation of the monomer sequence distribution indicates that I–DB shows the tendency to a block-type structure.

An analogous situation was found for isobutylene–butadiene copolymers.[1] But in that case the copolymerization system is more complex because the diene gives rise to different structural units and shows a great difference of reactivity relative to the olefin.[9] Conversely, I and DB exhibit a small difference of reactivity and hence the conclusions obtained concerning the copolymer structure surely reflect also the course of the copolymerization process. On the basis of the structural data obtained in this work, the product of the reactivity ratios of I and DB should be higher than one. Preferential solvation effects exerted by the monomers on the active centers[1] might explain these findings.

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50.3-MHz ^{13}C NMR Study of Chlorinated Poly(vinyl chloride) Microstructure and the Mechanism of Chlorination

Richard A. Komoroski,* Richard G. Parker, and Marvin H. Lehr

The BFGoodrich Research and Development Center, Brecksville, Ohio 44141.

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ABSTRACT: Carbon-13 NMR at 50.3 MHz has been used to study the microstructures of a series of solution-chlorinated PVC's (CPVC) in the earliest stages of the reaction (57–62% Cl) and the microstructure of a commercial CPVC (66% Cl). Resonances due to configurational isomers in sequences containing three adjacent CHCl carbons were observed for lightly chlorinated PVC and for a low molecular weight copolymer of vinyl chloride and 1,2-dichloroethylene. Configuration assignments were made on the basis of low molecular weight model compounds. At chlorine levels up to about 57.7% Cl only substitution at CH_2 carbons could be observed. However, CCl_2 carbons of isolated vinylidene chloride units were observed soon afterward (~58.3% Cl) in the product. This suggests that these structures were formed by a direct free-radical substitution mechanism rather than by a combined elimination–addition mechanism. Peak assignments for the commercial CPVC were made on the basis of calculated chemical shifts and the observed shifts of lightly chlorinated PVC and model copolymers. Results of spin–lattice relaxation experiments indicate that the chlorinated structures have restricted segmental mobility compared to PVC.

Introduction

The molecular structure of chlorinated poly(vinyl chloride) (CPVC) has been the subject of investigation for some time.[1,2] Although CPVC is simple in its basic composition, consisting predominantly of CCl_2, CHCl, and CH_2 groups, the many possible arrangements of these groups produce a very complex macromolecule. Both sequence distribution and CHCl configuration (in both the unchlorinated and chlorinated regions) must be taken into account to describe the microstructure of the polymer backbone.

The most powerful method available for characterizing the molecular structure of CPVC is nuclear magnetic resonance (NMR), particularly ^{13}C NMR. The sensitivity of the ^{13}C chemical shift to comonomer sequence distribution and tacticity makes it the method of choice for studying the microstructure of CPVC. The ability to directly observe CCl_2 carbons is a major advantage over ^{1}H NMR for CPVC. Unfortunately, the structural complexity of the polymers and the unfavorable NMR properties for CCl_2 carbons made the acquisition of high signal-to-noise ^{13}C spectra very difficult with the equipment available prior to the introduction of wide-bore, cryomagnet NMR systems.

We have prepared a series of CPVC's with very low degrees of chlorination and have examined the series using a cryomagnet-based, wide-bore NMR spectrometer operating at 50.3 MHz for ^{13}C. The relatively simple spectra, compared to that for commercial CPVC, facilitated some peak assignments and the observation of configurational isomers in the chlorinated segments. Identification of the first structures to appear during chlorination of PVC

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Table I
Composition and Glass Transition Temperatures of Some Lightly Chlorinated PVC's

sample no.	reaction time, min	T_g,[b] °C	% Cl[a]	% Cl (NMR)	mol % (111)	mol % (020)
1	0	91.0	56.15	56.8	0.0	0.0
2	10	91.0	56.72	57.3	1.1	0.0
3	20	94.0	57.75	57.7	1.7	0.0
4	30	97.5	58.28	58.7	3.3	0.5
5	40	99.5	57.99	59.5	4.0	0.5
6	50	105.5	57.88	60.1	5.6	0.6
7	60	106.5	59.40	60.6	7.1	1.4

[a] Schöniger oxygen flask method (±0.5%). [b] Recorded on second heat scan at 40 °C/min heating rate using a Perkin-Elmer DSC-2 differential scanning calorimeter.

provided insight into the mechanism of chlorination in the early stages. The above results, the spectra of model compounds, spin–lattice relaxation time (T_1) measurements, and previous results[2] are used to assign the 50.3-MHz ^{13}C spectrum of a commercial CPVC. The T_1 values also served as probes of mobility of the various chain segments.

Experimental Section

CPVC. The commercial CPVC examined here was Geon 603x560 (The BFGoodrich Co.) containing about 66% Cl. The lightly chlorinated PVC's were prepared by solution photochlorination of Geon 103EP PVC (The BFGoodrich Co.) in tetrachloroethane at 80 °C. Gaseous chlorine was fed (0.25 g/min) to the PVC solution (50 g/L) under ultraviolet irradiation (300-W Hg lamp; type H 3C/3A; Voltarc Tubes, Fairfield, CT).

Model Copolymers and Compounds. The vinyl chloride–1,2-dichloroethylene copolymer was prepared as follows: A 200-mL glass reactor was charged with vinyl chloride (15 g), *trans*-1,2-dichloroethylene (15 g), and *sec*-butyl peroxydicarbonate initiator (0.4 g). The mixture was agitated for 16 h at 50 °C and then poured slowly into rapidly stirred methanol (400 mL). The solid was collected on a Büchner funnel, washed with a large volume of methanol, and vacuum-dried for 6 h at 25–30 °C. The white powder weighed 13.2 g and contained 60.06% Cl by chemical analysis. GPC analysis in THF gave M_n = 3180 and M_w = 5830, with the peak at 5120. The vinyl chloride–vinylidene chloride copolymer was a commercial sample (Geon 202, The BFGoodrich Co.) and contained about 2.6 mol % vinylidene chloride. The *meso*- and *rac*-1,2,3,4-tetrachlorobutanes were obtained from ICN Pharmaceuticals, Inc., and were used without further purification.

NMR. Carbon-13 NMR spectra were obtained at 50.3 MHz on a Bruker WH-200 wide-bore, cryomagnet FT NMR spectrometer. The spectral data were acquired on 20 wt % solutions in 4:1 1,2,4-trichlorobenzene–benzene-d_6 at 110 °C using 20-mm sample tubes. Chemical shifts were measured relative to internal hexamethyldisiloxane at 2.00 ppm from tetramethylsilane. Typical accumulation conditions: pulse repetition rate, 7.5 s; 90° radiofrequency pulse, 35 μs; spectral width, 12195 Hz in 8192 points; line broadening from sensitivity enhancement, 2 or 3 Hz; time of accumulation, 5–15 h. Spin–lattice relaxation times (T_1) were measured by using the standard inversion–recovery sequence. Protonated and nonprotonated carbons were measured in separate experiments. Nuclear Overhauser enhancements (NOE) were measured by using inverse gated decoupling.

Results and Discussion

A. Lightly Chlorinated PVC and Model Copolymers and Compounds.

Samples were taken at regular intervals early in the solution photochlorination of PVC and examined by ^{13}C NMR at 50.3 MHz. Table I provides the glass transition temperatures and compositional data for the series. Figure 1 shows selected spectra from the series.

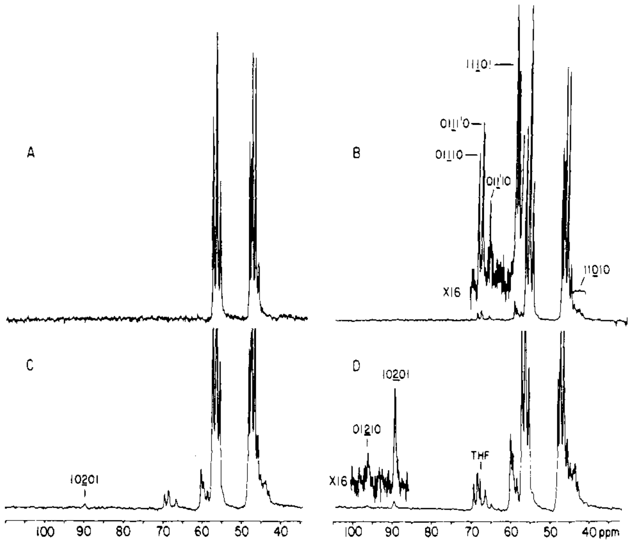


Figure 1. ^{13}C NMR spectra of lightly chlorinated PVC's at various stages of reaction in solution: (A) 0 min; (B) 20 min; (C) 30 min; (D) 50 min. Five-digit sequences indicate assignments. "THF" indicates peak due to residual tetrahydrofuran.

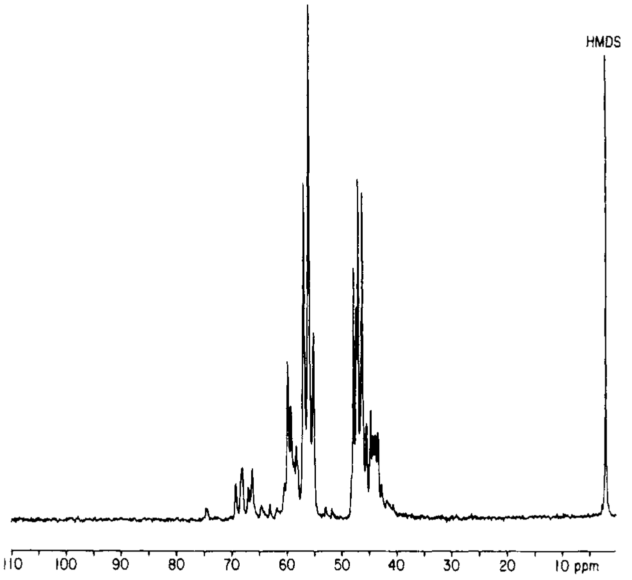


Figure 2. ^{13}C NMR spectrum of a vinyl chloride–1,2-dichloroethylene copolymer.

Additional peaks arising from the chlorination process were seen after only 10 min of reaction time (spectrum not shown). The spectrum obtained at 20 min (Figure 1B) is representative of the earliest stages of the reaction. Many new peaks appear compared to PVC (Figure 1A) but none are seen in the CCl_2 region (85–100 ppm). Hence we can ignore any CCl_2-containing structures when assigning the additional resonances of Figure 1B, which appear at (a) 66–70 ppm, (b) 58–60 ppm, and (c) 43–45 ppm. On the basis of substituent effects for chlorine,[2,3] the three regions can be assigned to carbons in structure I. This structure

$$\underset{c}{-CH_2}-\underset{b}{CHCl}-\underset{a}{CHCl}-\underset{b}{CHCl}-\underset{c}{CH_2-}$$

I

arises from adding a single chlorine atom to a methylene carbon in a PVC chain. The a:b:c areas are in the expected ratio of 1:2:2. Given the very low chlorine level (57.75%), it is unlikely that the peak multiplicity in the various regions is due to other chemically distinct structures.

Further confirmation of the assignment of I comes from the ^{13}C spectrum of a copolymer of vinyl chloride and 1,2-dichloroethylene (Figure 2). Random incorporation

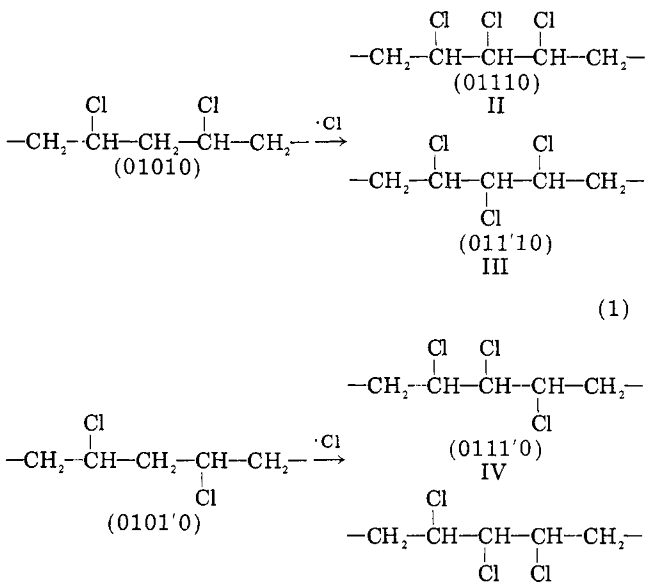
Table II
^{13}C Chemical Shifts of Model Compounds for 1,2 Structures in CPVC

compound		chemical shift, ppm		
		CHCl	CH$_2$Cl	CH$_3$
2,3-dichlorobutane[a]	m	61.6		22.1
	r	60.5		20.8
1,2,3,4-tetrachlorobutane	m	60.3	46.9	
	r	59.2	44.3	

[a] From ref 6. Converted to Me$_4$Si scale using $\Delta\delta$(CS$_2$ − Me$_4$Si) = 192.8 ppm.

of 1,2-dichloroethylene comonomer into a PVC chain should also produce I. The copolymer spectrum is very similar to that of very lightly chlorinated PVC (Figure 1B). The additional small peaks in the copolymer spectrum are probably due to chain end effects and defect structures in this low molecular weight material.

We believe the peak multiplicity for lightly chlorinated PVC arises from configurational isomerism in the chlorinated sequence I. The spectrum can be explained by considering the structures produced by direct substitution of one chlorine on a CH$_2$ carbon centering m and r dyads in PVC (01010 and 0101′0):[4]



$$\underset{(01010)}{-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-} \xrightarrow{\cdot\mathrm{Cl}} \begin{array}{c} \underset{\substack{(01110)\\ \mathrm{II}}}{-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-} \\ \underset{\substack{(011'10)\\ \mathrm{III}}}{-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-} \end{array} \tag{1}$$

$$\underset{(0101'0)}{-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-} \xrightarrow{\cdot\mathrm{Cl}} \begin{array}{c} \underset{\substack{(0111'0)\\ \mathrm{IV}}}{-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-} \\ \underset{\substack{(011'1'0)\\ \mathrm{V}}}{-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-} \end{array}$$

Since IV and V give the same NMR spectrum, we expect three peaks with an area ratio 1:1:2 for II:III:IV + V for carbon a, and four peaks of equal area for each carbon b and c. The above analysis assumes an equal concentration of m and r placements (actually r is favored slightly[5]) in the original PVC, a stereospecifically random chlorination, and no influence on chemical shifts from neighboring units in the chain. Conversely, the appearance of the expected pattern can be taken as evidence for a stereospecifically random chlorination.

For carbon a we see a 1:2:1 pattern with some multiplicity of the central peak attributable to neighboring sequence effects. For carbon b we see a 2:1:1 pattern, with the largest peak again split. For carbon c we observe at least five resonances, suggesting a strong influence of neighboring sequences on these "terminal" methylenes, as might be expected.

Configurational assignments can be made for the central carbon of I by analogy to low molecular weight model compounds. In Table II the ^{13}C chemical shifts are given for the diastereomeric pairs of 2,3-dichlorobutane[6] and 1,2,3,4-tetrachlorobutane. In both cases the chemical shift of the CHCl group in the meso isomer is downfield from that of the racemic isomer by about 1 ppm. On this basis we make the configurational assignments in Figure 1B. Configurational assignments for carbons b and c are not made due to the greater likelihood of influence from neighboring units.

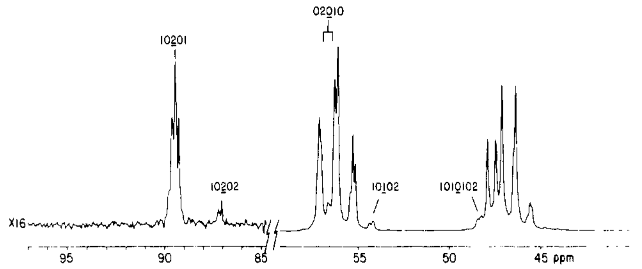
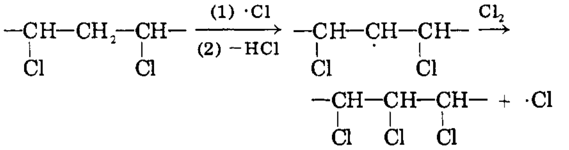


Figure 3. ^{13}C NMR spectrum of a 97.4:2.6 vinyl chloride–vinylidene chloride copolymer. Five-digit sequences indicate assignments.

Longer sequences of CHCl groups (e.g., 11*1*11) appear later (50 min) in the reaction (Figure 1D). These sequences give rise to additional peaks in the region 61–68 ppm[2] (see section B).

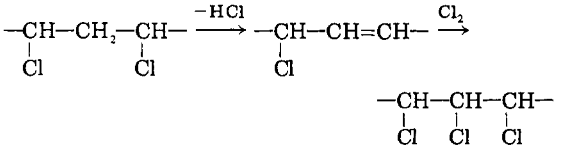
After 30 min of chlorination, CCl$_2$ groups begin to appear at about 89.5 ppm[2] (Figure 1C). On the basis of the work of Keller and Mügge,[7] Carman,[8] and ourselves (Figure 3) on vinyl chloride–vinylidene chloride copolymers, we attribute the peaks at 89.5 ppm and the shoulder at 54.3 ppm (Figure 1C,D) to isolated vinylidene chloride units. The shoulder at 54.3 ppm is due to a CHCl group of the type 10*1*02 while the CCl$_2$ of 10*2*01 appears at 89.5 ppm.

The presence of isolated vinylidene chloride units in lightly chlorinated PVC necessitates a reexamination of previous conclusions concerning chlorination mechanisms and the generation of CCl$_2$ groups in CPVC. Kolínský and co-workers[1] have concluded from ^{1}H NMR and other studies of the chlorination of PVC-α-d and PVC-β,β-d_2 that several mechanisms are involved. In the early stages of the reaction (in either suspension or solution) two mechanisms were proposed to be operative in the production of 1,2-dichloroethylene units.[1] The direct-substitution mechanism (eq 2) was considered only for CH$_2$ carbons.



$$-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}- \xrightarrow[(2)\ -\mathrm{HCl}]{(1)\ \cdot\mathrm{Cl}} -\underset{\mathrm{Cl}}{\mathrm{CH}}-\dot{\mathrm{C}}\mathrm{H}-\underset{\mathrm{Cl}}{\mathrm{CH}}- \xrightarrow{\mathrm{Cl_2}} -\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}- + \cdot\mathrm{Cl} \tag{2}$$

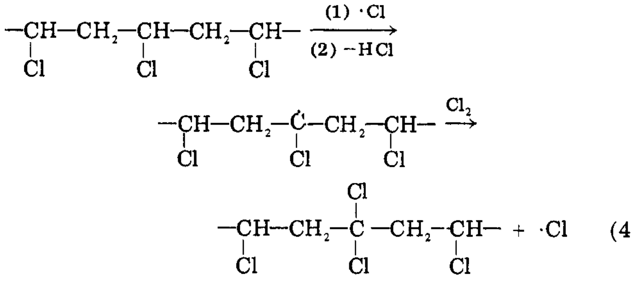
The elimination–addition (E–A) mechanism (eq 3) involved dehydrohalogenation of PVC followed by addition of Cl$_2$.



$$-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}- \xrightarrow{-\mathrm{HCl}} -\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH}{=}\mathrm{CH}- \xrightarrow{\mathrm{Cl_2}} -\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}- \tag{3}$$

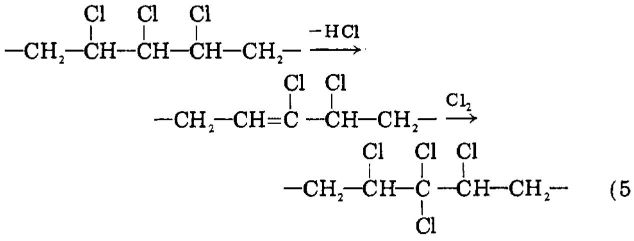
No CCl$_2$ groups were formed until later stages of the reaction and these groups were of the trichloroethylene type. The previous workers concluded that there was no evidence for CH$_2$ groups occurring in vinylidene linkages.

The formation of CCl$_2$ groups of isolated vinylidene chloride units in the early stages of our solution chlorination suggests to us that these groups (eq 4), like newly formed CHCl (eq 2), result from a direct free-radical substitution mechanism. No simple elimination–addition mechanism can be written for formation of isolated vinylidene chloride units. We found no direct evidence such



$$-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \xrightarrow[(2)\ -HCl]{(1)\ \cdot Cl} -\underset{Cl}{CH}-CH_2-\underset{Cl}{\dot{C}}-CH_2-\underset{Cl}{CH}- \xrightarrow{Cl_2} -\underset{Cl}{CH}-CH_2-\underset{Cl}{\overset{Cl}{C}}-CH_2-\underset{Cl}{CH}- + \cdot Cl \qquad (4)$$

as unsaturation to support an E–A mechanism at any stage of chlorination up to about 70% Cl.[9] However, a second type of CCl_2 did appear at about 96 ppm (Figure 1D) after 50 min of chlorination. We assign this CCl_2 at the center of the 01210 sequence (see section B),[2] which could arise from I by substitution or by an E–A mechanism (eq 5).[1]



$$-CH_2-\overset{Cl}{CH}-\overset{Cl}{CH}-\overset{Cl}{CH}-CH_2- \xrightarrow{-HCl} -CH_2-CH=\overset{Cl}{C}-\overset{Cl}{CH}-CH_2- \xrightarrow{Cl_2} -CH_2-\overset{Cl}{CH}-\underset{Cl}{\overset{Cl}{C}}-\overset{Cl}{CH}-CH_2- \qquad (5)$$

The structures 11210 and 11201, which are observed in commercial CPVC (see section B), can be produced by either substitution or an elimination–addition mechanism. The minor structure 10202 cannot be readily obtained via an E–A mechanism.

The relative rate of substitution of chlorine at the CH_2 and CHCl groups can be measured from the spectra of the series in Table I. Substitution at CH_2 groups is found to be about 5 times as likely to occur as substitution at CHCl groups. This is consistent with previous work[10] on chlorination of secondary chloroalkanes, where the chlorine-containing site is less reactive than adjacent CH_2 groups, but not by a large factor.

The measured tacticity of the residual PVC does not vary significantly among the samples in Table I.

B. ^{13}C NMR Assignments for Commercial CPVC. Figure 4 shows the 50.3-MHz ^{13}C spectrum of BFGoodrich Geon 603x560 CPVC containing about 66% Cl by weight. Considerably more detail is apparent than in previously reported spectra.[11,12] Peak assignments for five-carbon sequences are also indicated. The assignments are based on the results in section A, predicted shifts as calculated by Keller,[2] and T_1 values (Table III). Very highly chlorinated sequences are not considered but may contribute in certain cases.

At least five types of CCl_2 carbons are present in the commercial CPVC (Figure 4a). Effects of nearby CHCl stereosequence on CCl_2 chemical shifts are small (see CCl_2 resonance of Figure 3) and are not resolved for CPVC. The sequences 10201 (isolated vinylidene chloride) and 01210 are most prominent. Since it is the farthest downfield, the peak at 96 ppm is assigned to 01210, even though the observed and predicted values differ by about 2 ppm. The assignment for 11210 follows from that of 01210 with the expected upfield γ effect.[3] The 91-ppm peak is assigned to 11201 by comparison to vinyl chloride–trichloroethylene copolymers.[9,13] The peak at 87 ppm is assigned to 10202 based on vinyl chloride–vinylidene chloride copolymers (Figure 3).[7-9]

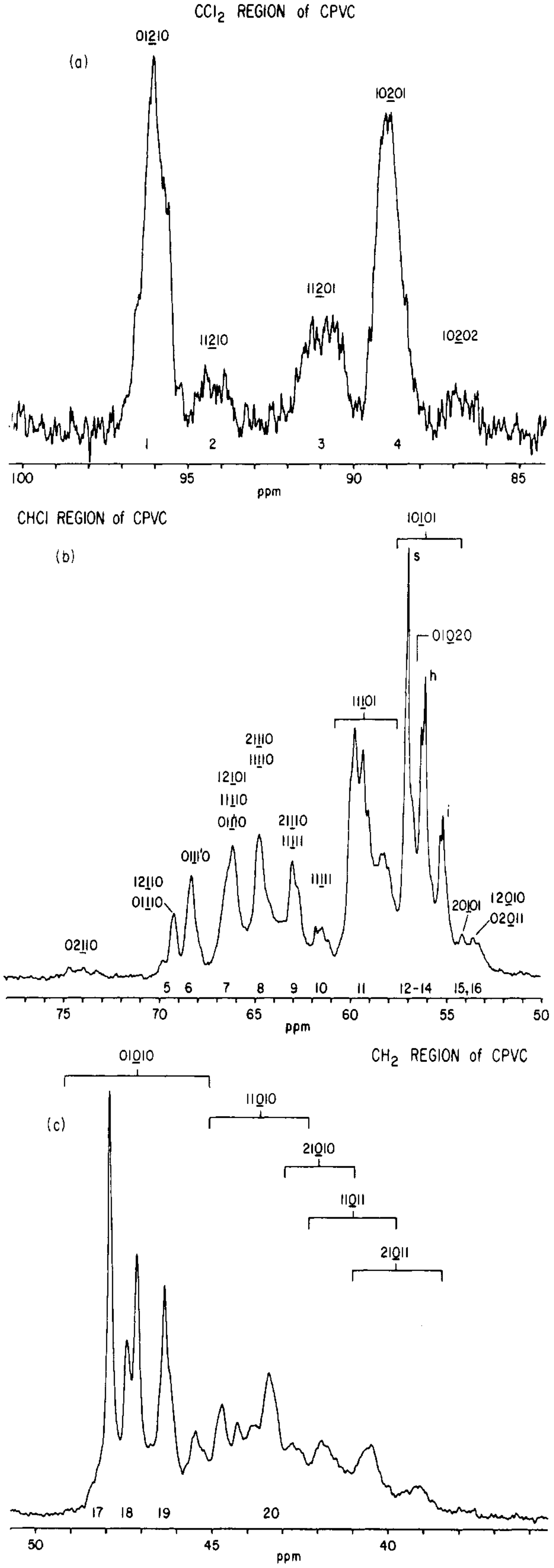


Figure 4. ^{13}C NMR spectrum of Geon 603x560 CPVC. Five-digit sequences indicate assignments. Numbers below each peak or band refer to Table III.

The results for lightly chlorinated PVC and the vinyl chloride–1,2-dichloroethylene copolymer indicate that configurational isomerism of the chlorinated segments plays a major role in both the CHCl and CH_2 spectral regions. Carbons in 1,2-dichloroethylene-type sequences appear to contribute to every peak between 58 and 70 ppm. Of course, more highly chlorinated, CCl_2-containing sequences also appear in this region. It is difficult to determine where, and to what extent, these latter structures

Table III
^{13}C T_1 and NOE Values for CPVC

peak no.	T_1,[a] s	NOE[b]	assignment
1	2.8	1.8 (96 ppm)	CCl_2
2	*c*	1.6 (89–96 ppm)	CCl_2
3	*c*		
4	2.8	2.4 (89 ppm)	CCl_2
5	0.25	2.5 (60–70 ppm)	mainly CHCl
6	0.31		
7	0.25		
8	0.25		
9	0.24		
10	0.22		
11	0.27	2.4 (55–60 ppm)	mainly CHCl
12	0.36		
13	0.34		
14	0.31		
15	0.26		
16	0.20		
17	0.24	2.4 (45–50 ppm)	CH_2
18	0.21		
19	0.21		
20	0.14	2.3 (35–45 ppm)	CH_2

[a] Estimated accuracy, ±15%. [b] Estimated accuracy ±0.1 for protonated carbons, ±0.2 for nonprotonated carbons. [c] Approximately several seconds.

contribute to the spectrum. Assignments in spectra 4b and 4c, beyond those made in section A, are our best guess given the predicted values and the known configurational influence. In the CH_2 region, we have assigned regions that overlap each other to a large extent due to configurational effects.

The residual PVC in the commercial CPVC sample appears higher in relative syndiotactic content than a typical PVC. Interferences in the PVC CHCl carbon region make the quantitative determination of tacticity difficult. Both Millan[14] and Keller[12] have observed the same behavior for nonsolution-chlorinated PVC.

C. Spin–Lattice Relaxation Times and Nuclear Overhauser Enhancements. Table III lists the ^{13}C T_1 values for the more prominent peaks in the spectrum of CPVC. The T_1 values of the residual PVC carbons of CPVC are in good agreement with those previously reported for PVC under similar conditions.[15] We do not feel our measurements are precise enough to detect T_1 differences due to stereoisomerism. The T_1 values of the peaks at about 89 and 96 ppm are an order of magnitude longer than those of the CHCl and CH_2 carbons, confirming the CCl_2 assignment for peaks in the 85–100-ppm region.

The T_1 values of the CHCl and CH_2 carbons in the chlorinated regions are reduced from the corresponding values in the PVC regions. Coupled with the substantial enhancements (see below) of the protonated carbons, this indicates a reduction of segmental mobility in the chlorinated regions.[16] This is not unexpected in view of the increasing T_g of the bulk polymer with degree of chlorination. Differences for T_1 are seen among the peaks in the 58–70-ppm region. Further work is necessary to determine if these differences can be useful for assignment purposes.

The T_1 experiment provides some additional assignment information. Figure 5 is a partially relaxed spectrum (τ = 0.14 s) of CPVC. From this spectrum and the calculated T_1 values, the peak at 54.3 ppm is identified as a CHCl-centered resonance, while that at 53.5 ppm is a CH_2-centered line. On the basis of this result, we assign the five-carbon sequences expected in this region as shown.

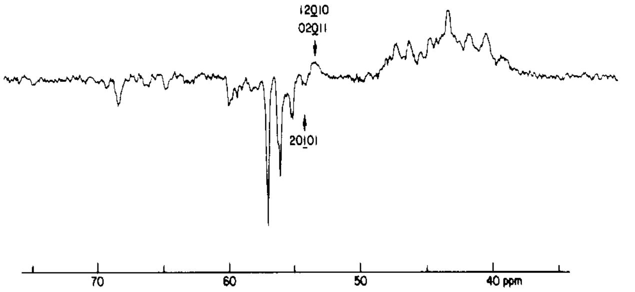


Figure 5. Partially relaxed (τ = 0.14 s) ^{13}C FT NMR spectrum of Geon 603x560 CPVC.

We have also measured the NOE values of individual CCl_2 carbons and other regions of the ^{13}C spectrum (Table III). The protonated carbon regions have substantial NOE values of 2.3–2.5, reduced somewhat from the theoretical maximum of 3.0. The CCl_2 peak at 89 ppm has a similar NOE, but the remainder of the CCl_2 carbons appear to have even lower NOE values. Lukáš et al.[17] have reported reduced NOE values for the CCl_2 carbons relative to the CHCl and CH_2 carbons of CPVC. Our average results for the CCl_2 region are in agreement with those of Lukáš et al. Reduced NOE values for nonprotonated backbone carbons have been observed for other polymers[18] and can complicate compositional and structural analyses. This is also true for CPVC and should be more severe at higher chlorine levels where CCl_2 groups are more abundant.

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