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^{13}C NMR Microstructural Analysis of Chlorinated Poly(vinyl chloride) in Terms of Three-Carbon Sequences

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ABSTRACT: Using previously determined peak assignments at 50.3 MHz, we have developed a quantitative ^{13}C NMR analysis of chlorinated poly(vinyl chloride) (CPVC) microstructure in terms of three-carbon sequences. The analysis is sensitive to chlorine level and yields the concentrations of 11 three-carbon sequences, the weight percent chlorine, the amount of tacticity of residual PVC, and the sequence lengths of unchlorinated vinyl chloride units and CHCl carbons. We have characterized a series of CPVC's (57–69% chlorine) prepared by solution photochlorination, as well as several 66%-chlorine CPVC's made by various processes. The sequence length of the vinyl chloride units ("residual PVC") for the solution-chlorinated polymers correlated well with the second heat of melting determined by DSC. This result confirmed that the heat of melting arises from the residual PVC in these polymers. The CPVC's (66% chlorine) prepared by using different processes had different levels of residual PVC, vinyl chloride sequence lengths, and total amounts and distributions of CCl_2-centered sequences. In solution, the various tactic sequences were chlorinated to approximately equal extents. For the heterogeneous processes, the residual PVC contained greater relative proportions of syndiotactic sequences, reflecting the reduced rate of chlorination of PVC crystallites relative to the amorphous regions. The use of higher frequency (100 MHz) did not significantly improve the peak resolution in much of the CPVC spectrum, even with computer resolution enhancement.

Introduction

In a previous report,[1] we described how the free-radical chlorination of poly(vinyl chloride) produces a polymer, chlorinated poly(vinyl chloride) (CPVC), for which no structural repeat unit can be written. On the basis of ^{13}C NMR data, we know that CPVC's are composed of CH_2, CHCl, and CCl_2 groups occurring in many sequence combinations along the polymer chain. Configurational isomerism of CHCl-containing sequences in both the chlorinated and unchlorinated regions must also be considered. A description of CPVC based on sequences of vinyl or other monomers, as is often done for chemically modified homopolymers,[2,3] is not readily feasible.

Many of the ^{13}C chemical shifts of three- to five-carbon sequences have been assigned in the 50.3-MHz spectrum.[1,4] Here we present a method for the quantitative characterization of CPVC based on the concentrations of 11 three-carbon sequences, residual PVC, the average sequence lengths of unchlorinated vinyl chloride units and CHCl groups, and the tacticity of the residual PVC. We use this analysis to characterize a series of CPVC's of different chlorine contents prepared by solution photochlorination. Several CPVC's made by different processes but at a single chlorine level are also compared. The effect of the chlorination process on the CPVC microstructure and the tacticity of the residual PVC is discussed, as well as the use of higher magnetic fields and resolution enhancement techniques to improve the CPVC analysis.

Experimental Section

CPVC. The CPVC's were prepared by solution photochlorination of Geon 103EP poly(vinyl chloride) (The BF Goodrich Co.) in tetrachloroethane at 80 °C. Gaseous chlorine was fed (0.25 g/min) to the poly(vinyl chloride) solution (50 g/L) under ultraviolet irradiation (300-W Hg lamp). The polymer was precipitated with methanol, recovered by filtration, washed with a large volume of methanol, and vacuum-dried overnight at 25–30 °C. The processes used to prepare the nonsolution CPVC's are referenced in Table IV.

NMR Spectra. The 50.3-MHz ^{13}C NMR spectra were obtained on a Bruker WH-200 wide-bore, cryomagnet Fourier transform NMR spectrometer. The spectral data were acquired on approximately 20 wt % solutions in 4:1 1,2,4-trichlorobenzene/benzene-d_6 at 110 °C by using 20-mm sample tubes. Chemical shifts were measured relative to internal HMDS at 2.00 ppm from Me_4Si. Typical accumulation conditions were as follows: pulse repetition time, 7.5 s; 90° pulse, 35 μs; spectral width, 12 kHz in 8K data points; line broadening from sensitivity enhancement, 1.5–3 Hz; time of accumulation, 5–15 h. Integrated areas were measured from electronic integrals.

The 100-MHz ^{13}C spectra were obtained on a Bruker WH-400 narrow-bore NMR spectrometer using 10-mm tubes. The accumulation conditions were as follows: pulse repetition time, 3.5 s; 90° pulse, 13 μs; spectral width, 15 kHz; transform size, 16K. Resolution enhancement was performed as previously described.[5]

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Table I
Possible Three-Carbon Sequences in Chlorinated Poly(vinyl chloride)[a]

CH_2-centered	CHCl-centered	CCl_2-centered
{101}	{010}	{020}
{201}	{110}	{120}
{202}	{111}	{121}
	{210}	{220}[c]
	{211}	{221}[c]
	{212}[b]	{222}[c]

[a] PVC = ...01010101... (tacticity ignored). [b] Sequence not observed. [c] A possible {22*X*} sequence has been observed in the spectra of CPVC prepared at high temperature under forcing conditions that resulted in chain cleavage.

Differential Scanning Calorimetry. Glass transition temperatures and second heats of melting were measured on a Perkin-Elmer DSC-2 instrument at a scan rate of 20 °C/min. The broad melting transition of the CPVC's was taken from about 100 to about 220 °C.

Results and Discussion

In Table I are presented the 15 possible three-carbon sequences that can occur for a "terpolymer" of CH_2, CHCl, and CCl_2 carbons. We use the numerical designation adapted from Keller[4] to identify each type of carbon (CH_2 = 0, CHCl = 1, CCl_2 = 2). Configurational isomers have not been distinguished in Table I. In addition, no chain direction has been specified since a sequence, such as {201}, will have the same chemical shift as its mirror image, {102}.

Only three CH_2-centered three-carbon sequences can occur in CPVC since adjacent methylenes do not normally occur in PVC (neglecting any small amount of head-to-head polymer postulated to be present). For longer sequences, those with an even number of carbons between methylenes cannot occur. Of the six possible CHCl-centered three-carbon sequences, all have been observed directly or indirectly except the highly chlorinated {212}. This structure is ignored in the analysis. Although structures with adjacent CCl_2 carbons are possible, resonances assignable to such sequences have been observed (at about 100 ppm) in only a few samples (see below). These samples all contained greater than 70% chlorine and were prepared at high temperatures under such forcing conditions that some chain cleavage occurred. Such sequences are not expected to occur in polymers containing less than 70% chlorine because of severe steric and electronic effects on their formation. Therefore, sequences with adjacent CCl_2 carbons are also ignored in the analysis. Thus, our sequence distribution analysis describes CPVC in terms of 11 of the 15 possible three-carbon sequences. Two of the three CCl_2-centered sequences we observe, {020} and {120}, must originate exclusively from {010} in PVC assuming that chlorination proceeds by a substitution mechanism, as demonstrated previously.[1] The third, {121}, can arise from either {010} or {101}.

CPVC Sequence Analysis. In a previous paper,[1] we assigned resonances in the 50.3-MHz ^{13}C NMR spectrum of CPVC to five-carbon sequences based on predicted chemical shifts,[4] substituent effects,[6] model polymers,[5,7] and CPVC with a low degree of chlorination. The use of five-carbon sequences reflects the initial sensitivity of the 50.3-MHz ^{13}C spectrum to sequence distribution at low chlorine content, at which point highly chlorinated sequences are absent. Some sequences, particularly in the CH_2 portion of the spectrum, were assigned to overlapping regions. This is due to the complexity of the spectrum arising from configurational isomerism present in many of the three- or five-carbon sequences. Thus, the analysis we present here is based on three-carbon sequences since this is the longest length for which we can develop a reasonable quantitative analysis containing all possible observed sequences. In certain cases, such as for CCl_2-centered sequences, the analysis can be partially extended to five-carbon sequences.

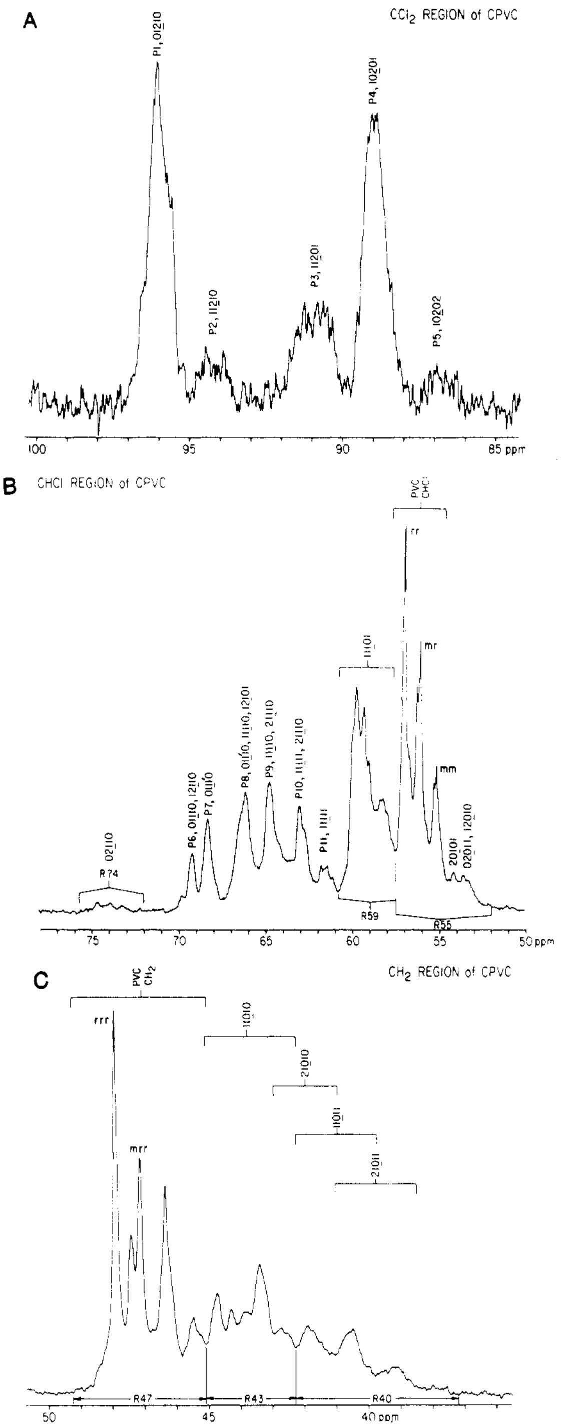

Figure 1. 50.3-MHz ^{13}C NMR spectrum of CPVC (Geon 603X560) showing peak assignments and designations used in the microstructural analysis: (A) CCl_2 region; (B) CHCl region; (C) CH_2 region.

Figure 1 shows the 50.3-MHz ^{13}C NMR spectrum of Geon 603X560 CPVC (The B. F. Goodrich Co.) with peaks (P) and regions (R) labeled as in the analysis. The primed notation designates configurational isomers.[1] Spectra were accumulated with nuclear Overhauser enhancement (NOE), necessitating normalization of the individual CCl_2 carbon areas for their reduced NOE's relative to the CH_2 and CHCl carbons.[1] We assume a single NOE of 2.4 for the CHCl and CH_2 carbons, as measured previously[1] for a sample containing about 66% chlorine. The CCl_2 carbon resonances were also corrected for partial saturation due to their long T_1's.[1] For a 7.5-s pulse repetition time, a 6% correction is applied. We also assume that the above conditions apply for all CPVC's at all chlorine levels between 57% and 70% chlorine at the concentration and temperature of the analysis.

The mole percent (F) of each of the three carbon types can be found by using eq 1–3. Here A is the total corrected area of the CPVC spectrum. Equations 2 and 3 reflect the fact that CH_2 carbons directly adjacent to CCl_2 carbons are shifted into the nominal CHCl region.[5] For each {11201} (P_3), one CH_2 is added to the nominal CH_2 area. The exact chemical shift of the methylene in {11201} is not known, but it is probably in the vicinity of 55 ppm. For each {10201} (P_4) and {10202} (P_5), two CH_2's are added to the CH_2 area. Methylenes in {02010} sequences are known to occur at 56.3 ppm from results on vinyl chloride–vinylidene chloride copolymers.[5] Other {201} sequences should occur nearby in the CHCl region. Methylenes in {202} sequences occur at 62–63 ppm.[5] Corresponding subtractions are made from the CHCl area.

$$F_{CCl_2} = [\sum_{i=1}^{5} P_i]/A \qquad (1)$$

$$F_{CHCl} = [\sum_{i=6}^{11} P_i + R_{55} + R_{59} + R_{74} - P_3 - 2(P_4 + P_5)]/A \qquad (2)$$

$$F_{CH_2} = [R_{40} + R_{43} + R_{47} + P_3 + 2(P_4 + P_5)]/A \qquad (3)$$

Equations 4–14 give the mole fractions of the 11 three-carbon sequences that we obtain in this analysis.

$$S_{101} = [R_{40} + R_{43} + R_{47}]/A \qquad (4)$$

$$S_{201} = [P_3 + 2P_4 + P_5]/A \qquad (5)$$

$$S_{202} = P_5/A \qquad (6)$$

$$S_{010} = [R_{55} - (P_3 + 2P_4 + P_5)]/A \qquad (7)$$

$$S_{110} = R_{59}/A \qquad (8)$$

$$S_{111} = [\sum_{i=6}^{11} P_i - 2(P_1 + P_2) - P_5]/A \qquad (9)$$

$$S_{210} = [2P_1 + P_2]/A \qquad (10)$$

$$S_{211} = [P_2 + P_3]/A \qquad (11)$$

$$S_{020} = [P_4 + P_5]/A \qquad (12)$$

$$S_{120} = P_3/A \qquad (13)$$

$$S_{121} = [P_1 + P_2]/A \qquad (14)$$

Equations 4–14 were derived from the assignments intuitively.[1] Equation 4 for S_{101} derives from the total CH_2 area between 37 and 50 ppm. Equation 7 for S_{010} is just the PVC CHCl area minus some corrections for known {201} interferences.[5] These corrections are derived from the CCl_2-carbon region as for eq 1–3. In this region, as in most others, small interferences due to highly chlorinated sequences may occur for which we cannot correct. The concentration of {110} is given by the group at 57.5–60.8 ppm and has no known correction. Equation 9 for S_{111} is corrected for {202} methylene at 62–63 ppm (P_5), for {210} methine somewhere between 61 and 70 ppm ($2P_1 + P_2$), and for {12$\underline{1}$1}, probably about 70 ppm (P_2). Equations 12–14 for the $\underline{2}$-centered triads derive from the CCl_2-peak areas. The {20202} sequence, known to occur at about 84 ppm,[5] is never seen and hence ignored. The position of the highly chlorinated sequence {11211} is assumed to occur with {01210} and {11210}, if at all. Any five-carbon sequence containing {212} at any position is assumed to be zero.

Equations 5, 6, 10, and 11 for certain 0- and 1-centered triads were derived in terms of CCl_2 carbon areas. No resonances are resolved for the on-center carbons of {201}, {202}, or {210} sequences. The region R_{74} from 72 to 76 ppm is assigned to {02$\underline{1}$10} sequences and may contain other {2$\underline{1}$1}-centered sequences. However, this band is very broad and difficult to measure accurately. We feel that a better estimate of {211} can be obtained from CCl_2 carbon areas. Equations 5, 6, 10, and 11 are not rigorous. They are only meant to provide estimates of the concentrations of sequences usually present at low levels. For the purpose of eq 11, the concentration of {11211} is assumed to be zero.

We tested eq 4–14 for consistency with triad necessary relationships for terpolymers (eq 3.89–3.91 in ref 8). Equations 10, 11, 13, and 14 were shown algebraically to be exactly consistent. Equations 5, 6, 12, and 13 were shown algebraically to be consistent with an error of only $P5/2$, a negligible quantity. A third relationship for the sequences given by eq 4, 5, 7, 8, and 10 could not be demonstrated algebraically, but could be tested numerically. Ideally the ratio $R = (2S_{010} + S_{110} + S_{210})/(2S_{101} + S_{201})$ should equal 1. The results of this calculation are presented below with the other numerical results for the solution polymers and those prepared by other processes. In most cases R is very close to 1. On average, agreement seems to be better for the solution polymers than for those prepared heterogeneously. This is probably due to the presence of higher concentrations of more highly chlorinated sequences in the heterogeneously prepared polymers.

Estimates of the residual, unchlorinated PVC remaining can be obtained from eq 15 and 16. By residual PVC we mean identifiable sequences of vinyl chloride units {10}. It does not mean totally unchlorinated chains of starting PVC. Equation 15 gives the mole percent of vinyl chloride units centering tetrads (or greater), PVC_{CT}. Equation 16 gives the mole percent of vinyl chloride units contained in diads or greater sequences, PVC_D. The weight percent chlorine is given by eq 17 and is based on the mole percent of each of the three types of carbons (eq 1–3).

$$PVC_{CT} = 200R_{47}/A \qquad (15)$$

$$PVC_D = 200[R_{43} + R_{47} + P_3]/A \qquad (16)$$

$$\text{wt \% Cl} = \frac{100(70.90F_{CCl_2} + 35.45F_{CHCl})}{82.92F_{CCl_2} + 48.47F_{CHCl} + 14.03F_{CH_2}} \qquad (17)$$

Equations for calculating number-average sequence lengths in copolymers and terpolymers have been given by Randall.[8] We have adapted these equations for CPVC. The complexity and limited peak resolution of the 50.3-MHz ^{13}C NMR spectrum of CPVC prevent an exact calculation of $\bar{n}_{10}$, the sequence length of vinyl chloride ({10}) units. Equation 18 provides a reasonable estimate of $\bar{n}_{10}$.

$$\bar{n}_{10} = \frac{R_{40} + R_{43} + R_{47} + P_3 + 2P_4 + P_5}{R_{40} + \frac{1}{2}(R_{43} + P_3 + 2P_4 + P_5)} \qquad (18)$$

In the calculation of $\bar{n}_{10}$, we took P_3, P_4, and P_5 to represent termination of {10} by conversion of {1} to {2}; R_{43} represents {10} terminated by conversion of {0} to {1} or {2}; R_{47} represents blocked {10} as interior units; and R_{40} represents isolated {10} (of {101} only). There are other types of isolated {10} which are not included in our analysis. The CH_2 carbon regions R_{40} and R_{43} were divided at a point considered to be the best compromise based on the overlap-

Table II
Microstructural Results for Solution-Chlorinated CPVC's

sample	T_g	wt % Cl		mol %			% residual PVC				mol %											
		chem	NMR	CH_2	CHCl	CCl_2	tetrad	diad	$\bar{n}_{10}$	$\bar{n}_1$	101	201	202	010	110	111	210	211	020	120	121	*R*
1	91.0	56.2	56.8	49.8	50.2	0.0	99.7	99.7		1.0	49.8	0.0	0.0	50.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.01
2	91.0	56.7	57.3	48.8	51.2	0.0	92.7	97.7	39	1.0	48.8	0.0	0.0	48.4	1.7	1.1	0.0	0.0	0.0	0.0	0.0	1.01
3	94.3	57.7	57.7	48.0	52.0	0.0	87.1	96.1	22	1.1	48.0	0.0	0.0	46.9	3.4	1.7	0.0	0.0	0.0	0.0	0.0	1.01
4	97.5	58.7	58.7	46.4	53.1	0.5	79.2	90.7	14	1.2	45.4	1.0	0.0	42.5	7.3	3.3	0.0	0.0	0.5	0.0	0.0	1.01
5	100.2	59.0	58.9	46.1	53.2	0.7	73.9	88.5	9.3	1.2	45.0	1.1	0.0	40.4	8.4	4.2	0.2	0.0	0.6	0.0	0.1	0.98
6	101.6	59.5	59.5	44.7	54.8	0.5	72.9	86.7	10	1.2	43.8	0.9	0.0	40.6	10.2	4.0	0.0	0.0	0.5	0.0	0.0	1.03
7	103.0	59.3	59.6	44.5	54.9	0.6	68.2	82.7	7.1	1.3	43.4	1.1	0.0	37.6	10.9	6.3	0.0	0.0	0.6	0.0	0.0	0.98
8	105.5	57.9	60.1	43.7	55.5	0.8	66.8	83.4	7.9	1.3	42.5	1.2	0.0	37.9	11.6	5.6	0.4	0.0	0.6	0.0	0.2	1.02
9	107.8	60.5	60.6	43.9	53.8	2.3	55.4	77.9	4.8	1.3	41.0	2.9	0.0	32.0	13.0	7.1	1.7	0.0	1.4	0.0	0.8	0.93
10			60.8	42.2	56.8	0.9	62.4	80.1	7.1	1.3	40.8	1.4	0.0	35.6	12.5	7.1	0.3	0.1	0.7	0.1	0.2	1.01
11	111.9	62.0	61.4	41.1	57.5	1.4	51.1	71.3	4.3	1.5	39.2	1.9	0.0	29.0	17.3	10.5	0.8	0.0	0.9	0.0	0.4	0.95
12	113.2		62.0	40.5	57.2	2.3	47.3	71.5	4.2	1.5	37.7	2.8	0.0	27.9	17.6	10.3	1.2	0.5	1.2	0.3	0.7	0.95
13	123.2	63.2	62.5	39.6	57.9	2.5	37.8	60.6	2.9	1.6	36.7	2.9	0.0	23.2	20.6	12.3	1.8	0.3	1.3	0.3	0.9	0.90
14	123.4		63.5	37.5	59.5	3.0	34.2	60.8	3.1	1.7	33.8	3.6	0.1	22.1	20.8	14.4	1.8	0.5	1.6	0.4	0.9	0.94
15	129.8	65.7	64.7	34.5	62.0	3.5	26.0	48.6	2.4	1.9	30.8	3.7	0.1	18.6	23.4	16.8	2.7	0.5	1.7	0.4	1.4	0.97
16	132.3		65.0	33.7	62.7	3.6	25.3	52.1	2.6	1.9	29.9	3.8	0.0	18.5	23.5	17.5	2.8	0.6	1.6	0.6	1.4	1.00
17	138.0	65.8	66.0	32.6	61.9	5.5	19.5	43.3	2.2	2.0	27.1	5.3	0.4	14.6	24.6	17.9	4.0	1.2	2.4	1.0	2.1	0.97
18	139.4		66.4	30.7	64.6	4.7	17.8	41.9	2.2	2.0	26.2	4.4	0.1	15.2	25.0	20.0	3.9	0.9	1.9	0.8	2.0	1.04
19	144.8	66.5	66.8	30.8	63.1	6.2	15.2	37.9	2.0	2.2	25.3	5.4	0.3	10.2	25.8	21.0	5.1	1.6	2.2	1.2	2.7	0.92
20	154.3	67.7	67.9	28.0	65.1	7.0	9.0	30.3	1.7	2.4	22.1	5.7	0.2	9.0	23.8	24.9	5.8	2.2	2.1	1.7	3.2	0.95
21	149.3		68.4	25.9	67.5	6.6	8.4	26.3	1.7	2.4	20.9	4.9	0.1	8.1	25.0	26.6	7.0	1.2	2.0	1.0	3.6	1.03
22	159		68.4	26.7	65.8	7.5	7.8	25.7	1.7	2.4	20.7	5.8	0.2	7.3	24.8	26.0	7.3	1.7	2.3	1.4	3.8	0.99
23	163.8	68.2	69.3	24.9	66.2	8.9	4.6	23.2	1.6	2.6	18.2	6.6	0.2	4.2	23.1	29.1	8.4	2.5	2.4	2.1	4.4	0.93
24	165.5	68.2	69.7	24.1	66.4	9.5	3.9	20.9	1.5	2.6	17.1	6.9	0.3	4.7	22.9	28.5	8.9	3.0	2.4	2.4	4.7	1.00
25	167.8	68.3	69.6	24.2	66.5	9.3	3.8	22.4	1.6	2.6	17.3	6.8	0.3	5.1	23.1	28.3	8.3	3.2	2.3	2.4	4.5	1.00

ping assignments previously determined.[1]

Equation 19 gives the sequence length of CHCl carbons

$$\bar{n}_1 = \frac{S_{010} + S_{210} + S_{212} + S_{111} + S_{110} + S_{211}}{S_{010} + S_{210} + S_{212} + \frac{1}{2}(S_{110} + S_{211})} \qquad (19)$$

$[\bar{n}_1]$, not 1,2-dichloroethylene units. It follows directly from the equation for sequence length in terpolymers.[8] The sequence distribution analysis outlined above was developed on the basis of peak assignments for sequences expected to occur in CPVC's of low and intermediate chlorine levels (57–67% chlorine). The exact positions of peaks due to highly chlorinated sequences centered on {1} or {0}, such as {*X*212*X*} or {21012}, are not known and may not be resolved from resonances due to lightly chlorinated sequences. Some peaks that occur in the 60–70 ppm region contain contributions due to sequences such as {12110}, a fact not taken into account here. Hence, this analysis is not expected to be as accurate for CPVC's of very high chlorine content as it is for CPVC's of low and intermediate chlorine content. The accuracy of the method may also be reduced somewhat for very heterogeneous polymers where some portions of the material are very highly chlorinated.

Analysis of Solution-Chlorinated Polymers. The ^{13}C NMR analysis developed here was used to characterize a number of CPVC's prepared by photochlorination in solution. Solution-chlorinated polymers have been characterized previously at low field,[9] but not is great detail. This low-field study was recently updated at 50.3 MHz.[10] The CPVC's studied here contain from 57% to 69% chlorine by chemical analysis and serve as a good test of the sensitivity of the NMR method to changes in composition. Table II gives the results of our analyses. The weight percent chlorine determined by ^{13}C NMR is in good agreement, for the most part, with that determined by chemical analysis. The concentration of CH_2 carbons decreases monotonically while the concentrations of CHCl and CCl_2 carbons increase with increasing chlorine content (Figure 2). No evidence is seen for an overall decrease in the concentration of CHCl groups due to formation of CCl_2 groups from CHCl groups, up to 69% chlorine. At this chlorine level the net result is that 65% of the chlorinated CH_2 groups have been converted to CHCl and 35% to CCl_2 groups.

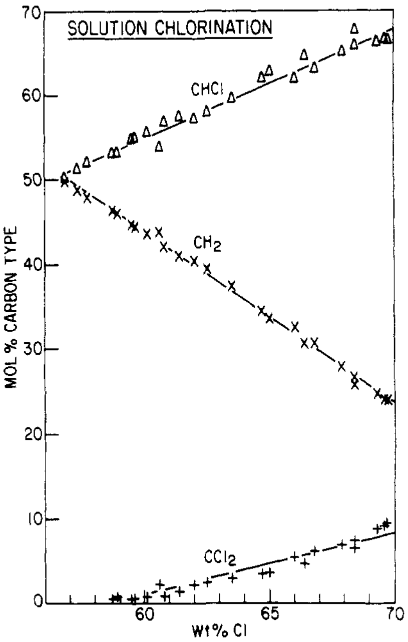

Figure 2. Mole percent carbon type vs. weight percent Cl for solution chlorination.

The amount of residual PVC centering tetrads, as given by the analysis, is reduced to only a few percent at about 69% chlorine. In fact, it is probably reduced very close to zero at somewhat lower chlorine contents, but intensity from other, non-PVC, sequences interferes slightly with the analysis. The amount of residual PVC in diads or greater is reduced more slowly, and a substantial amount is still remaining after chlorination to 69% chlorine. This remaining "PVC" in diads must consist in large part of isolated pairs and single units of vinyl chloride. This is supported by the behavior of the number-average sequence

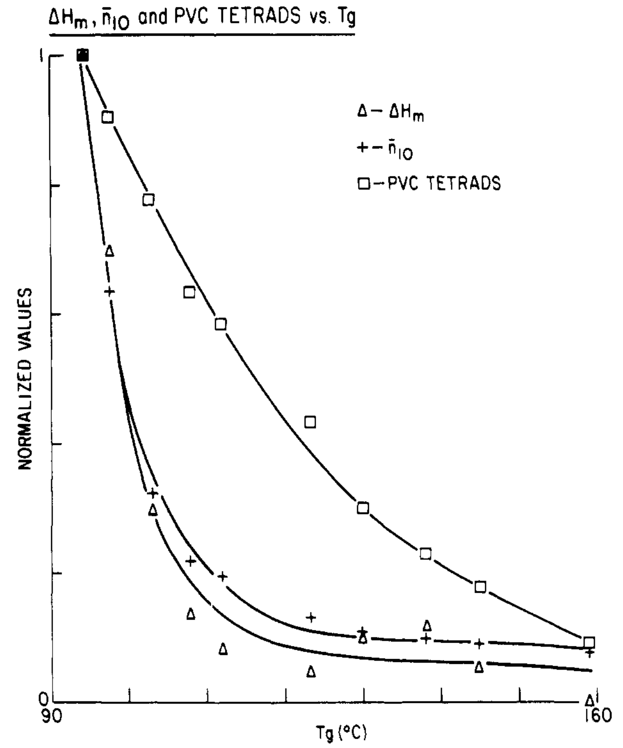

Figure 3. Heat of melting (ΔH_m), vinyl chloride sequence length ($\bar{n}_{10}$), and residual PVC centering tetrads vs. T_g for solution chlorination. Full scale for ΔH_m is 4.68 kJ/kg, for $\bar{n}_{10}$ is 22, and for residual PVC is 87.1%.

length of vinyl chloride units, $\bar{n}_{10}$, with chlorine content. The value of $\bar{n}_{10}$ decreases rapidly at first, as expected for random chlorination. At about 67% chlorine, the value of $\bar{n}_{10}$ becomes less than 2, indicating a high percentage of isolated vinyl chloride units.

The results obtained from this CPVC analysis can be correlated with thermal properties measured by differential scanning calorimetry (DSC). The variation in the second heat of melting ΔH_m of a number of prefused solution CPVC's as a function of glass transition temperature (T_g) is shown in Figure 3. Also shown is the variation of $\bar{n}_{10}$ as a function of T_g. The very similar behavior of the two curves shows that the residual crystallinity, as measured by the second heat of melting, correlates with the sequence length of the residual PVC. The quantity $\bar{n}_{10}$ should correlate with the average sequence length of syndiotactic placements, a critical quantity for formation of PVC crystallites (see following paper). Also shown is the behavior of the residual vinyl chloride units centering tetrads. This quantity, which falls off more gradually than either ΔH_m or $\bar{n}_{10}$, is not expected to follow the syndiotactic sequence length. We conclude from the above that the residual crystallinity in the solution CPVC's is indeed due to the residual PVC, and not from some newly formed, crystallizable sequence.

The sequence length of CHCl carbons, $\bar{n}_1$, varies from its initial value of 1.0 to 2.6 at about 70% chlorine. The small range of $\bar{n}_1$ suggests that it will not be as useful a parameter as $\bar{n}_{10}$ for characterizing CPVC structure. The narrow range of $\bar{n}_1$ is due to the simultaneous creation and destruction of CHCl carbons. Also, a growing sequence of CHCl's can be destroyed by additional chlorination within the sequence, or it can be terminated by encountering a preexistent CCl_2 carbon, such as in a {10201} sequence.

The behavior of various 1- and 2-centered three-carbon sequences with chlorine content is shown in Figures 4 and 5. While the change in concentration of some sequences appears to be linear, others change in nonlinear fashion because they are being created and destroyed in consecutive reactions. The amount of {110} (Figure 4) actually decreases at high chlorine content due to its further chlorination to other sequences. It is also interesting that the {121} and {120} sequences are produced at increasing rates, while the increase of {020} is approximately linear. The concentration of {121} surpasses that of {020} at about 65% chlorine for the solution-chlorinated polymers. Similar behavior was seen in a very recent study of solution-chlorinated polymers prepared at other temperatures.[10] We are not able to explain why the more highly chlorinated {121} is always more prevalent than {120}. It may be that the various configurational isomers of {111} possess one or more conformations readily susceptible to chlorination at the central carbon atom.

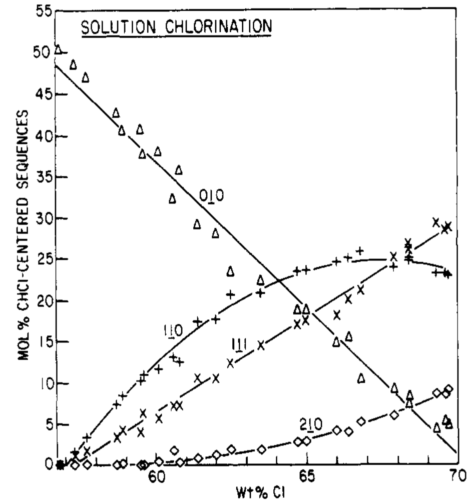

Figure 4. Mole percent CHCl-centered sequences vs. weight percent Cl for solution chlorination.

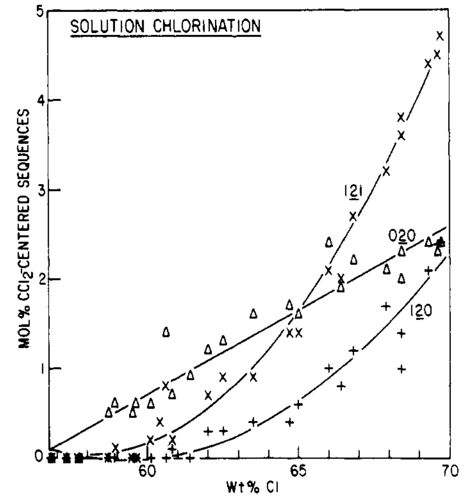

Figure 5. Mole percent CCl_2-centered sequences vs. weight percent Cl for solution photochlorination.

A question in past CPVC structural studies has been the relative rates of chlorination of CH_2 and CHCl groups in PVC. We have already shown[1] that both CH_2 and CHCl carbons are substituted by chlorine in the very early stages of the chlorination. Measurement of the ratio of the concentration of {111} to that of {020}, at low chlorine contents, should provide an excellent estimate of the initial relative reactivity of chlorine radicals toward CH_2 and CHCl carbons in PVC. The ratio {111}/{020} is found to be initially 9.8 for solution chlorination under our conditions. This is consistent with previous work on chlorination

Table III
Tacticity of Residual PVC in Solution-Chlorinated and Other CPVC's[a]

		tactic triad, mol %				
sample[b]	residual PVC (tetrad)	mm(CHCl)	mr(CHCl)	rr(CHCl)	rr(CH_2)	rrr(CH_2), mol %
1	99.7	23.1	47.5	29.4	28.1	15.8
2	92.7	20.4	48.7	30.8	28.9	16.6
3	87.1	22.2	48.7	29.1	27.3	15.2
4	79.2	20.6	48.4	31.0	29.8	18.0
5	73.9	23.5	46.7	29.8	27.9	17.9
6	72.9	20.5	48.7	30.8	29.3	18.6
7	68.2	22.2	47.7	30.1	24.2	18.4
8	66.8	19.8	46.6	33.6	30.8	21.1
9	55.4	21.8	47.4	30.8	25.5	16.2
10	62.4	20.5	46.4	33.1	28.5	18.5
11	51.1	20.3	45.7	34.0	28.7	20.2
12	47.3	20.4	46.5	33.1	27.1	19.5
13	37.8	21.8	44.6	33.6	24.0	17.7
14	34.2	25.9	43.5	30.6	26.5	19.2
15	26.0	22.2	41.5	36.3	25.6	19.3
16	25.3	24.4	44.7	30.9	23.4	19.5
17	19.5	20.0	39.8	40.2	21.6	18.0
18	17.8	24.7	40.3	35.0	21.3	18.4
19	15.2	23.1	33.2	43.6	24.3	21.1
L Cl_2 1	22.5	22.0 (25.1)	43.9 (49.4)	34.1 (25.4)[d]	(22.7)	(16.6)
L Cl_2 2	18.9	22.4 (23.4)	39.8 (44.5)	37.8 (32.1)	35.1 (36.2)	29.8 (28.7)
H_2O 1	26.2	20.7 (20.8)	35.8 (36.7)	43.6 (42.5)	40.1 (42.4)	33.3 (33.7)
H_2O 2	27.5	21.5 (24.0)	36.1 (38.0)	42.4 (38.0)	40.8 (39.0)	32.8 (29.5)
fluid bed	28.5	22.1	34.1	43.8	43.4	33.5
HCPVC[c]		18	17	65	62	56

[a] Values in parentheses from resolution-enhanced spectra. [b] See Table II and footnotes, Table IV. [c] Very highly chlorinated CPVC (see text). Reference 21. [d] Highly inaccurate because of the low level of residual PVC and the homogeneity of the process.

of secondary alkanes.[11] It is also consistent with the results of Keller et al.[10] for other solution-chlorinated polymers. By contrast, the ratio for a series of water-slurry chlorinated resins was found to be 5.3.[12] Thus, in solution, where all carbons should be equally available for substitution, CH_2 carbons are initially chlorinated about 10 times faster than CHCl carbons. In the water-slurry system, where chlorine (or chlorine radicals) must diffuse through solid PVC particles, the selectivity is reduced so that CH_2 carbons are chlorinated only 5 times faster than CHCl carbons. As a result, at the same degree of chlorination, a water-slurry CPVC would be expected to contain more CCl_2 carbons than a solution CPVC. In addition, many of these CCl_2 carbons might occur near the surface of the particles.[13]

Stereochemical Analysis. Table III gives the tacticity of the residual PVC in a number of solution and other CPVC's. The CHCl carbon region of the residual PVC (55–57.5 ppm) was used to obtain the concentrations of isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads. The triad concentrations were obtained directly from the corresponding peak areas[14] without any correction for the known interfering resonances. The concentrations of the syndiotactic triad were also estimated from the tetrad peaks rrr and mrr in the CH_2 carbon region[14] using the necessary relationship[15]

$$(\mathrm{rr}) = (\mathrm{rrr}) + (\mathrm{mrr})/2 \qquad (20)$$

The concentration of the promiment rrr tetrad is also listed in Table III.

The concentrations of syndiotactic triads and tetrads in sample 1, the starting PVC, are nearly the same as those previously reported.[14] With increasing chlorine content, there is very little change in the amount of syndiotactic triads, although there is considerable scatter in the data. At about 30% residual PVC, the apparent concentration of syndiotactic triads, as measured in the CHCl region, increases. However, this change is not reflected in the mole percent rr from the CH_2 region, where the apparent syndiotacticity decreases with about 30% PVC remaining. The mole percent rrr tetrad (15.8% in PVC) appears to increase quickly to 18–20% at 80% residual PVC and remains in that range as the residual PVC approaches 15%.

The discordant results among the various tacticity analyses for the solution CPVC's are largely due to the presence of interfering resonances. In the CHCl region, interference due to CH_2 carbons next to CCl_2 carbons in {01020} sequences, which appear at about 56.3 ppm,[5] is the major factor. This interference increases the apparent concentration of syndiotactic triads. Since it occurs between the rr and mr CHCl peaks, it also contributes somewhat to the mr peak. Hence, it is impossible to apply a correction procedure by subtracting an area equal to that of the interfering peak from the peak due to rr triads. When we attempted such a correlation by subtracting twice the area of the CCl_2 peak at 89 ppm,[5] we did obtain reasonable values at low chlorine contents where the correction is small. However, at higher chlorine contents (62.5% and greater), the values for mole percent rr were very erratic and much lower than expected. It is also apparent from spectra of very high chlorine content CPVC (>67%) that there is a small interference to the mm triad peak.

The interference in the PVC CH_2 carbon region appears to be less than in the CHCl region for a given chlorine content. It is for this reason that we use the CH_2 region to represent the amount of residual PVC. Even so, some interference does occur toward the high-field (45 ppm) end of this region. Thus, at the higher chlorine contents the amount of residual PVC appears to be overestimated. This partially explains the decrease in the syndiotactic triads at the higher chlorine contents. There appears to be no direct interference to the rrr tetrad peak at 47.7 ppm. The variation in the concentration of this tetrad is probably due to its small area relative to the total area. Another possible complication in the tacticity analyses is that chlorination adjacent to a PVC triad may cause a small chemical shift change for the central carbon, moving the

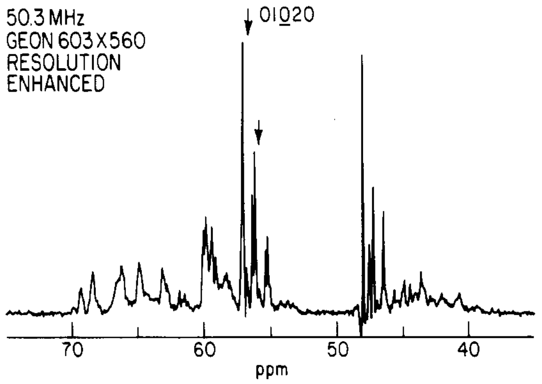

Figure 6. Resolution-enhanced, 50.3-MHz ^{13}C spectrum of Geon 603X560. The arrow at about 57 ppm shows the interfering peak due to {01$\underline{0}$20} sequences. The arrow at about 56 ppm shows an unidentified interfering peak.

resonance of that carbon into that of some other sequence.

We conclude from the results in Table III that a reasonable estimate of PVC tacticity in solution CPVC's can be made at residual PVC contents of about 25% or greater. This corresponds to a weight percent chlorine of about 65%. For CPVC's prepared by heterogeneous processes, it may be possible to measure tacticity at lower PVC levels since the residual PVC occurs in longer sequences on the average and would give a better resolved spectrum in the PVC regions (see below). We also conclude that in solution there is no strong preference for chlorination of a particular tactic sequence, at least at residual PVC levels where tacticity can be accurately measured. At low levels of residual PVC, the stereochemical preference of chlorination may be influenced by the presence of highly chlorinated sequences. Close inspection of the CH$_2$ region as a function of the degree of chlorination does show that the mrr peak at 47.0 ppm disappears more quickly than the remaining PVC CH$_2$ peaks. Apparently the mrr tetrad is chlorinated at a somewhat faster rate than the others.

Although under normal data processing conditions the major interference in the CHCl region of PVC is not resolved, resolution enhancement provides total separation of the {01020} peak. Figure 6 shows this peak resolved from the residual PVC rr peak. The interfering peak is resolved more easily at 100 MHz (Figure 7B). It does appear that other, smaller peaks are interfering slightly with the peaks from the mr and mm triads.

The stereochemistry in some chlorinated sequences can also be followed at the early stages of the reaction. We previously found that solution chlorination yields relative amounts of {111}, {11′1}, and {11′1′} sequences that are approximately consistent with equal chlorination rates for m and r diads of PVC.[1]

100-MHz ^{13}C NMR Spectra of CPVC. The ^{13}C NMR analysis for CPVC structure developed here is limited to a large extent by the peak resolution available in the 50.3-MHz spectrum. A more detailed analysis, including all or most five-carbon sequences, and stereochemical information, requires a substantial increase in spectral resolution. The use of higher magnetic fields might be expected to greatly increase the amount of structural information available in the ^{13}C spectrum. Unfortunately, this is not the case. We have obtained 100-MHz ^{13}C NMR spectra of sample 17 and Geon 603X560 CPVC under conditions comparable to those used to obtain the spectrum shown in Figure 1. Very little, if any, improvement in spectral resolution is seen at the higher field. Resolution enhancement by computer improves the situation somewhat in the residual PVC regions, and in the CH$_2$ region (40–46 ppm). No improvement is seen in the region from 58 to 70 ppm, and in the CCl$_2$ carbon region (not shown). Figure 7, A and B, shows the 40–70 ppm regions of the resolution-enhanced 100-MHz spectra of sample 17 and Geon 603X560 CPVC, respectively. It is clear from the spectra in Figure 7, A and B, that very high fields will not dramatically improve the overall CPVC structural analysis.

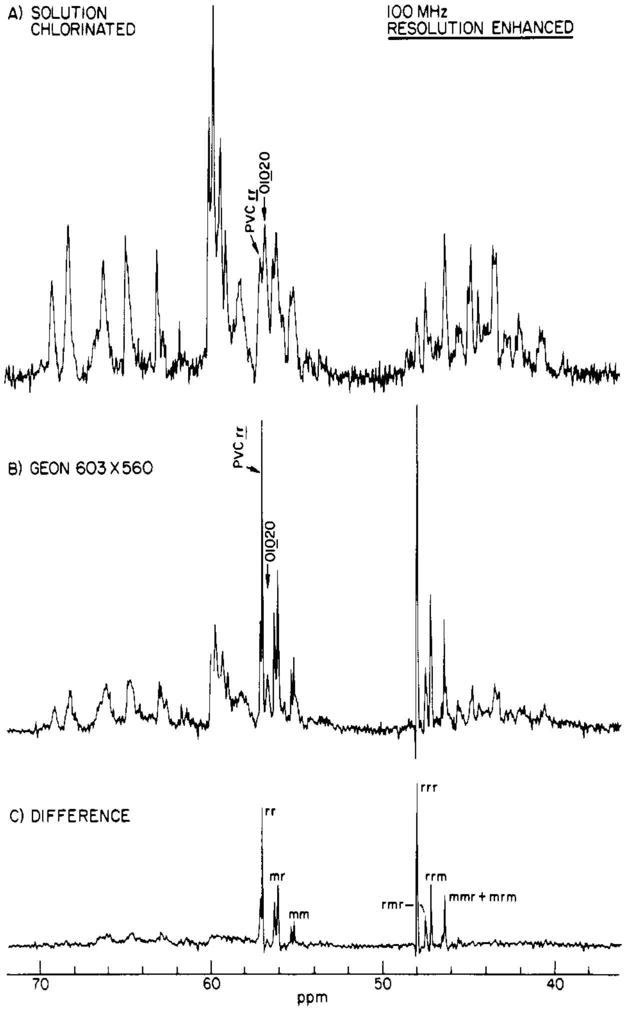

Figure 7. Resolution-enhanced, 100-MHz ^{13}C spectra of CPVC's: (A) sample 17 (Table II); (B) Geon 603X560 (process H$_2$O 1); (C) difference spectrum, B − A.

Differentiation of CPVC's Made by Various Processes. The sensitivity of the ^{13}C NMR spectrum of CPVC to the chlorine level and to the variety of three-carbon sequences suggests that the method can be used to differentiate CPVC's made by various processes. In this regard, progress has already been made at 22.6 MHz.[16] Table IV gives the results of our ^{13}C NMR analysis applied to CPVC's made by six different processes.[17-20] Ideally, it would be desirable to follow each process as a function of degree of chlorination. Here we only compare the processes at one chlorine level—about 66%. While all of the spectra are grossly similar, many detailed differences can be noted. Figure 8 shows a comparison of the CCl$_2$ regions of the ^{13}C spectra for the various processes, along with the total CCl$_2$ contents. Clearly both the total CCl$_2$ content and the distribution of CCl$_2$ types are sensitive to the chlorination process. In the heterogeneous processes (last three) more CCl$_2$ groups are formed than for the homogeneous processes at the same percent Cl, and the distribution of types is weighted more toward very highly chlorinated sequences.

It has been known for some time that the amount and tacticity of the residual PVC in CPVC are strongly influ-

Table IV
Microstructural Results for CPVC's Prepared by Various Processes

	wt % Cl		mol %			% residual PVC				mol %											
process	chem	NMR	CH_2	CHCl	CCl_2	tetrad	diad	$\bar{n}_{10}$	$\bar{n}_1$	101	201	202	010	110	111	210	211	020	120	121	*R*
solution[a]	65.8	66.0	32.6	61.9	5.5	19.5	43.3	2.2	2.0	27.1	5.3	0.4	14.6	24.6	17.9	4.0	1.2	2.4	1.0	2.1	0.97
L Cl_2 1[b]	65.3	65.2	33.3	63.0	3.7	22.5	42.6	2.1	1.9	30.6	2.6	0.1	17.9	21.7	18.8	3.9	0.7	1.1	0.5	2.1	0.96
L Cl_2 2[c]	65.5	67.0	29.7	64.0	5.6	18.9	40.7	2.2	2.0	25.6	4.0	0.2	15.4	21.5	21.3	5.7	1.3	1.6	1.0	3.0	1.05
H_2O 1[d]		66.5	32.4	60.9	6.7	26.2	45.8	2.6	1.9	26.7	5.5	0.4	15.6	19.5	19.0	5.4	2.0	2.2	1.5	2.9	0.95
H_2O 2[e]		66.6	32.9	59.7	7.4	27.5	43.9	2.6	1.8	26.1	6.6	0.4	17.6	17.1	17.9	5.2	2.6	2.5	2.1	2.9	0.98
fluid bed[f]	66.5	66.5	36.8	52.2	11.1	28.5	49.8	2.6	1.7	26.9	9.5	0.8	14.5	14.9	13.0	6.6	5.3	3.2	3.8	4.0	0.80
HCPVC[g]		72.5	18.8	65.3	15.9																

[a] Sample 17, Table II. [b] Reference 17. [c] Reference 18. [d] Reference 19; Geon 603X560. [e] Reference 21. [f] Chlorine concentration ramped 2–100% over 360 min at 40 °C, UV initiation. [g] Reference 25. Very highly chlorinated CPVC (see text).

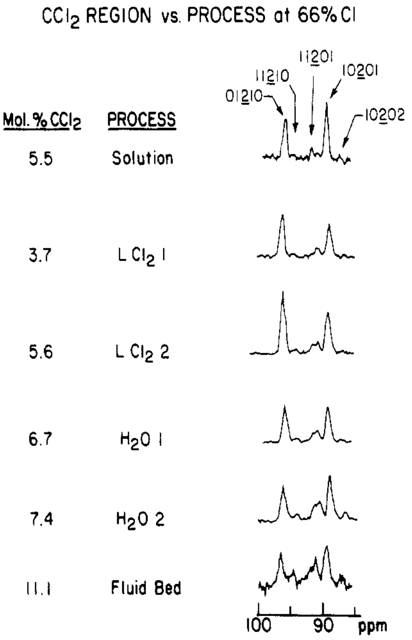

Figure 8. Effect of process on the amount and type of CCl_2 carbons in CPVC at about 66% Cl.

enced by the chlorination process.[16,21] Our results in Table IV confirm this. Although all the samples in Table IV contain about the same level of Cl (L Cl_2 1 is slightly lower), they have different amounts of residual PVC. This is also reflected in the sequence lengths. The heterogeneous processes, having more residual PVC, have larger values of $\bar{n}_{10}$ than the homogeneous processes. The heterogeneous processes also have smaller $\bar{n}_1$ values.

We[1] and others[22,23] had previously concluded, on the basis of ^{13}C NMR evidence, that the residual PVC in CPVC prepared by using a heterogeneous process was higher in syndiotactic content than the starting PVC. This has been attributed to a reduced rate of chlorination of the PVC crystallites, primarily composed of longer syndiotactic sequences, relative to the amorphous regions. Recently, doubt has been cast on this interpretation by Dorrestyn and co-workers,[24] who concluded, on the basis of their own and previous work, that peak overlap made it impossible to accurately measure the tacticity of the residual PVC in CPVC's. While such may be the case for spectra obtained at 25 MHz, we find that spectra obtained at 50 MHz and higher can be used for reasonably accurate quantitative measurement of tacticity within the limits defined above. This is particularly true when resolution enhancement is used.

Inspection of the 54–58 and 46–48 ppm regions of the 100-MHz spectrum (Figure 7B) of Geon 603X560 CPVC, produced in a heterogeneous process,[19] shows that the residual PVC is much higher in syndiotactic content than a typical PVC. This is demonstrated more dramatically by digital subtraction of the normalized spectrum of a solution-chlorinated polymer of the same chlorine content (sample 17, Figure 7A) from that of Geon 603X560. The solution-chlorinated polymer has approximately the same concentrations of most chlorinated sequences (Table IV). The difference spectrum shown in Figure 7C confirms that most of the CPVC spectrum has been canceled out, except for the residual PVC portions. The Geon 603X560 CPVC sample has a syndiotactic triad content of 40–44% based on our analyses at 50 MHz. The same is true for the other heterogeneous processes (Table III, "H_2O 2" and "fluid bed"). Moreover, the use of resolution enhancement at 50 MHz yields tacticity values that are in reasonable agreement with those obtained without resolution enhancement.

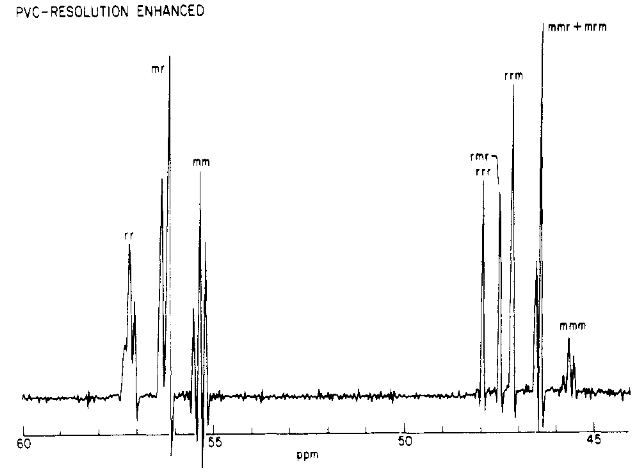

Figure 9. Resolution-enhanced, 50.3-MHz ^{13}C spectrum of PVC for comparison to Figure 7C. Tacticity assignments are from ref 14.

The peak resolution in the residual PVC regions of Figure 7 shows that the relative rates of chlorination of long stereochemical sequences can be followed. Figure 9 shows the 50.3-MHz spectrum of PVC resolution enhanced to the point where it can be compared to the 100-MHz spectrum of Figure 7C on a resolution basis. Comparison of the difference spectrum of Figure 7C to that of PVC reveals changes of relative peak intensities at the tetrad and pentad levels. Assuming all sequences are chlorinated at about equal rates in solution, the relative overall rate of chlorination in the heterogeneous process used for Geon 603X560 CPVC decreases in the order (rmr) = (mmr) + (mrm) > (rrm) ≫ (rrr). This is consistent with the triad results from the CHCl region ((mr) > (rr)).

Chlorination to a very high degree using a heterogeneous process can produce a polymer whose residual PVC is essentially all syndiotactic. Figure 10 shows the spectrum

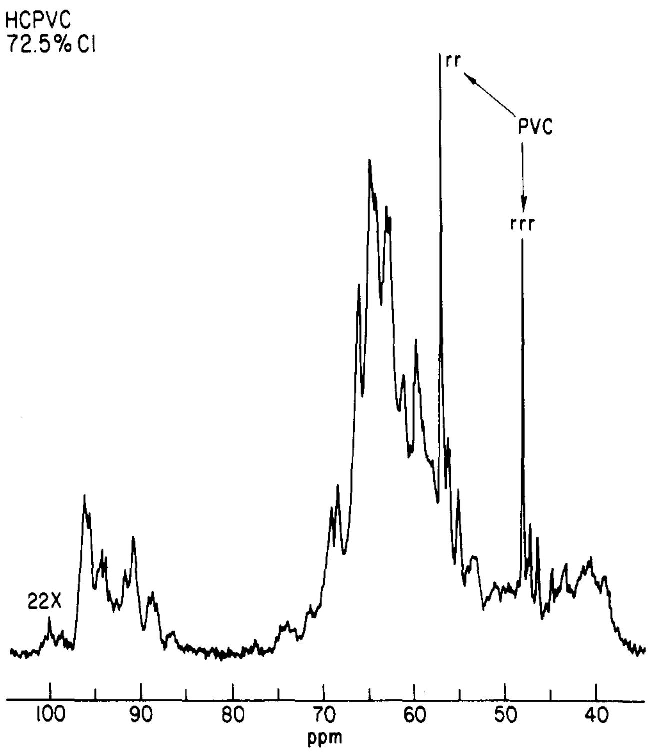

Figure 10. Very highly chlorinated CPVC prepared by a fluid bed process.

of a 73% chlorine CPVC produced by an experimental fluid-bed process.[25] Although our detailed analysis is not applicable at such a high chlorine level, two important observations can be noted from the spectrum. First, the syndiotactic PVC peaks are clearly visible and constitute at least 62-65% of the total area attributable to residual PVC (Table III). The results for this polymer confirm the reduced chlorination of the PVC crystallites relative to the amorphous regions in a heterogeneous process. In addition, a new CCl_2 peak appears at about 100 ppm which we assign to the presence of $\{22X\}$ sequences. Obviously such sequences will be difficult to generate in measurable concentration under all but the most forceful chlorination conditions. No evidence for adjacent CCl_2 carbons was seen in a recent study of the chlorination of poly(vinylidene chloride).[26]

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Thermal Property-Structure Relationships of Solution-Chlorinated Poly(vinyl chlorides)

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ABSTRACT: The specific heat capacity increment (Δc_p) at T_g for the chlorinated poly(vinyl chlorides) (CPVC's) studied decreased almost continuously with increasing chlorine substitution. The decrease exceeded that calculated from the "constant molar bead heat capacity rule". This is interpreted as evidence that chlorine substitution stiffens the CPVC chain. At first chlorination up to 59% chlorine caused an increase in Δc_p, which coincided with the large initial decrease in PVC crystallinity. The crystallinity dropped to less than one-tenth the value in PVC when the chlorine level reached 61%. The relative drop in crystallinity coincided with the decrease in PVC syndiotactic sequences containing 12 or more monomer units as calculated from random chlorination statistics. Detectable crystallinity persisted until the chlorine content was about 67.5%. The Δc_p for 100% amorphous PVC was found to be in good agreement with theory.

Introduction

The early characterization and uses of solution-chlorinated poly(vinyl chloride) have been described by Bier[1] and Trautvetter.[2] They concluded that chlorine substitution was random or homogeneous compared to water-slurry or solvent-swollen chlorination processes, which gave