

¹³C NMR Chemical Shifts and the Microstructure of Propylene-Vinyl Chloride Copolymers with Low Propylene Content

Alan E. Tonelli* and Frederic C. Schilling

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. Received January 12, 1984

ABSTRACT: ¹³C NMR chemical shifts expected for the carbon atoms in propylene-vinyl chloride (P-VC) copolymers of low propylene content are calculated as a function of copolymer stereosequence. Mark's conformational model of P-VC copolymers is coupled with the γ -gauche effect, which results in upfield chemical shifts for those carbon atoms in a gauche arrangement with carbon or chlorine substituents in the γ position, to calculate the ¹³C NMR chemical shifts of the carbon atoms in the vicinity of a propylene unit surrounded by vinyl chloride units. Agreement between the calculated chemical shifts and those we observe in the 50-MHz ¹³C NMR spectrum recorded for a P-VC copolymer containing 5 mol % propylene units is excellent. As an example, the chemical shifts calculated for the CH₃ carbons are sensitive to pentad but not to heptad or longer stereosequences. This is confirmed in the ¹³C NMR spectrum of our P-VC copolymer with low P content and contrasts with the predicted and observed heptad sensitivity of the CH₃ resonances in the ¹³C NMR spectra of atactic polypropylene. The agreement achieved between calculated and observed chemical shifts for our P-VC copolymer enables us to assign its ¹³C NMR spectrum, to evaluate the statistics of stereochemical placements during the copolymerization of P with VC monomers, and to compare these stereochemical statistics to those resulting from the homopolymerization of P and VC.

Introduction

Polymer microstructure is most fruitfully studied by ¹³C NMR spectroscopy.¹ This is a consequence of the extreme sensitivity of the observed ¹³C chemical shifts to the local elements of polymer structure, such as stereoregularity, sequence of comonomer units, inverted monomer addition, branching, etc. The full potential of structural information contained in the ¹³C chemical shifts observed for synthetic polymers has recently² been realized through our ability to predict the relative chemical shifts produced by different polymer microstructures.

The numbers and kinds of substituents attached to a carbon atom determine its relative chemical shift. ¹³C NMR studies³⁻⁶ of hydrocarbons and their derivatives have led to substituent rules that can be used to produce accurate estimates of the observed chemical shifts. Each carbon substituent α or β to the observed carbon produces a downfield shift (deshielding effect) of ca. +9 ppm relative to an unsubstituted carbon. In contrast γ -carbon substituents three bonds removed from the observed carbon result in an upfield shift (shielding effect) of ca. -2 to -3 ppm.

Shielding of the observed carbon by a γ substituent has been demonstrated² to require their gauche arrangement (see Figure 1). The microstructure of the polymer in the vicinity of the observed carbon atom determines the frequency of such γ -gauche arrangements. It is possible to evaluate the frequency of γ -gauche interactions and the resultant relative ¹³C chemical shifts from a knowledge of the polymer chain conformational characteristics and the magnitude of the upfield shift produced by each γ -gauche interaction.

¹³C NMR chemical shifts expected for the various carbon atoms in polypropylene⁷ and its oligomers,^{8,9} ethylene-propylene copolymers,¹⁰ poly(vinyl chloride)¹¹ and its oligomers,¹¹ ethylene-vinyl chloride copolymers,¹² polystyrene¹³ and its oligomers,¹⁴ and several fluoro polymers¹⁵ have been successfully predicted by the γ -gauche effect method. The effects of stereosequence, comonomer distribution and sequence, and defect structures have all been successfully accounted for, thereby providing detailed microstructural descriptions of these polymers.

Here we extend this approach to the copolymers of propylene with vinyl chloride (P-VC) containing small

amounts of propylene. We limit our consideration to P-VC copolymers possessing P units isolated by long runs of VC units, because the low reactivity ratios of P and VC and the chain-transfer characteristics of P limit^{16,17} the incorporation of P units into P-VC copolymers to ca. 15 mol %. Though incorporation of P units in P-VC is limited to ca 15 mol %, P-VC copolymers containing even fewer P units exhibit^{16,17} processing and thermal stability characteristics superior to those of pure poly(vinyl chloride) (PVC).

Calculation of ¹³C NMR Chemical Shifts

The rotational isomeric state (RIS) model of P-VC copolymers developed by Mark¹⁸ is used to calculate bond rotation probabilities¹⁹ necessary to the evaluation of the number of γ -gauche interactions involving a given carbon atom. On the basis of our previous studies of polypropylene (PP)⁷ and PVC¹¹ homopolymers, we adopt the following γ -gauche upfield chemical shifts, where $\gamma_{a,b}$ is the upfield shift at carbon a produced by γ -substituent b when in a gauche arrangement: $\gamma_{CH, CH_2 \text{ or } CH_3} = -5$ ppm, $\gamma_{CH, Cl} = -3$ or -7 ppm, $\gamma_{CH_2, CHCl} = -2.5$, $\gamma_{CH_2, CH(CH_3)} = -4$ ppm, and $\gamma_{CH_3, CH} = -5$ ppm.

¹³C NMR chemical shifts were calculated for methine carbons in the isolated P unit (see Figure 2) and in the VC units that neighbor or are next-nearest neighbors to the P unit. The ¹³C chemical shifts of methylene carbons adjacent to and separated from -CH(CH₃)- by one -CHCl- unit are considered. Methyl carbon chemical shifts were also calculated (see Figure 2 for details). ¹³C NMR chemical shifts calculated and observed for P-VC copolymer with low propylene content were compared to the chemical shifts calculated and observed for the parent homopolymers polypropylene (PP) and poly(vinyl chloride) (PVC).

Calculated chemical shifts only reflect differences in conformational probabilities produced by different configurations and are not absolute. When comparison is made to observed resonances, the calculated chemical shifts are placed as a group to achieve agreement.

Experimental Section

Materials. The sample of P-VC copolymer is a product of Airco, Inc. (resin no. 470) and was used as received. ¹³C NMR

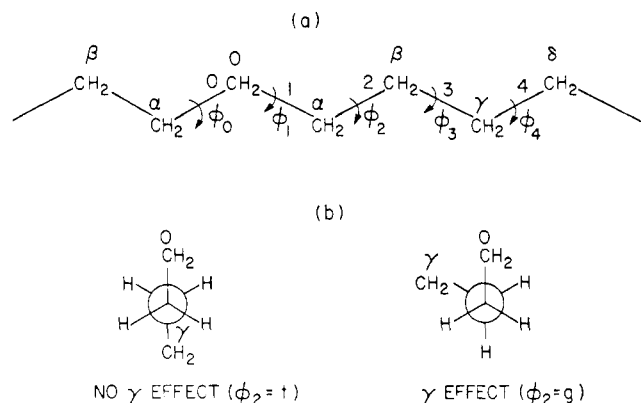


Figure 1. (a) Portion of a paraffinic hydrocarbon chain in the all-trans, planar zigzag conformation. (b) Newman projections along bond 2 in (a) illustrating the γ effect.

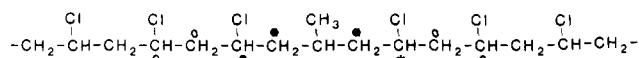


Figure 2. Schematic representation of P-VC copolymer showing an isolated P unit surrounded by sequences of VC units.

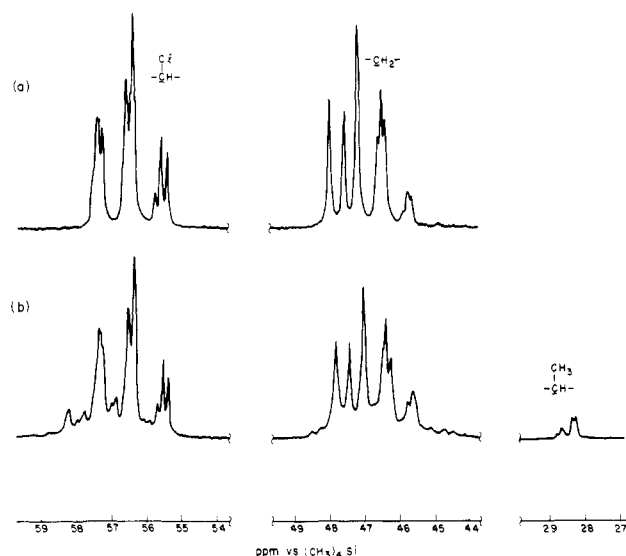


Figure 3. (a) 50-MHz ^{13}C NMR spectrum of PVC. (b) VC and P methine and methylene carbon portions of the 50-MHz ^{13}C NMR spectrum of P-VC copolymer.

measurements indicate a propylene content of 5.1 mol %. Detailed physical properties of this material have been reported by Deanin¹⁶ and Cantow et al.¹⁷ The PVC sample was purchased from Aldrich Chemical Co. PP sample A is Epolene X-3259-11B manufactured by Eastman Chemical Products Inc. and sample B is a heptane fraction of a research product of Hercules Co.²⁰ The 2-chloro-4-methylpentane and 2,4-dichloropentane were obtained from Wiley Organics Co.

^{13}C NMR Measurements. The 50.31-MHz spectra were recorded on a Varian XL-200 spectrometer. Broad-band proton-decoupled spectra were collected with a 90° sampling pulse, a spectral window of 8000 Hz, and 32K data points. Hexamethyldisiloxane (HMDS) was employed as an internal reference (2.0 ppm vs. Me_4Si). The polymer samples were observed as 18–24% (w/v) solutions in 4:1 mixtures of 1,2,4-trichlorobenzene-*p*-dioxane-*d*₈ at 110 $^\circ\text{C}$. Between 3000 and 10000 scans were accumulated for each sample, with 3–10-s delay between sampling pulses. The longest delay was selected in order to make quantitative measures of polymerization statistics.²¹

Results and Discussion

The methine and methylene carbon portions of the ^{13}C NMR spectra of our sample of P-VC and an atactic PVC both measured at 50 MHz are presented in Figure 3.

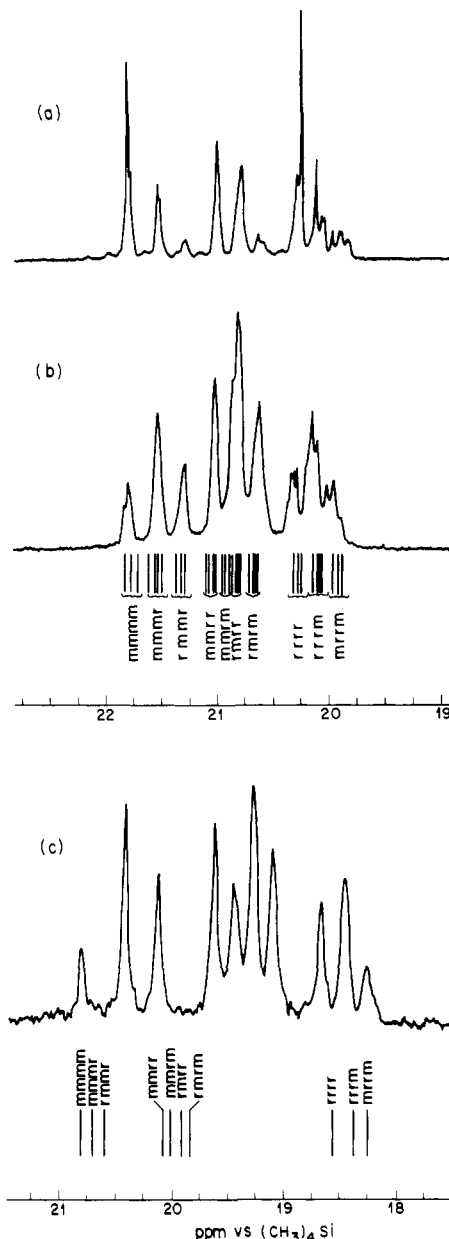


Figure 4. (a) Methyl carbon region of the 50-MHz ^{13}C NMR spectrum of PP sample A. (b) Methyl carbon region of the 50-MHz ^{13}C NMR spectrum of PP sample B with stick spectrum of ^{13}C chemical shifts calculated⁷ for the methyl carbons in atactic PP. (c) P methyl carbon region of the 50-MHz ^{13}C NMR spectrum of P-VC copolymer with stick spectrum of ^{13}C chemical shifts calculated for the methyl carbons in P-VC.

From the ratio of P to VC methine carbon intensities in Figure 3b we determine that 5.1 mol % of the repeat units in our P-VC are P. The combination of low P content with the observation¹⁶ that P does not homopolymerize under the conditions used to form the P-VC copolymer virtually ensures that all P units in our P-VC copolymer are isolated by long runs of VC units.

In Figure 4a,b we present the methyl carbon regions of the ^{13}C NMR spectra of two PP samples, and in Figure 4c we show the P methyl carbon region of our P-VC copolymer. The stick spectra of chemical shifts calculated for the methyl carbons in PP and P-VC are displayed below parts b and c, respectively. There is a good correspondence between the chemical shifts calculated and the resonances observed for the methyl carbons in P-VC. Comparison of the methyl resonances in P-VC and PP reveals a decreased sensitivity to stereosequence for P-VC.

Table I
¹³C NMR Chemical Shifts Calculated for the Methyl Carbons in Several Heptad Stereosequences of P-VC and PP

heptad	$\Delta\delta^a$	
	P-VC	PP
r(rmr)r	0	0
m(rmr)r	-0.01	-0.07
r(rmr)m	-0.01	-0.05
m(rmr)m	-0.03	-0.10
r(mrr)r	0	0
m(mrr)r	-0.04	-0.07
m(mrr)m	-0.07	-0.12

^a $\Delta\delta$ is the difference in chemical shift in ppm among the various heptads containing the same central pentad stereosequence.

The methyl carbon resonances in P-VC are sensitive to pentad stereosequences, while in PP, heptad sensitivity is observed.

In Table I the ¹³C NMR chemical shifts calculated for the methyl carbons in several heptad stereosequences of P-VC and PP are compared. As observed, the methyl carbon chemical shifts calculated for P-VC are sensitive to pentads, while PP methyl carbons show significant heptad sensitivity. The difference in stereosequence sensitivity between methyl carbons in P-VC and PP is directly attributable to the differences in their conformational behavior as embodied in their RIS models. Local bond conformations reflect pentad sensitivity in P-VC and heptad dependence in PP. In addition, the overall spreads in methyl carbon chemical shifts observed in P-VC and PP are 2.7 and 2.0 ppm, respectively, with the methyl carbons in P-VC resonating upfield from those in PP. These are reproduced by the calculated chemical shifts which employ the same γ effect ($\gamma_{\text{CH}_3\text{CH}_2} = -5$ ppm) and further indicate differences in the conformational behavior between P-VC¹⁸ copolymer and PP²² homopolymer.

The methine region of the ¹³C NMR spectrum of PP is shown in Figure 5a. Part b of Figure 5 presents the region of the P-VC ¹³C NMR spectrum belonging to methine carbons in P units. Chemical shifts calculated for these P methine carbons are given in parts c and d of the same figure and correspond to $\gamma_{\text{CH}(\text{CH}_3)\text{Cl}} = -7$ and -3 ppm, respectively. Our ¹³C NMR studies¹¹ of PVC and its oligomers indicate $\gamma_{\text{CH,Cl}} = -3$ ppm, while comparison of the ¹³C NMR chemical shifts observed²³ in alkanes and their monochlorinated derivatives lead to $\gamma_{\text{CH,Cl}} = -7$ ppm. Comparison of the observed $\text{CH}(\text{CH}_3)$ resonances with the calculated chemical shifts shows a close correspondence for $\gamma_{\text{CH}(\text{CH}_3)\text{Cl}} = -7$ ppm (see Figure 5b,c) while $\gamma_{\text{CH}(\text{CH}_3)\text{Cl}} = -3$ ppm leads to calculated chemical shifts disparate from the observed (see Figure 5b,d). This assignment is further supported by the observation that $P_m = P_r = 0.5$ from the methyl carbon resonances (cf. seq.), leading to a 1:3 ratio of mm:(mr + rr)-centered pentad intensities, which is consistent with the chemical shifts calculated for the P methine carbons using $\gamma_{\text{CH}(\text{CH}_3)\text{Cl}} = -7$ ppm (see Figure 5b,c).

The small differences between some observed resonances and the chemical shifts calculated for the methyl and P methine carbons in P-VC (see Figures 4 and 5) are due to minor imperfections in the RIS model for P-VC.¹⁸

Methine carbons C*HCl belonging to VC units adjacent to P units (see Figure 2) resonate downfield from or partially overlap the downfield methine resonances in long VC sequences (see Figure 3b). Chemical shifts calculated for C*HCl carbons show the opposite behavior and are predicted to resonate slightly upfield from the PVC-like methine carbons. This observation is confirmed by the

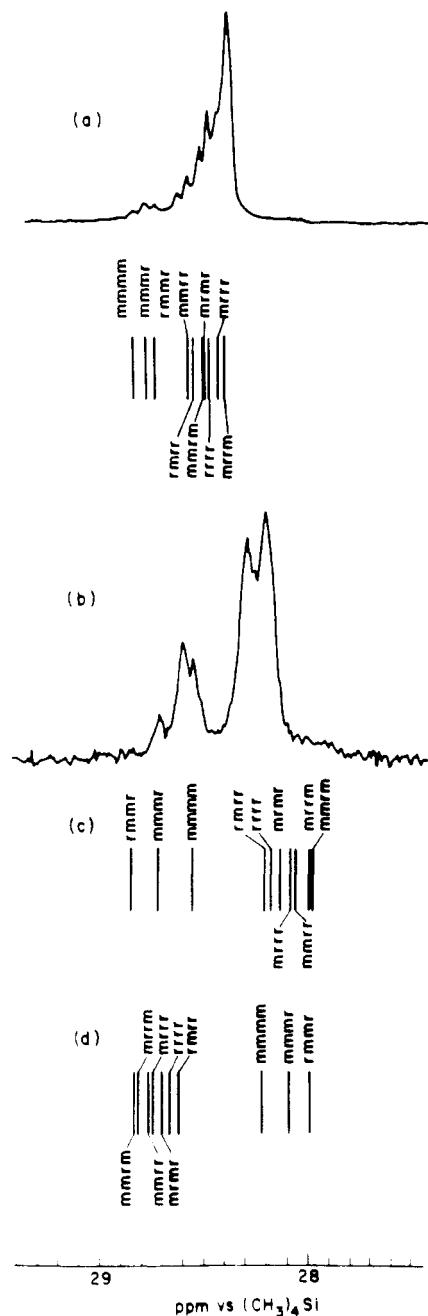


Figure 5. (a) Methine carbon region of the 50-MHz ¹³C NMR spectrum of PP sample B with stick spectrum of ¹³C chemical shifts calculated for PP shown below. (b) P methine carbon region of the 50-MHz ¹³C NMR spectrum of P-VC copolymer. (c, d) Stick spectra of ¹³C chemical shifts calculated for the P methine carbons in P-VC with $\gamma_{\text{CH}(\text{CH}_3)\text{Cl}} = -7$ and -3 ppm, respectively.

chemical shifts measured for the C₂ carbons in the 2,4-dichloro- and 2-chloro-4-methylpentanes, where C₂ in the dichloropentane resonates upfield from its position in 2-chloro-4-methylpentane. As was the case in P-VC, chemical shifts calculated for these model compounds show the reverse order. We are presently unable to explain this discrepancy.

A large number of resonances of minor intensity, which reside downfield from, upfield from, and overlap the major resonances, is evident in the methylene carbon region of the P-VC spectrum (see Figure 3). ¹³C NMR chemical shifts calculated for the methylene carbons C*H₂ and C°H₂ (see Figure 2), which are nearest and next-nearest neighbors of the methylated methine carbons, are predicted for C*H₂ to come upfield and overlap and for C°H₂ to come downfield and overlap with the methylene carbons further

removed from the methylated methine carbon. Thus, the resonances observed in the methylene carbon region are in excellent agreement with the ^{13}C chemical shifts calculated for the methylene carbons in our P-VC copolymer. In addition, all three types of methylene carbons, i.e., C^*H_2 , C°H_2 , and CH_2 further removed from $-\text{CH}(\text{CH}_3)-$, are expected to show the same dependence on P-VC stereosequence based on their calculated chemical shifts.

If we focus on the regions of the P-VC ^{13}C NMR spectrum corresponding to the methyl and methylated methine carbons, it is possible to determine the stereochemical statistics governing the addition of a P unit to a sequence of VC units and the addition of a VC unit to an isolated P unit. From the integrals of the ten CH_3 pentad peaks in Figure 4c we have determined the concentration of mm, mr, and rr triads centered about the isolated P unit. If the stereochemical placement is Bernoullian, then $P_m^2 = (\text{mm})$, $P_r^2 = (\text{rr})$, and $P_m + P_r = 1.0$. We find $P_m = P_r = 0.50$, indicating that the additions of P to VC units and VC to the isolated P unit are completely stereorandom.

This conclusion is supported by the intensities of the resonances in the methylated methine region of the ^{13}C NMR spectrum of P-VC in Figure 5b, which also leads to $P_m = P_r = 0.50$ for the addition of P and the next VC units. By contrast, long runs of VC units, though also described²⁴ by Bernoullian statistics, favor the addition of racemic units with $P_r = 1 - P_m = 0.56$.

Clearly, stereochemical statistics for the copolymerization of propylene and vinyl chloride are Bernoullian as is observed for PVC homopolymerization.¹¹ The homopolymerization of propylene, on the other hand, is not normally a Bernoullian process.²⁵ Thus the addition of P and VC to VC is stereochemically Bernoullian, while the addition of P to P is not.

The agreement between the calculated chemical shifts and the resonances observed in the ^{13}C NMR spectrum of P-VC implies that Mark's¹⁸ RIS model for P-VC adequately describes their conformational characteristics. Without this conformational description it would have been difficult to assign the observed resonances to the various P-VC microstructures and to draw conclusions about the stereochemical statistics governing the copolymerization of P and VC monomer units.

Acknowledgment. We are grateful to W. H. Starnes, Jr., for providing the sample of P-VC copolymer and to D. S. Pearson for making available to us the atactic PP (sample B).

Registry No. PP (homopolymer), 9003-07-0; PVC (homopolymer), 9002-86-2; (P-VC) (copolymer), 25119-90-8.

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- (24) Because the methylene and methine resonances neighboring a P unit in P-VC overlap with corresponding resonances in the long VC runs, we are unable to directly measure the P_m of these long VC runs. Instead we assume the long runs of VC units in our P-VC copolymer have the same $P_m = 0.44$ as the atactic PVC homopolymer whose ^{13}C NMR spectrum we presented for comparison (see Figure 3a). From the area measurement of the methyl pentad resonances we find the stereochemistry of the vinyl chloride dyad which follows the propylene unit is not Bernoullian and, therefore, does not provide a measure of the P_m of long VC runs.
- (25) Atactic PP is normally⁷ characterized by the ^{13}C NMR spectrum shown in Figure 4a for PP sample A. It is not a Bernoullian polymer but instead has runs or blocks of m dyads or r dyads present in much greater than random or Bernoullian amounts. Atactic PP sample B is atypically Bernoullian.