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^{13}C NMR Characterization of Vinyl Chloride–Vinylidene Chloride Copolymers

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ABSTRACT: Carbon-13 NMR at 50.3 MHz has been used to reexamine a series of vinyl chloride–vinylidene chloride copolymers previously studied at 22.6 MHz. The increased spectral resolution and signal-to-noise ratio and the use of resolution enhancement, partially relaxed spectra, and APT spectra allowed additional copolymer sequence and configurational assignments to be made. Vinyl chloride configuration across an intervening vinylidene unit was observed in a high vinylidene chloride copolymer. Full triad sequence distributions were generated for these commerical copolymers and were compared to calculated distributions based on Bernoullian and first-order Markov statistics. The reasonably good agreement between the experimental and Bernoullian values is consistent with the method of preparation of the polymers. Spin–lattice relaxation times showed little influence of composition on polymer chain mobility for a particular carbon type.

Introduction

The characterization of the configuration isomerism and sequence distribution of vinyl polymers and copolymers by ^{13}C NMR has become commonplace.[1] The ^{13}C spectra of vinyl copolymers can be complicated by the combined effects of tacticity and distribution of comonomer sequences. Vinyl chloride–vinylidene chloride (VC–VDC) copolymers have been studied previously by ^{13}C NMR at 22.6 MHz.[2,3] Some comonomer triad assignments were made at low field even though peak overlap was severe in many cases.

VC–VDC copolymers, in addition to being interesting in their own right, are good model polymers for certain structures in chlorinated poly(vinyl chloride) (CPVC).[4,5] As part of a program to characterize the molecular structure of CPVC and other chlorinated polymers, we reexamine a series of VC–VDC copolymers at 50.3 MHz. We demonstrate the use of some supplementary techniques such as resolution enhancement, partially relaxed spectra, and the attached proton test (APT) to aid in peak assignments. Spin–lattice relaxation times (T_1) are measured for most resolved peaks in the copolymer spectra.

Experimental Section

The three high vinyl chloride copolymers and the poly(vinyl chloride) were commerical materials (BFGoodrich Co.). The high vinylidene chloride copolymer was obtained from Polysciences Inc.

Carbon-13 NMR spectra were run at 50.3 MHz on a Bruker WH-200 wide-bore cryomagnet spectrometer. Samples were 20 wt % in 1,2,4-trichlorobenzene–benzene-d_6 (80:20) with hexamethyldisiloxane as internal chemical shift standard and were run in 20-mm-o.d. NMR tubes at 110 °C. Spectra for quantitative analysis of triad concentrations were acquired with inverse gated decoupling to remove the effects of nuclear Overhauser enhancement and with the following conditions: pulse delay, 25 s; spectral width, 13 158 Hz in 16 384 points; 90° radio-frequency pulse, 38.5 μs; number of accumulations, 1500–3200. Spin–lattice relaxation times were measured by using the standard inversion–recovery sequence. J-modulated spin-echo spectra for X nucleus (APT = attached proton test) were acquired as in ref 6 and were optimized for J_{CH} = 125 Hz.

Results

Figure 1 shows the ^{13}C spectra of four VC–VDC copolymers of different comonomer content in the CCl_2 carbon region. The CHCl and CH_2 region for the same four polymers and poly(vinyl chloride) (PVC) is shown in Figure 2. The 50.3-MHz spectra of Figures 1 and 2 have better peak resolution and signal-to-noise ratio than spectra acquired at 22.6 MHz.[2,3] Further improvement in resolution can be obtained by computer resolution enhancement. Before Fourier transformation the free induction decay (FID) can be multiplied by an increasing exponential or other suitable function to reduce resonance line width at the expence of signal-to-noise ratio. Using the software available with our Bruker WH-200 spectrometer, we perform a Lorentzian-to-Gaussian transformation with the optimum resolution enhancement function proposed by Ernst.[7] The FID is multiplied by a two-term exponential $\exp[-\pi(\mathrm{LB})t(1 - t/2(\mathrm{GB})(\mathrm{AQ}))]$, where AQ is the data acquisition time, LB is negative, and GB is positive. Since a Gaussian line has less extensive wings than a Lorentzian line, resolution of overlapping resonances is improved. Proper choice of LB and GB can lead to a reduction of line width at half-height. An example is shown in Figure 3.

The 53–58-ppm region of the VC–VDC copolymer spectra is complicated by the effects of tacticity, sequence distribution, and the presence of both CH and CH_2 carbons.[2] Techniques that can discriminate between CH and CH_2 carbons can be valuable for unraveling such regions in the ^{13}C spectra of vinyl polymers. One such method is the use of partially relaxed spectra[8] to take advantage of the spin relaxation time difference between CH and CH_2 carbons in similar motional environments. Figure 4 shows a partially relaxed spectrum of copolymer B (τ = 0.2 s). At this value of τ, the delay between the 180° and 90° pulses in the inversion–recovery experiment, the known CH_2 peaks from 45 to 48 ppm have relaxed to positive intensity, while the known CHCl peaks are still negative. The presence of CH_2 peaks in the 56–58-ppm region is clearly indicated. Unfortunately, depending on motional differences within the molecule studied or the τ value chosen, peak intensities in partially relaxed spectra can be severely distorted, possibly leading to incorrect assignments.

A more reliable and more generally applicable technique is the recently developed APT sequence.[6] In APT spectra a 180° phase shift is introduced between CH and CH_3 carbons on the one hand and CH_2 and nonprotonated carbons on the other. This technique can be handy for assigning the ^{13}C spectra of vinyl and related polymers, where CH–CH_2 carbon overlap can be severe. Figures 5 and 6 show APT spectra of polymers C and B, respectively. We believe that APT spectra are easier to interpret than partially relaxed spectra and provide more detailed information (compare Figure 4 to Figure 6B,C). The spin-echo nature of the APT experiment provides some built-in resolution enhancement, but this may also be a problem since artifacts can be introduced (see Figure 6B,C), particularly if additional resolution enhancement is employed. Processing under several degrees of resolution enhancement will usually clarify matters. Recently developed

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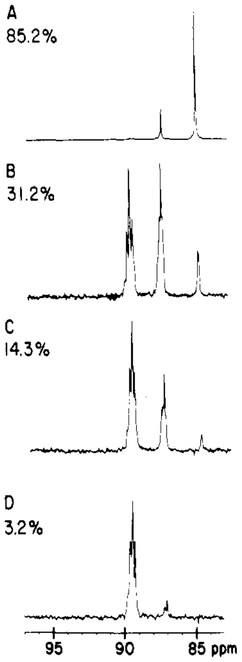


Figure 1. CCl_2 carbon region of the 50.3-MHz ^{13}C NMR spectra of four vinyl chloride–vinylidene chloride copolymers. Mole percent vinylidene chloride is indicated.

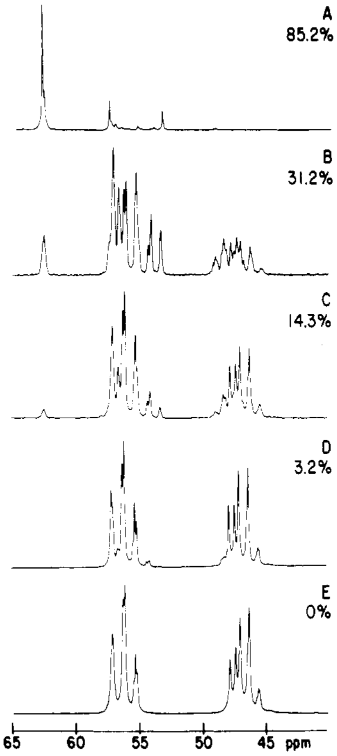


Figure 2. CHCl and CH_2 carbon region of the ^{13}C spectra of the same copolymers as in Figure 1 plus PVC. The spectra in Figure 1 are not plotted at the same vertical gain as here.

techniques for producing subspectra consisting of only one carbon type (e.g., CH_2) should prove very powerful for ^{13}C spectra of vinyl polymers.[9]

Discussion

(A) Resonance Assignments. Using the variation of peak intensities with composition and the assignment aids discussed above, we have assigned the spectra of the VC–VDC copolymers (Table I). Since slight differences in chemical shift can occur among the polymers for the resonances of a particular sequence, most chemical shifts listed in Table I are from the most complex spectrum, that of polymer B.

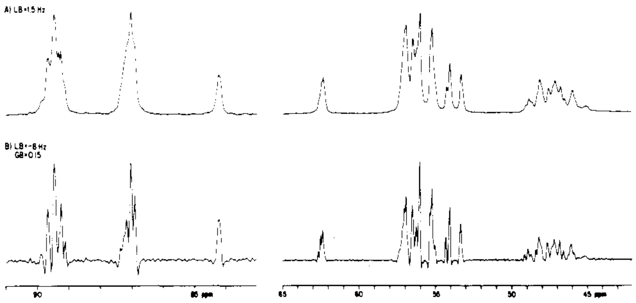


Figure 3. Comparison of the ^{13}C spectra of copolymer B under (A) normal sensitivity enhancement and (B) resolution enhancement. Enhancement parameters are indicated. Vertical gain is different in the two regions shown.

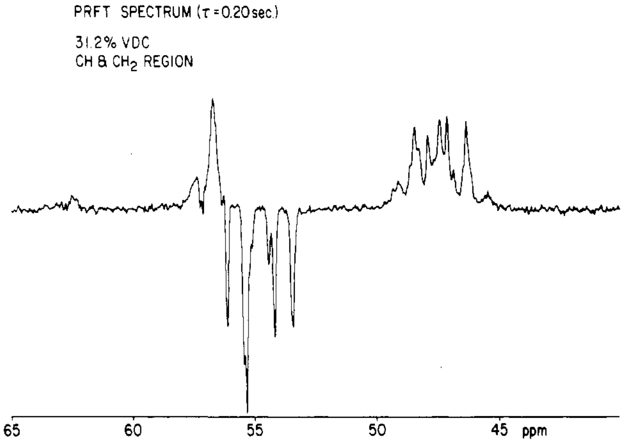


Figure 4. Partially relaxed ^{13}C NMR spectrum of copolymer B showing CH_2 carbon peaks in the vicinity of 57 ppm.

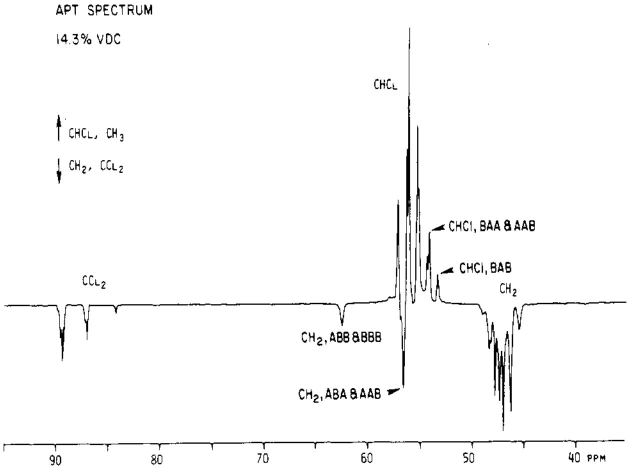


Figure 5. APT ^{13}C spectrum of copolymer C.

The assignments of the various configurational isomers of PVC (AAA) have been given previously and are not listed here.[10] In the CCl_2 region resolution enhancement reveals fine structure due to configurational isomerism and pentad sequences for the ABA and BBA triads. The CCl_2 carbon of BBB sequences is not sensitive to pentad sequences. The CH_2 carbons of BBB and ABB can be resolved as can the CH_2 of pentad sequences for BBB around 62 ppm.

The partially relaxed and APT spectra of the copolymers indicate a number of CH_2 resonances in the region 56–58 ppm. Chlorine substituent effects on ^{13}C chemical shifts[2] indicate that these CH_2 carbons can arise from ABA, BBA, and BAB sequences. Unfortunately, severe overlap occurs

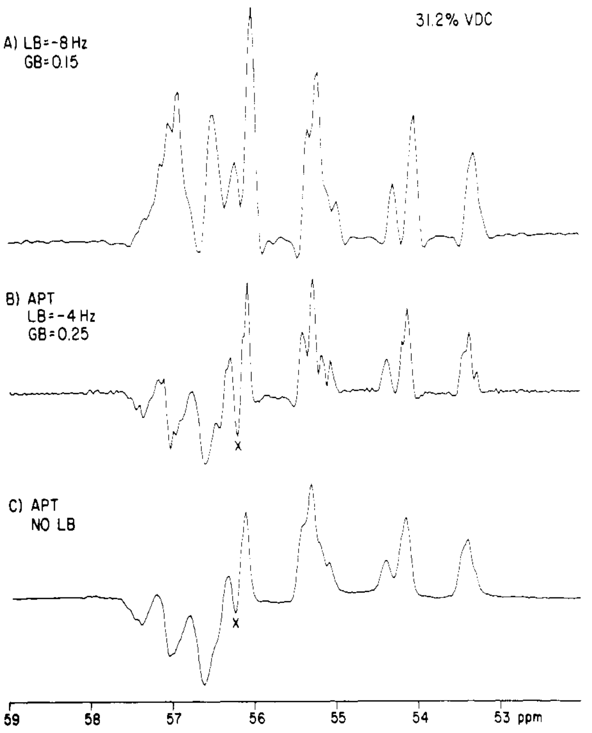


Figure 6. Comparison of the (A) normal resolution enhanced, (B) APT resolution enhanced, and (C) APT unenhanced 52-59-ppm region of the ^{13}C spectrum of copolymer B. The "X" in (B) marks an artifact of APT plus resolution enhancement.

Table I
^{13}C Chemical Shifts and Peak Assignments for Vinyl Chloride-Vinylidene Chloride Copolymers^a

sequence	carbon	δ_C, ppm
$\mathrm{BABA^mA}$	$\mathrm{CCl_2}$	89.91
$\mathrm{A^mABA^mA}$	$\mathrm{CCl_2}$	89.69
$\mathrm{A^rABA^mA}$	$\mathrm{CCl_2}$	89.48
BABAB^b	$\mathrm{CCl_2}$	89.35, 89.09
$\mathrm{A^rABA^rA}$	$\mathrm{CCl_2}$	89.26
$\mathrm{BABA^rA}$	$\mathrm{CCl_2}$	89.12
$\mathrm{BBBA^rA}$	$\mathrm{CCl_2}$	87.38
$\mathrm{ABBA^mA}$		87.18
$\mathrm{BBBA^mA}$		86.92
$\mathrm{ABBA^rA}$, BBBAB	$\mathrm{CCl_2}$	87.05
$\frac{\mathrm{A}}{\mathrm{B}}\mathrm{BBB}\frac{\mathrm{A}}{\mathrm{B}}$	$\mathrm{CCl_2}$	84.24
BBBB	$\mathrm{CH_2}$	62.9
ABBB	$\mathrm{CH_2}$	62.5
AABB	$\mathrm{CH_2}$	62.4
$\mathrm{BAB}\frac{\mathrm{A}}{\mathrm{B}}$	$\mathrm{CH_2}$	57.66
$\mathrm{BBA}\frac{\mathrm{A}}{\mathrm{B}}$	$\mathrm{CH_2}$	56.94
$\mathrm{ABA}\frac{\mathrm{A}}{\mathrm{B}}$	$\mathrm{CH_2}$	56.61
$\mathrm{AAB}\frac{\mathrm{A}}{\mathrm{B}}$	$\mathrm{CH_2}$	56.51
AAAAA^c	CHCl	57.1, 56.3, 55.4, 55.1, 57.0, 56.1, 55.3
$\mathrm{A^rAB}$, $\mathrm{BA^rA}$	CHCl	55.25
$\mathrm{A^mA^mAB}$, $\mathrm{BA^mA^mA}$	CHCl	54.31
$\mathrm{A^rA^mAB}$, $\mathrm{BA^mA^rA}$	CHCl	54.05
BAB	CHCl	53.48
BAAA	$\mathrm{CH_2}$	48.2-48.4
BAAB	$\mathrm{CH_2}$	48.7-49.3
AAAA^c	$\mathrm{CH_2}$	47.5, 47.1, 46.4, 45.6, 47.9

^{a} A = vinyl chloride; B = vinylidene chloride. ^{b} For polymer A. See text. ^{c} From ref 10.

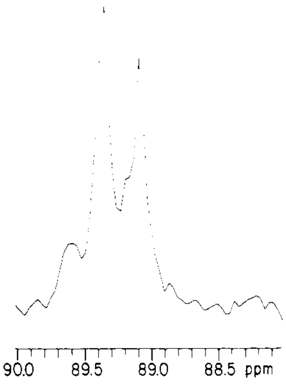
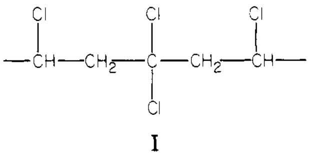


Figure 7. Blowup of the ABA triad region for copolymer A.

with the CHCl peak of AAA triads. From peak intensity variations with composition and APT spectra we have made the assignments listed in Table I. The BAB sequence was assigned from the spectrum of polymer A. Tacticity and pentad sequence sensitivity almost certainly make the situation in this region more complicated than implied by Table I.

The peaks at 54-55 ppm are assigned to CHCl carbons of some BAA + AAB sequences. The remaining sequences of AAB + BAA appear at about 55.3 ppm along with the isotactic configurational triad of PVC. The variation of the area of the 55.3-ppm peak with composition confirms this point, as does the ratio of the ABA $\mathrm{CCl_2}$ peak area (89-90 ppm) to that at 54-55 ppm. The APT spectrum of Figure 6B shows an additional peak in the vicinity of 55 ppm relative to PVC.

The configurational assignments given in Table I only involve sequences of adjacent VC units. It is of interest to know if ^{13}C NMR can discriminate configurational isomers across a monomer unit not containing a pseudoasymmetric center, such as vinylidene chloride (structures I and II).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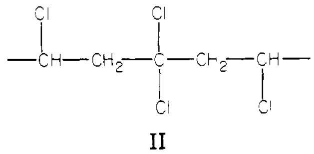
II

Previous discussion of this question centered around ethylene-propylene copolymers where, if propylene configuration across an ethylene unit can be distinguished, conclusions concerning the nature of stereoregular polymerization of propylene can be reached.[11,12] For ethylene-propylene copolymers such isomerism is predicted to have little effect on the ^{13}C chemical shifts, even for the central unit.[13] Figure 7 shows an expanded portion of the $\mathrm{CCl_2}$ region for copolymer A. Peaks in the vicinity of 89 ppm are due to ABA triads and for polymer A should arise overwhelmingly from BABAB pentads. Pentads of the type AABAB should be very small given the copolymer composition and the reactivity ratios of the monomers.[14] We assign the two peaks at about 89 ppm to structures I and II. The shift differences of about 0.3 ppm is larger than that predicted for an analogous situation in ethylene-propylene copolymers.[13] The two isomers appear to be present in approximately equal amounts, although overlap with small peaks (AABAB?) somewhat obscures the true intensities.

(B) Sequence Distribution and Statistical Analyses. The assignments in Table I can be used to quantitatively characterize the four copolymers studied here in terms of triad sequence of monomer units. The $\mathrm{CCl_2}$ carbons give well-resolved bands at about 89, 87, and 84 ppm for the B-centered sequences ABA, BBA + ABB, and BBB, respectively. The CHCl carbon of BAB is a well-

Table II
Compositions and Comonomer Triad Concentrations of Four Vinyl Chloride-Vinylidene Chloride Copolymers

	polymer			
	A	B	C	D
mol % VDC	85.2	31.2	14.3	3.2
triad concn, mol %				
ABA	2.4	15.2	9.6	3.1
BBA + ABB	18.8	13.3	4.0	0.1
BBB	63.9	2.7	0.7	0.0
AAB + BAA	3.6	24.0	14.4	5.0
BAB	9.1	7.9	2.5	0.2
AAA	2.1	37.0	68.8	91.6

resolved peak at 53.5 ppm, while the PVC CH_2 carbon region from 45 to 48 ppm is a measure of AAA. For AAB + BAA, overlap of both the CHCl and CH_2 carbon peaks with the CHCl region of AAA prevents an accurate quantitation. Part of the CHCl intensity (A^mAB) occurs at 54.0–54.3 ppm, with the remainder (A^rAB) at about 55.2 ppm. For our triad analysis we assume that a reasonable estimate of AAB + BAA is given by 2.2 times the intensity of the peaks at 54.0–54.3 ppm. The factor 2.2 comes from the known ratio of r to m dyads in a typical PVC.[10]

Since the concentrations of the various triads rely on the relative areas of CH_2, CHCl, and CCl_2 carbons, the possibility exists for response differences due to variable nuclear Overhauser enhancements (NOE) or partial saturation of resonances with long T_1's. An NOE measurement on sample B showed that under our conditions all peaks have the same NOE of 2.55 ± 0.2. However, since NOE's can vary with composition[15] and cannot be measured very accurately, for our analysis we use spectra with inverse gated decoupling to remove the effect of NOE. A 25-s pulse delay eliminates any partial saturation problems for the CCl_2 carbons (see section C).

Compositions and comonomer triad concentrations are given in Table II for the four copolymers. The experimental number-average sequence lengths of vinyl chloride and vinylidene chloride are listed in Table III.[1]

In a batch polymerization of vinyl chloride and vinylidene chloride, a heterogeneous mixture of copolymers of different compoisition is obtained.[14] The vinylidene chloride will tend to be highly blocked because of the reactivity ratios ($r_B = 3.2$, $r_A = 0.3$)[14] of the two comonomers in this situation. Commercial polymers are usually prepared to high conversion with continuous addition of vinylidene chloride to maintain constant comonomer compositions and give a homogeneous polymeric product.[14] As a result of the high conversion, the commerical polymers characterized here cannot be expected to conform to simple copolymerization models. Table III gives the sequence lengths predicted from application of Bernoullian and first-order Markov statistics. The predicted sequence lengths were obtained as previously described.[1,3,16] For low sequence lengths, the predictions of Bernoullian and first-order Markov statistics are little different from each other and are close to the experimental sequence lengths. The two models diverge somewhat at high sequence lengths, where Bernoullian statistics gives a better match to the experimental results than first-order Markov statistics. This is not unexpected in view of the method of polymerization, which was designed to produce a homogenous product.

(C) Spin–Lattice Relaxation Behavior. The ^{13}C T_1's are listed in Table IV for the major resonances or groups of resonances in the spectra of the copolymer and PVC. All the polymers were run at the same concentration and temperature, and hence at least semiquantitative com-

Table III
Experimental and Calculated Number-Average Sequence Lengths of Vinyl Chloride-Vinylidene Chloride Copolymers

		$\bar{n}_B$			$\bar{n}_A$		
polymer	mol % VDC	exptl	Bernoullian	1st-order Markov	exptl	Bernoullian	1st-order Markov
A	85.2	7.2	6.8	4.8	1.36	1.17	1.20
B	31.2	1.42	1.45	1.43	3.5	3.2	2.5
C	14.3	1.23	1.17	1.20	8.9	7.0	3.9
D	3.2	1.02	1.03	1.02	35	31	14

Table IV
^{13}C Spin-Lattice Relaxation Times of Some Vinyl Chloride-Vinylidene Chloride Copolymers

		T_1,[a] s				
carbon	sequence	A 85.2% VDC	B 31.6% VDC	C 14.3% VDC	D 3.2% VDC	PVC 0% VDC
CCl_2	ABA		4.9			
CCl_2	ABB + BBA		4.6			
CCl_2	BBB		5.4			
CHCl	A^rA^rA		0.32[b]	0.35[b]	0.44	0.37
CHCl	A^mA^rA		0.41	0.39	0.45	0.39
CHCl	A^mA^mA		0.45[c]	0.44[c]	0.46	0.40
CHCl	$A^mAB + BA^mA$		0.46	0.47	0.52	
CHCl	BAB	0.52	0.54	0.53		
CH_2	BBB, ABB	0.42	0.31	0.31		
CH_2	ABA, AAB		0.27[d]	0.27[d]		
CH_2	BAAB		0.26			
CH_2	BAAA		0.24	0.23	0.29	
CH_2	BAB	0.37				
CH_2	AAA		0.24 0.24 0.21 0.20	0.22 0.21 0.21 0.20 0.23	0.26 0.25 0.26 0.25 0.26	0.19 0.19 0.18 0.18 0.19

[a] Estimated accuracy ±10%, except as noted. [b] Contains a sizable contribution from the CH_2 carbon of ABA and AAB sequences. [c] Contains a sizable contribution from the CHCl carbon of A^rAB and BA^rA sequences. [d] Strongly overlapping with other sequences. Estimated accuracy ±20%.

parisons can be made among the polymers. Due to peak overlap in the spectra and the narrow range of T_1 values for a given carbon, we have not generated correlation times for segmental motion using an appropriate model. The relatively high NOE of 2.55 indicates that the correlation times for segmental motion are on the high-temperature side of the T_1 minimum, and hence increasing T_1 indicates increasing segmental mobility.

As expected the CCl_2 carbon T_1's are an order of magnitude longer than those of the CHCl or CH_2 carbons. Our results for PVC are in good agreement with those of Schilling.[17] However, we made no attempt to observe the small T_1 difference for carbons in the various stereochemical sequences in PVC or the copolymers. Comonomer composition only slightly affects the motional behavior of a given sequence. Differences are seen for the same carbon type in different sequences. For example, the CHCl and CH_2 carbons of BAB sequences have longer T_1's than the corresponding carbons of AAA or AAB sequences. On the whole there are no clear trends for these copolymers, and the T_1's are uninformative. The T_1 measurements serve mainly to establish the proper conditions for obtaining quantitatively useful spectra.

Registry No. Vinyl chloride/vinylidene chloride copolymer, 9011-06-7.

References and Notes

(1) J. C. Randall, "Polymer Sequence Determination: Carbon-13 NMR Method", Academic Press, New York, 1977.

(2) F. Keller and C. Mugge, *Faserforsch Textiltech.*, **27**, 347 (1976).

(3) C. J. Carman, *ACS Symp. Ser.*, **No. 142**, 81 (1980).

(4) R. A. Komoroski, R. G. Parker, and M. H. Lehr, *Macromolecules*, **15**, 844 (1982).

(5) F. Keller and B. Hosselbarth, *Faserforsch. Textiltech.*, **29**, 152 (1978).

(6) S. L. Patt and J. N. Shoolery, *J. Magn. Reson.*, **46**, 535 (1982).

(7) R. R. Ernst, *Adv. Magn. Reson.*, **2**, 1 (1966).

(8) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).

(9) D. M. Doddrell, D. T. Pegg, and M. R. Bendall, *J. Magn. Reson.*, **48**, 323 (1982).

(10) C. J. Carman, *Macromolecules*, **6**, 725 (1973).

(11) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, and J. D. Roberts, *Macromolecules*, **4**, 475 (1971).

(12) J. M. Sanders and R. A. Komoroski, *Macromolecules*, **10**, 1214 (1977).

(13) A. E. Tonelli, *Macromolecules*, **11**, 634 (1978).

(14) G. Talamini and E. G. Peggion, in "Kinetics and Mechanism of Polymerization," G. E. Ham, Ed., Marcel Dekker, New York, 1967, Vol. 1, Part I, Chapter 5, p 331.

(15) P. M. Henrichs, J. M. Hewitt, L. J. Schwartz, and D. B. Bailey, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 775 (1982).

(16) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1975 (1975).

(17) F. C. Schilling, *Macromolecules*, **11**, 1290 (1978).