Determination of Tetrad Concentration in Poly(vinyl chloride) Using Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Pulsed Fourier transform carbon-13 nmr spectra were obtained for poly(vinyl chloride) and interpreted in terms of tetrad sequences for the methylene carbons and pentad sequences for the methyne carbons. Five distinct resonances can be assigned to the six possible tetrads. The relative areas are in agreement with the Bernoullian statistics used to fit earlier 220-MHz proton nmr spectra reported by Heatley and Bovey. The tetrad assignments for the methylene carbon-13 chemical shifts differ from those previously proposed. Local chain conformation is suggested as an explanation for the observed relative methylene ^{13}C chemical shifts.

Extensive proton nuclear magnetic resonance investigations[1-18] have been used to determine the configuration and conformation of poly(vinyl chloride) (PVC) in solution. The analyses for tacticity have been difficult because of the complexity of the proton spectrum. The complexity is the result of proton spin coupling and the overlapping of the many proton chemical shifts. The least ambiguous proton nmr analysis of tetrad and pentad sequences in PVC was obtained from 220-MHz spectra.[17] Even so, it was necessary to carefully select proton coupling constants, chemical shifts, and line widths to calculate theoretical spectra containing overlapping resonances. The carbon-13 nuclear magnetic resonance (^{13}C nmr) spectra of PVC[19-22] have shown some advantage over proton spectra for determining triad concentrations. In *o*-dichlorobenzene[20,21] three distinct methyne carbon resonances were assigned to syndiotactic, heterotactic and isotactic triad configurations.[20] These continuous wave (CW) ^{13}C nmr spectra obtained in *o*-dichlorobenzene at 130° had sufficient resolution to allow peak area measurement of the triad sequences.[21] But, the resolution was not sufficient to allow an interpretation of the methylene spectral region. An interpretation of the methylene carbon resonances was proposed in a later report of CW ^{13}C nmr spectra of PVC.[22]

This present work reports the discrimination of stereochemical configurations in PVC that is obtained from Fourier transforms of pulsed ^{13}C nmr spectra obtained in *o*-dichlorobenzene at 100°. The present spectra have discrete methylene resonances that can be assigned to tetrad sequences. These assignments are significantly different than those previously proposed.[22] The interpretation is compared to the reported proton nmr analyses obtained at 220 MHz. In addition, pentad structure is also evident in the methyne resonances. The possible effect of polymer chain conformation on ^{13}C chemical shifts are considered.

Experimental Section

The pulsed ^{13}C nmr spectra were obtained in natural abundance at 25.2 MHz from the Fourier transform of the ^{13}C free induction decay using a Varian XL-100-15. All spectra were obtained at the Major Analytical Insrument Facility at Case Western Reserve University. Instrument conditions for Figure 1 were: spectrum width, 710 Hz; acquisition time, 5.6 sec; 43 μ sec 90° pulse; 2191 transients; and 100°. For Figure 2 they were: spectrum width, 1300 Hz; acquisition time, 0.8 sec; 42-μsec pulse; 71,790 transients; and 60°. The spin-lattice relaxation time may not be equal for the methyne and methylene carbons. Consequently when 0.8-sec acquisition time is used, error could be introduced into an analysis that relied upon a relative comparison of methyne and methylene integrated areas. Such error is not likely in this present analysis as only relative area measurements are made between methyne carbon resonances or between methylene carbon resonances. One might expect little difference to exist between the T_1 of methylene carbons which differ only in their configuration. The same might be expected for relative comparison of methyne integrated intensities. Within experimental error, the relative methylene resonance areas were found to be the same if 0.8-, 4.0-, or 5.6-sec acquisition times were used to produce the spectra. The relative methyne areas also did not change under these different instrument conditions. The relative methylene (or methyne) areas were equivalent if the spectra were obtained using a spectrum width of 710, 1300, or 5000 Hz. The spectra were obtained using 12-mm tubes and 10 (w/v) % solutions in *o*-dichlorobenzene. Spectra were obtained at 60, 100, and 110° with no measurable change in chemical shifts or areas. The chemical shifts were measured relative to internal hexamethyldisiloxane (Me_6Si_2) and converted to internal Me_4Si. The conversion factor, measured from a mixture, was $Me_4Si\text{–}Me_6Si_2 = -1.94$ ppm. All areas were measured with a K&E compensating polar planimeter. The samples of PVC were made at 55° and were similar to those used previously.[21]

Results

A high-resolution pulsed Fourier transform ^{13}C nmr spectrum of poly(vinyl chloride) is shown in Figure 1. The improvement in resolution of the pulsed FT spectrum over the previously reported[20,21] CW spectrum of PVC shows a great deal of methylene carbon chemical shift discrimination, as well as, pentad sequence information from the methyne resonances. The relative areas and ^{13}C chemical shifts of the methyne and methylene resonances are given in Table I. Also shown in Table I are theoretical resonance areas based on Bernoullian statistics if the probability of

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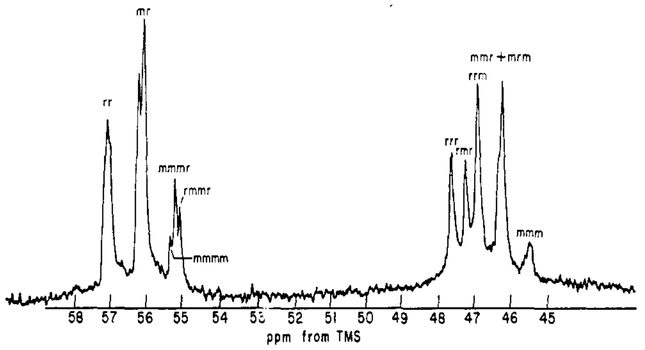

Figure 1. Pulsed FT ^{13}C nmr spectrum of poly(vinyl chloride). The chemical shifts are in ppm downfield from Me_4Si. Spectrum was obtained at 100° in *o*-dichlorobenzene.

Table I
^{13}C Chemical Shifts[a] and Relative Areas for Poly(vinyl chloride)

Assignment	$\delta\ ^{13}C$	Obsd (Mole Fraction)	Bernoullian Distribution[23] $P_m = 0.43$[c]	$P_m = 0.45$[c]
		Methyne		
rr	57.15			
	57.06			
		0.291	(0.325)[b]	(0.303)
mr	56.29			
	56.13			
		0.520	(0.490)	(0.496)
mmmm	55.42		0.034	0.041
mmmr	55.29		0.091	0.100
rmmr	55.16		0.060	0.061
		0.188	(0.185)	(0.202)
		Methylene		
rrr	47.74	0.161	0.185	0.166
rmr	47.35	0.146	0.140	0.130
rrm	47.01	0.282	0.279	0.272
mmr + mrm	46.33	0.320	0.316	0.334
mmm	45.59	0.092	0.080	0.091

[a] ±0.02 ppm downfield from internal Me_4Si in *o*-dichlorobenzene Me_4Si-Me_6Si_2 = −1.94 ppm). [b] Triad concentration in parentheses. [c] P_m is the probability of isotactic monomer placement during propagation.

isotactic monomer placement during propagation, P_m is 0.43 or 0.45. A comparison of theoretical concentrations and observed peak areas were used to assign the ^{13}C chemical shifts to the designated pentad and tetrad sequences shown in the table. The nomenclature for the designation of dyad, triad, pentad, and tetrad configuration in Table I are those described by Bovey.[23]

Discussion

The pulsed FT ^{13}C nmr spectrum shown in Figure 1 clearly demonstrates the potential of ^{13}C nmr as a method for determining polymer molecular structure. The resulting ^{13}C nmr determination of tacticity in PVC confirms the proton nmr analysis reported earlier by Heatley and Bovey.[17] The ^{13}C spectra have an advantage over the ^{1}H spectra because discrete resonance areas can be measured and assigned to the individual tetrad or triad sequences directly, without the necessity of simulating a resonance area which is a composite of many chemical shifts.[17] Within experimental error, the observed ^{13}C relative peak areas fit Bernoullian statistics. The triad concentrations agree with the triad concentrations measured from the earlier CW ^{13}C spectrum,[21] even though the CW spectrum did not provide pentad or tetrad information.

Both the triad and tetrad concentrations seem to be most consistent for $P_m = 0.45$. P_m is defined[22] as the probability of isotactic monomer placement during propagation. However, $P_m = 0.43$ as previously suggested[17] is not out of line for these data. The agreement between methyne and methylene relative areas is not unexpected as Schaefer and Natusch[24] have shown that carbon atoms within a polymer system have equal nuclear Overhauser enhancement. Consequently, there should not be an error in comparing the quantitative areas of the different kinds of PVC carbon resonances.

There are several considerations one can make about the assigned methylene ^{13}C chemical shifts. The assignments shown in Figure 1 and Table I were based on comparing the observed relative areas with theoretical tetrad concentrations for Bernoullian statistics. Clearly five of the six possible tetrads are resolved. Also the resonance at 46.33 ppm is certainly composed of at least two peaks. Carbon-13 spectra of low molecular weight fractions of PVC did have resolution which showed a definite peak (not a shoulder) in both the syndiotactic methyne resonance and the methylene resonance at 46.33 ppm. A typical spectrum is shown in Figure 2. Note that the sum of the mmr and mrm tetrads (sum = 0.33 for $P_m = 0.45$) agrees with the observed area at 46.33 ppm. A reasonable alternate interpretation would be that all r-centered tetrads would have their resonances in one region of the spectrum and all m-centered tetrad resonances would be grouped in a different region of the spectrum. Thus, the r centered tetrad resonances would be on the low-field side of the methylene resonances and the m centered tetrad resonances on the high-field side of the methylene resonances. This is the interpretation proposed by Inoue, Ando, and Nishioka.[22] Such an interpretation produced very poor agreement between observed and theoretical areas. This interpretation would mean that the resonance at 46.33 ppm would be due to the m centered tetrads, mmr and rmr, and should have a tetrad fractional area of 0.353. Similarly the resonance at 47.35 ppm would not be due to the rmr tetrad but would be due to the mrm tetrad and should have a tetrad fractional area of 0.111. All of the pulsed FT ^{13}C nmr spectra observed for the PVC made near 50° had a resonance at 47.33 ppm with a methylene relative area in the range of 0.13–0.16, never 0.11. Likewise the resonance at 46.33 ppm was in the range of 0.31–0.32, never 0.35. These spectra were obtained using the various combination of temperature, pulse cycle, and spectrum width given in the Experimental Section. Consequently, the assignment shown in Table I seems most valid.

The differences between the present tetrad chemical shift assignments and those of other workers[22] may be the result of differences in observed spectral resolution. The resolution shown in Figures 1 and 2 is much higher than that obtained from (CW) spectra.[19-22] Consequently, the resulting area measurements will be more accurate and one can more reliably test Bernoullian statistics. As mentioned earlier, the measured methylene areas do not fit Bernoullian statistics if the assignments of Inoue, Ando, and Nishioka are envoked. One should also consider the possibility that the broad resonance assigned by Inoue, Ando, and Nishioka to branching may be the same reso-

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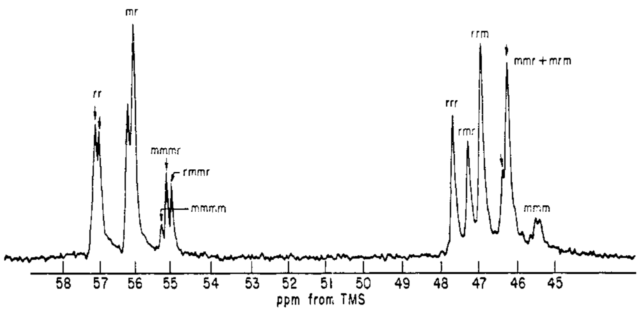

Figure 2. Pulsed FT ^{13}C nmr spectrum of low molecular weight PVC showing two syndiotactic methyne resonances and two resonances for the mmr and mrm tetrads.

nance assigned in the present work to mmm tetrads. It is not likely that the resonance, shown in Table I as a mmm tetrad, is in fact due to branching. This resonance had the same relative methylene area in high and low molecular weight polymers. One might expect the stereoconfiguration of PVC made at 50° to be independent of molecular weight. But one would not expect the per cent branching to be the same in a high and low molecular weight sample.

The relative ^{13}C chemical shifts of the methylene resonance in meso and racemic 2,4-dichloropentane appeared to be dependent upon the population of rotational conformations.[20] Gauche 1-4 interactions produce a more upfield ^{13}C chemical shift than does a trans 1-4 interaction.[25] Consequently, it was postulated that in 2,4-dichloropentane the relative difference in ^{13}C chemical shifts was a function of the amount of trans and gauche interactions that a carbon was experiencing in the overall average population of conformations. Based on infrared,[26] proton nmr[17] and othr studies[27,28] of the conformational population of PVC, the most stable conformation for the rrr tetrad would have tt interactions. Consequently, the methylene carbon in a rrr tetrad would experience more trans interactions on an average than the other tetrads. On the other hand, the most stable conformation for the mmm tetrad should involve a 3_1 helix with tg conformation.[26] Consequently, there could be more gauche interactions, on an average, for the methylene carbon in a mmm tetrad than for the other tetrads. It is therefore reasonable that the methylene carbon in the mmm tetrad should be the most shielded and that conversely, the methylene carbon in a rrr tetrad should be the most deshielded. Based on the postulate that the more gauche interactions a methylene carbon is experiencing in its average conformational environment the more shielded the carbon becomes, I would predict that the following tetrads are in the order of increasing gauche interaction: rrr < rmr < rrm < mmr ~ mrm < mmm.

It is interesting that the ^{13}C chemical shifts of the rmr and the rrr tetrads are more alike than are the ^{13}C chemical shifts of the rrm and rrr tetrads. This suggests that the average conformational interactions of the rmr and the rrr tetrads are more similar than for the two r-centered tetrads, rrr and rrm. Using the same argument, the conformation of the mmr and mrm tetrad would be more similar than for the m-centered tetrads, mmr and rmr. The consequence would be that the relative ^{13}C chemical shifts observed for the methylene carbons in tetrad sequences are a function of the average conformational environment of the tetrad and not primarily upon whether the central dyad is meso or racemic. The relative separation in hertz between the ^{13}C chemical shifts should be a function of the fractional trans or gauche contribution. Thus it seems that ^{13}C chemical shifts could be useful in deducing some information about the average conformational population in polymers. Of course, as opposed to infrared frequencies where direct measurements of individual conformers can be made,[26] these resonance areas at a particular chemical shift are a composite of the total conformers a methylene carbon is experiencing. ^{13}C resonance areas are not a measurement of individual tt, tg, gg, or other conformations.

The resonance assigned to the methylene carbon in a mmm tetrad at 45.59 ppm is broader than the other methylene resonances. Conceivably, this may be due to either a difference in chain mobility of this segment, since it would prefer to form a helix rather than a planar zigzag. Or, because of the preferred helix, this segment is more compressed and the methylene carbon may be more sensitive to the configuration of the monomer on each end of the tetrad. Therefore the mmm tetrad may be broader because of slightly different chemical shifts reflecting hexad structures.

The relative areas of the three resonances at 55.42, 55.29, and 55.16 ppm were used to assign methyne carbons to isotactic centered pentads. The observed concentration of isotactic triads is 0.19 mol fraction of the total methyne area. Assuming, Bernoullian statistics, the relative proportion of the three possible isotacic centered pentads should be approximately 4:10:6 for mmmm:mmmr:rmmr, respectively. The observed intensities seen in Figure 1 fit this ratio. Consequently, the assignments shown in Table I and in Figure 1 were made. Based on the argument that is proposed to explain the relative chemical shifts for the methylene carbons, one might expect that the mmmm pentad would be the most shielded. This is because of the gauche interactions with the methylene carbons in the backbone of the polymer chain. However, the methyne carbon differs greatly from the methylene carbon in that the methyne carbon has gauche or trans 1-4 interactions with the chlorine atoms that the methylene carbons do not experience. The 3_1 helix formed in a mmmm pentad has trans 1-4, chlorine–methyne carbon interactions. Perhaps the contribution of trans conformational interactions relative to the chlorine atoms have a slight deshielding effect on the methyne carbon.

Certainly the observation does caution one not to make ^{13}C chemical shift assignments for methyne carbons based solely on empirical relationship assumed for methylene carbons. The sensitivity of the ^{13}C nucleus to its environment reflects a more complicated interaction than simply the conformation of the polymer backbone chain. The conformation relative to the chlorine branches must also be considered.

Since there are four pentads with heterotactic centered triads, no unambiguous assignment can be made for the two observed nonequivalent heterotactic methyne carbons at 56.29 and 56.13 ppm. Likewise, no attempt was made to speculate on which syndiotactic centered pentads might be nonequivalent and thus, producing the shoulder in the syndiotactic methyne carbon resonance.

It has been demonstrated[29] that any discussion of PVC tacticity based on proton nmr analysis must be limited to the portion of PVC that is soluble in *o*-dichlorobenzene. Wilkes[29] has shown that as the crystallinity of PVC increases, there is an increasing concentration of insoluble

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PVC, probably highly syndiotactic, that is not detected by proton nmr. The tacticity analysis in Table I based on ^{13}C data, at this time, should also be considered as an analysis of the portion of PVC soluble in *o*-dichlorobenzene. Future work may establish what effect crystalline PVC has on its ^{13}C nmr spectrum.

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Nuclear Magnetic Resonance Relaxation in a Radiation Cross-Linked Poly(vinyl chloride) System

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ABSTRACT: Nmr relaxation measurements were employed to investigate the effect of mixing and subsequent irradiation on the segmental mobility of a 2:1 mixture of poly(vinyl chloride) (PVC) and bifunctional tetraethylene glycol dimethacrylate (TEGDMA). Mixing decreases TEGDMA mobility while the glass transition of PVC is markedly depressed. As a PVC–TEGDMA mixture is initially heated above room temperature, there is a decrease in number of mobile molecular segments. The cause is attributed to development of paracrystalline order in the PVC. Irradiation produces strong motional hindrances, even impeding methyl group rotation. The effect becomes important at a dose of about 0.05 Mrad.

In recent studies[1,2] the chemistry and some physical properties of a commercially useful electron-irradiated poly(vinyl chloride)-tetraethylene glycol dimethacrylate (PVC–TEGDMA) cross-linked system were investigated. Added to increase the sensitivity of PVC to cross-linking, the bifunctional TEGDMA self-polymerizes in the early stage of cross-linking, but with increasing irradiation forms a network with PVC. The effects of composition and electron dosage upon gel formation were observed, and morphological, calorimetric, and dynamic mechanical findings were related to the chemistry of the cross-linking. In the present work, we have studied the segmental mobility of the PVC–TEGDMA network system at a molecular level as seen by nmr relaxation measurements.

Experimental Section

Materials. The PVC used was Opalon 660 (Monsanto) which is reported to have a weight-average molecular weight of 120,000 and a number average of 50,000. The tetraethylene glycol dimethacrylate, a liquid, is a product of the Ware Chemical Corp.

The PVC–TEGDMA mixtures were prepared by W. A. Salmon using a weight composition ratio of PVC to TEGDMA of 2:1. The substances were mixed with heat stabilizers in a blender at 80°, compression molded under 15-tons ram force at 140° for 3 min, and irradiated by 1-MeV electrons at a rate of 0.01 Mrad/sec to attain the desired radiation dosage.[1] Uniformity of composition and morphology is difficult to achieve within a batch or from batch to batch through this series of processes. Except for the 5-Mrad sample which was red, all samples were colorless. Sample thickness was about 0.04 in.

Procedure. The nmr measurements determined the spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2, as functions of temperature and radiation dose.[3] The pulse method of nmr was used at a resonance frequence of 30 MHz in an apparatus previously described.[4] T_1 was determined using a conventional 180-90° pulse sequence, while T_2 was obtained by measurement of the free induction decay following a 90° pulse.

In all the samples of this study, it was found that at sufficiently high temperature the free induction decay could be decomposed by computer analysis into a weighted sum of two exponential decays.[5] These decay components were separated and the calculated T_2 relaxation times and their relative intensities which are referred to hereafter as the mobile and immobile fractions plotted *vs.* temperature.[6] The terms mobile and immobile are to be understood as relative to each other. Computer calculated uncertainty ranges for the decay curve fits were too small to warrant inclusion on the data plots. In the case of a two component relaxation, the longer T_2 is associated with the mobile protons while the shorter T_2 is associated with the relatively immobile protons. Coincidentally, for the PVC–TEGDMA composition used in this study the protons residing on the PVC and the TEGDMA molecules are nearly equal in number.

Sample temperature was maintained suitably constant by means of a Leeds and Northrup 6261 controller; 5 min was necessary for an observation while 20 min was allowed between observation for the purpose of sample temperature equilibration.

Results

We have sought to resolve the effect of the mixing and subsequent irradiation on the segmental mobility of these PVC–TEGDMA mixtures. To do so we have examined the nmr behavior of the individual components and of a series of mixtures exposed to irradiation doses varying from 0 to 5 Mrad.

T_2 Relaxation Time. The T_2 and mobile fraction variations with temperature for PVC, TEGDMA monomer, and its polymer are given in Figure 1. The poly(TEGDMA) was produced by heating the monomer at 120° overnight to polymerize thermally into a three-dimensional network.

The mobile fraction *vs.* temperature dependence of PVC resembles the pattern of the stiffness modulus–temperature data published by Reding *et al.*[7] for a PVC polymerized at 40°. In that study the stiffness modulus dropped steeply at the glass transition, but then decreased gradually with increasing temperature. The existence of this "plateau" region was attributed to paracrystallinity (two-dimensional chain alignment). The PVC used in this work begins to display molecular motion on the T_2 scale at 120°. The initial steep rise in mobile fraction presumably is caused by the amorphous portions. The gradual ascent between 130 and 200° may be due in

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