High-Temperature Carbon-13 Nuclear Magnetic Resonance Spectra of Poly(vinyl chloride)

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ABSTRACT: Random-noise, proton-decoupled carbon-13 nmr spectra were obtained in *o*-dichlorobenzene at 130° for poly(vinyl chloride) which had been polymerized at 50°. These spectra exhibited narrower line widths and better defined methylene and methine resonances than ^{13}C spectra obtained at 48°. Triad concentrations, based on the methine carbons, were 31% syndiotactic, 50% heterotactic, and 19% isotactic. The ^{13}C analysis is compared to reported proton nmr analyses.

We have reported[2] that carbon-13 nuclear magnetic resonance (^{13}C nmr) is very sensitive to stereochemical configuration in chlorinated hydrocarbons. We also showed that random-noise, proton-decoupled, ^{13}C nmr spectra could be used to discriminate stereochemical configurations in poly(vinyl chloride) (PVC). Based on model compounds, methine carbon chemical shifts were assigned to syndiotactic, heterotactic, and isotactic triad sequences. The relative intensities of these three resonances for a commercial PVC made at +50° were shown to be different from those of a more syndiotactic PVC. Those data[2] were obtained at 48°, which was found to be the normal spectrometer probe temperature with proton noise decoupling. At that time we did not attempt to make a quantitative measurement of tacticity, based on the areas of methine carbon resonances, because base-line definition between the methine carbon resonances was not adequate to enable us to neglect peak overlap. The methylene carbon resonance region in the spectra obtained[2] at 48° showed a broad and poorly defined resonance. We concluded that this region was an envelope of resonances resulting from all possible tetrad sequences. Schaefer has recently reported similar results from Fourier transforms of pulsed ^{13}C nmr spectra.[3]

It has been well established,[4] in proton nmr studies of polymer solutions that high temperature is required for most polymers in order to obtain spectra of adequate resolution for maximum structural analysis. However, to date, any advantages that high temperature may offer ^{13}C nmr analysis of polymer solutions have not been reported. Since our earlier report,[2] we have been successful in obtaining random-noise, proton-decoupled, ^{13}C nmr spectra at +130° for a commercial PVC polymerized at 50°. Our results show that the use of high temperature may be as valuable when obtaining ^{13}C nmr spectra of polymers as it has been for proton nmr studies of polymers.

Carbon-13 nmr spectra of the same PVC polymerized at 50°, used in our previous study,[2] were obtained at 130° using a Bruker HFX-90 spectrometer operating at 22.62 MHz. The polymer sample was prepared as a 10% (w/v) solution in *o*-dichlorobenzene. 1,4-Dibromotetrafluorobenzene was used for a ^{19}F lock and was contained in a 5-mm tube inserted into a 10-mm tube containing the PVC solution. Proton noise decoupling was employed, and the spectra were time averaged using a Fabri-Tek 1074. All ^{13}C chemical shifts are relative to external CS_2.

The improvement in resolution in the ^{13}C spectrum of PVC is shown in Figure 1. The three resonances at 135.3, 136.2, and 137.2 ppm upfield from CS_2 are due to methine carbons which are in syndiotactic, heterotactic, and isotactic triads, respectively. The methylene carbon resonances near 148 ppm are much better defined in the spectrum obtained from an *o*-dichlorobenzene solution at 130° than in the spectrum obtained from an *o*-dichlorobenzene solution at 48°.[2] Structural features are now evident in the methylene carbon resonances which suggest that proper model compounds might enable one to make chemical shift assignments. Thus, dyad or tetrad concentrations might also be measured from ^{13}C nmr spectra, in addition to the triad concentrations. The ^{13}C nmr data for the +50° PVC are summarized in Table I. The improved resolution at +130° is reflected in the narrower line widths.

The PVC solution in *o*-dichlorobenzene was a gel at 48°, whereas it was a mobile solution at 130°. The more defined methylene resonance at high temperature is probably a result of reduced dipolar interactions because the molecular chains are tumbling more rapidly.[4] Duch and Grant[5] found that motional narrowing for *cis*-1,4-polybutadiene as well as for *cis*- and *trans*-1,4-polyisoprene was rapid enough, relative to the carbon-13 time scale, to obtain high-resolution spectra on the bulk rubber at room temperature. In contrast to polyisoprene or polybutadiene, the glass transition temperature for PVC is +82°[6] and consequently high-resolution ^{13}C spectra on the bulk polymer are not possible. However, it has been shown that the T_g of PVC decreases with the degree of plasticization.[7] Consequently, the rubbery chains in PVC gels have enough mobility at normal instrument operating temperatures to allow the accumulation of high-resolution spectra.[2,3] Our data at +130° were obtained at a temperature sufficient to decrease the correlation time[4a] for the segmental motion of the polymer chains and cause motional narrowing. One should also be able to obtain spectra with improved resolution at 48° by using a better room-temperature solvent for PVC, thus decreasing the correlation time for segmental motion. It is possible that some contribution to

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TABLE I
^{13}C METHINE CHEMICAL SHIFT DATA[a] FOR PVC POLYMERIZED AT 50°

Carbon –CHCl–	^{13}C chemical shift +130°	Δ^{13}C (S − H); (H − I)[b] +130°	48°	Line width,[d] Hz +130°	48°
Syndiotactic	135.3	−0.92	−1.03[c]	6.4	13.2
Hetereotactic	136.2	−0.94	−0.94[c]	6.6	12.4
Isotactic	137.1			5.5	12.0

[a] ^{13}C chemical shifts are in parts per million upfield from external CS_2; obtained from a 10% (w/v) solution in *o*-dichlorobenzene. [b] The difference in ^{13}C chemical shifts in parts per million between syndiotactic–heterotactic carbons and heterotactic–isotactic carbons. [c] Reference 2. [d] Peak width at half-height for each methine resonance.

TABLE II
PVC TACTICITY BASED ON TRIAD CONCENTRATIONS

Polymerization temp, °C	% S	% H	% I	Method of nmr analysis	Calcd dyads[a] % m	% r	Ref
55	30.6	50.3	19.1	^{13}C at 22.62 MHz; {^{1}H} decoupled; methine peak areas	44.2	55.8	This work
55	31.0	50.2	18.8	^{1}H at 220 MHz; no decoupling; methine peak areas	43.9	56.1	*b*
40	32.2	48.7	19.1	^{1}H at 60 and 100 MHz; {D} decoupled; β,β-*d*$_2$-PVC; methine peak areas	43.4	56.6	*c*
58	35	48	17	^{1}H at 60 and 100 MHz; no decoupling; β,β-*d*$_2$-PVC; methine peak areas	41	59	*d*
55	35	49	16	^{1}H at 60 MHz; {^{1}H} decoupled; methine peak areas	41	59	*e*
52.5	29	52	19	^{1}H at 56.4 MHz; {^{1}H} decoupled; methine peak areas	45	55	*f*
50	36	28	36	^{1}H at 60 MHz; no decoupling; empirical equations and peak heights of methine multiplet	50	50	*g*

[a] Dyad concentrations are calculated from the measured triad concentrations, assuming Bernoullian statistics (see ref 8). [b] C. J. Carman and C. E. Wilkes, unpublished results, B. F. Goodrich Co., Research Center. [c] L. Cavalli, G. C. Borsini, G. Carraro, and G. Confalonieri, *J. Polym. Sci., Part A-1*, **8**, 801 (1970). [d] S. Enemoto, M. Asahina, and S. Satoh, *ibid., Part A-1*, **4**, 1373 (1966). [e] S. Satoh, *ibid., Part A*, **2**, 5221 (1964). [f] J. Bargon, K. H. Hellwege, and U. Johnson, *Makromol. Chem.*, **95**, 187 (1966). [g] W. C. Tincher, *ibid.*, **85**, 20 (1965).

the broad methylene resonance at room temperature could result from the polymer not being completely in solution at room temperature.

Figure 2 shows the methine carbon resonances using a narrower sweep width. The high-resolution spectrum exhibits a high degree of discrimination between stereochemical configurations. Again, the discrimination is not due to an increase in chemical shift differences, but to motional narrowing. The areas of the three methine carbon resonances shown in Figure 2 were measured with a planimeter. The calculated triad concentrations for the PVC polymerized at 50° were 30.6% syndiotactic, 50.3% heterotactic, and 19.1% isotactic. Our results are compared in Table II with a partial listing of previous nmr analyses of PVC polymerized near 50°C. The first three entries in Table II are very consistent. Since these data are based on three different types of nmr analyses (*i.e.*, ^{13}C nmr, 220-MHz ^{1}H nmr, and 100-MHz ^{1}H nmr), one can conclude that the average triad concentrations of PVC polymerized at 50° are 31% S, 50% H, and 19% I. (The agreement among these methods of analyses is about ±0.6%.) We assumed Bernoullian statistics and calculated the dyad concentrations[8] using the equations $m = I + H/2$ and $r = S + H/2$. Based on the ^{13}C nmr data, the dyad concentrations for PVC polymerized at 50° would be 44% m (isotactic) and 56% r (syndiotactic). Confidence in the ^{13}C nmr analysis is increased since the calculated dyad concentrations agree with both 220-[9] and 100-MHz[10] proton nmr data.

We should insert a word of caution for use of nmr to measure stereoregularity in PVC. Wilkes[11] has found, using internal standards with a wide range of PVC's, that proton

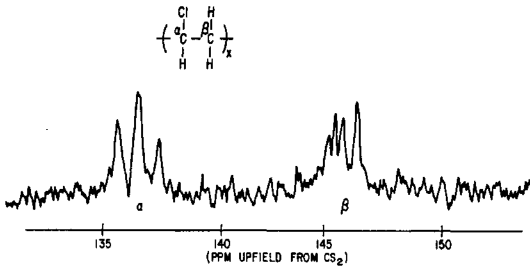

Figure 1. Proton-noise-decoupled, natural-abundance, 22.62-MHz ^{13}C nmr spectrum of commercial PVC made at +50°. The spectrum was obtained at +130° from a 10% (w/v) solution in *o*-dichlorobenzene, and was time averaged for 250 scans using a sweep width of 10 Hz/cm and a sweep rate of 15 Hz/sec. Resonance positions are given in parts per million upfield from CS_2.

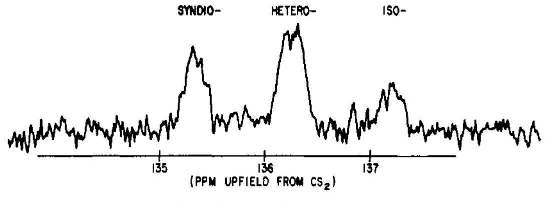

Figure 2. Proton-noise-decoupled, natural-abundance, 22.62-MHz ^{13}C nmr spectrum of the methine carbons in a commercial PVC made at +50°. The spectrum was obtained at +130° from a 10% (w/v) solution in *o*-dichlorobenzene, and was time averaged for 400 scans using a sweep width of 2.0 Hz/cm and a sweep rate of 3 Hz/sec. Resonance positions are given in parts per million upfield from CS_2.

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nmr is often not examining the total polymer. He found that the solubility of PVC decreased as the crystallinity of PVC increased and, consequently, a fraction of the polymer was not contributing to the proton nmr spectrum. At this point, we do not know what effect regions of crystallinity might have on the ^{13}C nmr spectra of PVC obtained at 130°. As has been suggested for *trans*-1,4-polyisoprene at 45°,[5] the presence of crystalline regions may result in a loss in signal intensity and broadening of the lines.

Carbon-13 nmr analysis of PVC for tacticity has an advantage over either 220- or 100-MHz proton nmr analyses in that there are no peak overlap effects in the decoupled methine resonances. Consequently, tacticity can be measured by measuring individual, isolated methine carbon peaks.

A Nuclear Magnetic Resonance Analysis of the Steric Course of Propagation of Vinyl Methyl Ether

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ABSTRACT: Stereospecifically deuterated cis and trans isomers of vinyl methyl ether have been polymerized under several conditions with various initiators. Some observations on initiation are recorded. It was found that only minor differences resulted in the proportion of erythro- and threo-meso protons produced within the isotactic sequence when a few different initiators and solvents were used. The presence of both erythro- and threo-meso protons defines the isotactic polymerization process as occurring by both syndiotactic-like and isotactic-like presentation of the monomer to the polymer cation. Polymers prepared with BF_3 and various etherates are more stereoregular at both the α and β positions than polymers prepared with PF_5 catalyst under the same conditions. From our proposed assignment of the downfield and upfield meso tetrad resonances to threo- and erythro-meso configurations, respectively, we suggest that isotactic-like approach of monomer is slightly preferred. Definition of the transition state is handicapped by a lack of knowledge of the nature of the ionic species, but some mechanistic interpretations are presented.

The homogeneous stereospecific polymerization of vinyl methyl ether has been of great interest since Schildknecht and coworkers first described the preparation of crystalline polymer by boron trifluoride etherate catalysis at low temperature.[1] Early studies directed at obtaining information concerning the distribution of configurational sequences in the polymer were hampered by the lack of any quantitative experimental technique.[2–4] However, since Bovey and Tiers first demonstrated that nuclear magnetic resonance could be used as a sensitive probe for the determination of polymer tacticity and homotactic sequence length,[5] many studies of the steric structure of poly(vinyl methyl ether) by this technique have been reported.[4,6–11]

Following Schildknecht's initial preparation of stereoregular poly(vinyl methyl ether), many workers have investigated various aspects of the synthesis of this stereoregular polymer and several mechanisms have been proposed to account for its formation. These involve formation of cyclic intermediates,[12] coordination of growing chain end with counterion and monomer,[13,14] and various steric and penultimate effects.[15,16] However, because of the large number of variables which must be explained, many of these mechanistic proposals do not have widespread applicability. Furthermore, only one proposal attempts to distinguish between possible cis or trans opening of the olefin bond of vinyl ethers,[16] even though this information should be basic in postulating a transition state.[16a] Although both cis and trans opening of the monomer double bonds have been reported for a variety of polymerization systems, it has been found that cis opening is the more common occurrence in homogeneous cationic polymerization. Natta, *et al.*, showed that cis opening of the olefin bond occurs for *trans*-isobutyl propenyl ether[17] as well as for *cis*- and *trans*-β-chlorovinyl ethers[18] when polymerized with homogeneous cationic catalysts. The same conclusion was reached by Ohsumi,[19,20] *et al.*, for the homogeneous polymerization of *trans*-methyl propenyl ether with boron trifluoride etherate.

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