

Nuclear Magnetic Resonance and Stereoregularity of PVC

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Synopsis

The decoupled α -proton spectrum of PVC was examined using a 220 MHz NMR spectrometer. All of the ten possible pentads were detected and an assignment is given based on Bernoullian statistics. This assignment is in general agreement with conclusions reached by previous workers except for some modifications in the heterotactic resonances. Triad tacticity data were obtained from the pentads and were used to estimate the differential enthalpy and entropy changes for bulk PVC polymerized in the temperature range 70°C to -50°C.

THEORY

Chain Sequence Stereoregularity

When a vinyl chloride monomer unit adds on to a growing chain during free-radical polymerization in a tail-to-head fashion, the carbon-carbon bond of this molecule still rotates even after the molecule tail (CH_2 -) has been attached. The chlorine atom assumes different spatial positions due to this rotation, and its configuration relative to the rest of the chain is undefined until the next monomer unit adds on. When this happens, the configuration of that particular chlorine atom is fixed. Whether there is or there is not any influence of this configuration on the configuration of the next chlorine atom is a matter of the statistical pattern of addition. Basically, there are two possible configurations for the chlorine atom. If it lies to the same side of the zigzag chain as the preceding chlorine, an isotactic placement has occurred. If it lies opposite to the preceding one, a syndiotactic placement has occurred. Subsequent additions may result in the same configuration or a switch can take place.

Figure 1 is a schematic representation of the possible configurations that result from the stepwise addition of four monomer units. Sequences made up of two monomer units are called diads, those of three units are called triads, four monomer units are called tetrads, five are called pentads, and so on. As shown in the figure in triads and higher sequences, we can define a third configuration called heterotactic. This may not be called heterotactic placement. There are only two possible placements, i.e., isotactic and syndiotactic and that is strictly correct for diads. For higher sequences, the word configuration should be used rather than placement. At the bottom of the figure, the possible number of each of the three configurations is shown and also the total number of configurations possible for any sequence length. Thus, there are two diads, three triad configurations, six tetrads, and ten pentads. It should be noted

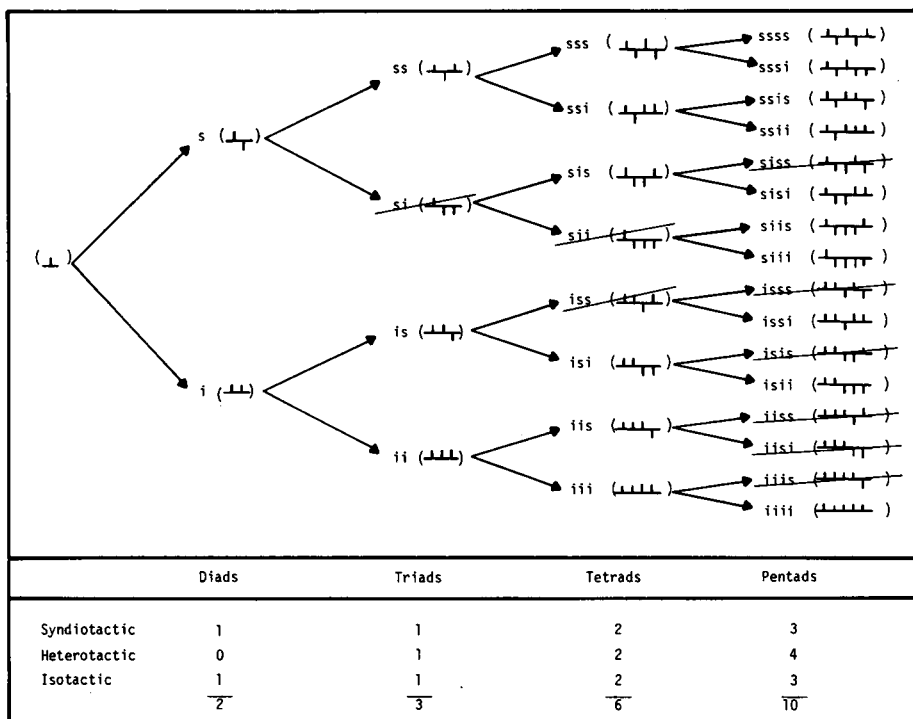


Fig. 1. Configurations obtained on the subsequent addition of four monomer units.

that some configurations are mirror images of others, and these are counted as one as shown in Figure 1.

For each sequence length, the fractions of the polymer with different configurations must add up to one. In terms of probabilities,¹ this can be written as

$$P(s) + P(i) = 1.0 \quad (1)$$

For triads

$$P(ss) + P(si \& is) + P(ii) = 1.0 \quad (2)$$

Similarly, for tetrads:

$$P(sss) + P(ssi \& iss) + P(sis) + P(isi) + P(sii \& iis) + P(iii) = 1.0$$

where $P(y)$ is the normalized probability of the configuration y .

Because diad and triad tacticities are the most familiar to workers, they were given easier nomenclature. For example, capital I and capital S are used for diad isotacticity and syndiotacticity, respectively. Small s , i , and h are used for triad syndiotacticity, isotacticity, and heterotacticity, respectively. Thus,

$$I + S = 1.0 \quad (3)$$

$$i + h + s = 1.0 \quad (4)$$

Since is and si are mirror images, we conclude:

$$P(is) = P(si) = \frac{1}{2}P(si \& is). \quad (5)$$

Such relationship enables us to convert higher order sequence tacticities to lower ones, for example:

$$P(s) = P(ss) + P(st)$$

$$\therefore S = s + h/2 \quad (6)$$

and

$$I = i + h/2. \quad (7)$$

Similar relationships between tacticities of different orders were reported by Frish et al.²

Statistical Distributions

As mentioned above, the configuration of one chlorine atom may or may not affect the configuration of the next chlorine atom.

If the configuration of a monomer unit is independent of the preceding configuration, it is called Bernoullian, i.e., it follows random Bernoulli trial statistics. It is convenient here to introduce the concept of conditional probabilities,¹ for example:

$$P(s/s) = P(ss)/P(s). \quad (8)$$

$P(s/s)$ is the probability that a third monomer unit will add in a syndiotactic mode to a syndiotactic diad to produce a syndiotactic triad.

Similarly, other conditional probabilities can be defined:

$$P(s/i) = P(is)/P(i) \quad (9)$$

$$P(i/s) = P(st)/P(s) \quad (10)$$

$$P(i/i) = P(ii)/P(i). \quad (11)$$

Also,

$$P(s/ss) = P(sss)/P(ss) \dots \text{and so on.}$$

Clearly,

$$P(s/s) + P(i/s) = 1.0$$

and

$$P(s/i) + P(i/i) = 1.0.$$

The specific persistence ratios are defined as follows:²¹

$$\rho_t = \frac{P(s)}{P(s/i)} = \frac{P(s)P(i)}{P(is)} \quad (12)$$

$$\eta_s = \frac{P(s/s)}{P(s)} = \frac{P(ss)}{P(s)P(s)} \quad (13)$$

$$\eta_{ss} = \frac{P(s/ss)}{P(s)} = \frac{P(sss)}{P(s)P(ss)}$$

$$\eta_{ts} = \frac{P(s/is)}{P(s)} = \frac{P(is)}{P(s)P(is)}$$

For Bernoullian statistic which is characterized by one probability and does not depend on the preceding configuration,³

$$P(s) = P(s/s) = P(s/is) = P(s/ii) = \dots$$

or

$$\rho_i = \eta_s = \eta_{is} = \eta_{ss} = 1.0.$$

If previous units have an effect, the statistics are called Markovian of order n , the order being the number of previous units that contribute to the influence. In the first-order Markovian statistics (simple Markovian), only the penultimate monomer unit has an effect, and in this case the statistics are described by two independent parameters. Generally,³

$$P(u^n/v^m) = P(u^n/v^m w^y).$$

The probability of the sequence u^n of n units to occur depends on the previous sequence v^m of m units and does not depend on the preceding sequence w^y of y units. A simple Markovian statistic is one for which $m = 1$. For that case,

$$P(s) \neq P(s/s) = P(s/ss) = P(s/is) \neq P(s/i) = P(s/ii) = \dots$$

or

$$\rho_i \neq \eta_s = \eta_{is} = \eta_{ss} \neq 1.0.$$

For higher-order Markovian statistics ($m > 1$) and non-Markovian statistics,

$$\rho_i \neq \eta_s \neq \eta_{is} \neq \eta_{ss} \neq 1.0.$$

Values of ρ_i and η_s less than unity indicate higher chance for switching between isotactic and syndiotactic placements which leads to shorter isotactic and syndiotactic sequences than the Bernoullian case for which $\rho_i = \eta_s = 1.0$. The opposite is true for ρ_i and η_s larger than one.

The simple Markovian statistic is analogous to copolymerization. Four propagation constants can be defined, k_{it} , k_{st} , k_{is} , and k_{ss} , where

$$P(i/s) = \frac{k_{st}}{k_s} = \frac{k_{st}}{k_{st} + k_{ss}}$$

$$P(s/s) = \frac{k_{ss}}{k_s} = \frac{k_{ss}}{k_{st} + k_{ss}}$$

$$P(i/i) = \frac{k_{it}}{k_I} = \frac{k_{it}}{k_{it} + k_{is}}$$

$$P(s/i) = \frac{k_{is}}{k_I} = \frac{k_{is}}{k_{it} + k_{is}}$$

Two parameters r_1 and r_2 can be defined analogous to the reactivity ratios:

$$r_1 = \frac{P(i/s)}{P(s/s)} = \frac{k_{st}}{k_{ss}} \quad (14)$$

$$r_2 = \frac{P(i/i)}{P(s/i)} = \frac{k_{it}}{k_{is}} \quad (15)$$

Reinmöller and Fox⁴ defined the ratio $G = r_1/r_2$ and used it as a measure of the strength of penultimate effect in the polymerization of methyl methacrylate. G less than unity indicates a tendency to form stereoblocks, i.e., same effect as ρ_i and η_s larger than one.

The effect of polymerization temperature on the parameters r_1 and r_2 is given by the Arrhenius relationships

$$r_1 = \frac{k_{s't}}{k_{ss}} = \exp \left\{ \frac{\Delta(\Delta S)_{ss}{}^{s't}}{R} - \frac{\Delta(\Delta H)_{ss}{}^{s't}}{RT} \right\} \quad (16)$$

$$r_2 = \frac{k_{t'i}}{k_{ts}} = \exp \left\{ \frac{\Delta(\Delta S)_{ts}{}{t'i}}{R} - \frac{\Delta(\Delta H)_{ts}{}{t'i}}{RT} \right\} \quad (17)$$

where $\Delta(\Delta H)$ and $\Delta(\Delta S)$ are differential enthalpy and entropy changes, respectively, between the subscript configuration and the superscript configuration.

NMR of Poly(vinyl Chloride)⁵

Nuclear magnetic resonance is the most extensively used method to study stereoregularity of polymers. Proton resonance is by far the most important to date. Different configurations are expected to give different peaks in the spectrum. A 220-MHz spectrometer resolves resonances from higher sequences better than a 100-MHz or 60-MHz spectrometer. In the PVC molecule there are two types of carbon atoms. Accordingly, there is one α -proton and two β -protons. In the NMR spectrum, the β -protons resonate at higher field than the α -proton. Even ads, e.g., diads and tetrads, are resolved in the β -proton spectrum, while odd ads, e.g., triads and pentads, are resolved in the α -proton spectrum. Accordingly odd ads have lower chemical shifts (τ) than even ads since the chemical shift is defined as

$$\tau = 10 + \delta \text{ ppm, where } \delta = \frac{H_n - H_r}{H_0} \times 10^6 \text{ ppm.}$$

H_0 is the applied field, H_n is the resonance field for the nucleus, and H_r is the resonance field for the internal reference ($H_r = H_0$).

Because of the spin coupling between the α -proton and the β -proton, NMR spectra of PVC are relatively complicated. To facilitate analysis, it is better to decouple the protons. Generally, there are two methods to achieve this. If some of the hydrogens are replaced by deuterium atoms, the spectrum is simplified considerably because $^1\text{H}-\text{D}$ coupling constants are much smaller than $^1\text{H}-^1\text{H}$ ones. This method is known as "deuteration." Thus, the spectrum of poly(α - d_1 -vinyl chloride) or poly(β - β - d_2 -vinyl chloride) is much easier to analyze than the spectrum of poly(vinyl chloride).

The other method is called "double irradiation" where one of the protons is decoupled from the other by secondary irradiation with appropriate frequency. This causes the multiplet resonances to collapse to singlets.⁵ Many NMR spectrometers are equipped with spin-decouplers that perform this function.

While the analysis of decoupled spectra are much easier, they only yield the chemical shifts but not the coupling constants.

In the past decade, a considerable amount of work has been done in the field of NMR spectroscopy of PVC.⁶⁻¹⁵ These studies aimed at throwing some light on chain configuration and conformation and also on the possible statistics

describing the propagation mechanism. At first, the attention was drawn mainly to the methylene β -proton spectrum. Johnsen⁶ used a 60-MHz spectrometer and interpreted his results as two overlapping triplets representing meso and racemic structures. Tincher⁹ offered a different interpretation viewing the β -proton resonance as the AB part of an ABX₂ spectrum. Doskocilova¹⁵ supported that view by using 2,4-dichloropentane as a model compound. Bovey et al.^{7,10} disagreed, however, with that view. The main point of controversy was the appearance of some extraneous peaks in the spectra and whether these were due to branching¹² or fine splitting of different resonances.¹³ This controversy was partially solved by Shimanouchi et al.,¹⁶ who showed that the chain length could have an effect on the chemical shifts, thus the model compounds would not necessarily reflect the behaviour of long chains. Bovey et al.¹⁷ then interpreted the β -proton spectrum of poly(α -d₁-vinyl chloride) using the tetrad assignments of Yoshino.¹³ They were able to calculate the spectrum including the small extraneous peaks by assuming the validity of Bernoulli trial statistics.

Later, the α -proton resonance spectrum began to gain attention. Heatley and Bovey¹⁸ calculated the spectra of uncoupled undeuterated PVC. They were able to obtain the chemical shifts and coupling constants for both the α - and the β -proton spectra by comparing the calculated and experimental scans. Cavalli et al.¹⁹ and Johnsen and Kolbe²⁰ have also reported deuterium-decoupled 100-MHz spectra of the α -proton resonance. They were able to assign the different pentad resonances for poly(β - β -d₂-vinyl chloride).

Recently, Fourier transform ¹³C-NMR was used to study PVC. Schaefer²¹ and Carman et al.²² measured triads while Inoue et al.²³ measured tetrads. Carman²⁴ measured both tetrads from the β -carbons and pentads from the α -carbons and was able to assign five distinct resonances to the six possible tetrads. He showed that Bernoullian statistics agreed with his assignments which differed from those of Inoue et al.²³

Pham et al.²⁵ estimated values of differential enthalpies and entropies of activation from triads and tetrads measured by ¹³C-NMR. They showed that Bernoullian statistics apply to PVC made by free-radical bulk polymerization at 0°C.

In the present study, the decoupled α -proton spectrum is examined. A VARIAN 220-MHz spectrometer equipped with spin proton-proton decoupler was employed. Due to the high resolution power of such an instrument, all ten of the possible pentad resonances were identified compared to eight identified at lower frequencies.^{19,20} The pentad assignments reported here are based on excellent agreement with Bernoullian statistics, and they are in general agreement with Cavalli et al.,¹⁹ except for some modification in the heterotactic region of the spectrum.

Triad tacticity data were then used to estimate differential enthalpies and entropies of activation for the free-radical polymerization of vinyl chloride.

EXPERIMENTAL

PVC Samples

Prepared in the temperature range of 30–70°C in bulk using the chemical initiator 2,2'-azobisisobutyronitrile (AIBN). Low-temperature PVC samples were polymerized in bulk using γ -ray initiation at -10°, -30°, and -50°C and

were supplied for this investigation by G. Palma, Laboratorio di Fotochimica e Radiazioni d'Alta Energia C.N.R., Padova, Italy. Initiation involved a dose rate of 2.2 rad/sec giving conversions in the range of 78% to 90%.

NMR Measurements

Measurements were done at the Ontario Research Foundation by Dr. Arthur Grey of the NMR center. Specifications were: a VARIAN 220-MHz spectrometer equipped with spin decoupler; solvent = *o*-dichlorobenzene (15 mg/ml); 2% HMDS as internal references; and temperature = 120°C. Areas of peaks were measured by actual count and by the triangular method; both agreed within 2% on the average.

Measurements for the 70°C and the -50°C PVC were repeated four times each to establish the pure error variance needed for the statistical analysis.

PVC solutions were prepared following the heat treatment procedure recommended in previous publications.^{27,28} This was necessary in order to disintegrate the aggregates found in bulk PVC which may affect NMR measurements.

RESULTS AND DISCUSSION

Figure 2 is the decoupled α -proton spectrum of PVC polymerized at 50°C. This sample has an isotacticity of 0.441. The upper curve (A) is the measured spectrum. The "stick" diagram (C) was drawn using the assignments in Table I. Probabilities were calculated for the different pentads assuming Bernoullian statistics. Expression for Bernoullian pentad probabilities are given by Cavalli et al.¹⁹ and are presented in Table I.

Curve (B) was obtained from the "stick" diagram by spreading the lines into "Lorentzian" peaks. A half-height width of 6 Hz gave the best match between experimental and calculated spectrum.

Basically, there are three peaks corresponding to syndiotactic, heterotactic, and isotactic configurations with decreasing field frequency, respectively. Both the syndiotactic and isotactic peaks are further split into three peaks which is the possible number of peaks for pentad resonances. The heterotactic

TABLE I
Pentad Assignments and Chemical Shifts

Assign- ment	Bernoullian probability ^a	Calculated		Observed		Pentad chemical shift τ , ppm	
		Pentads	Triads	Pentads	Triads		
<i>issi</i>	$I^2(1 - I)^2$	0.061	} $P(ss) =$ 0.313	0.062	} $P(ss) =$ 0.318	5.468	
<i>sssi</i>	$2I(1 - I)^3$	0.154		0.156		5.491	
<i>ssss</i>	$(1 - I)^4$	0.098		0.100		5.523	
<i>ssii</i>	$2I^2(1 - I)^2$	} 0.242	} $P(si + is)$ = 0.492	0.214	} $P(si + is)$ = 0.482	5.591	
<i>isis</i>	$2I^2(1 - I)^2$			} 0.250		0.268	5.618
<i>ssis</i>	$2I(1 - I)^3$					0.038	0.039
<i>isii</i>	$2I^2(1 - I)$	0.096	} $P(ii) =$ 0.195	0.098	} $P(ii) =$ 0.200	5.750	
<i>iiii</i>	I^4	0.038		0.039		5.723	
<i>siii</i>	$2I^2(1 - I)$	0.096		0.098		5.750	
<i>siss</i>	$I^2(1 - I)^2$	0.061		0.063		5.773	

^a I is the diad isotacticity.

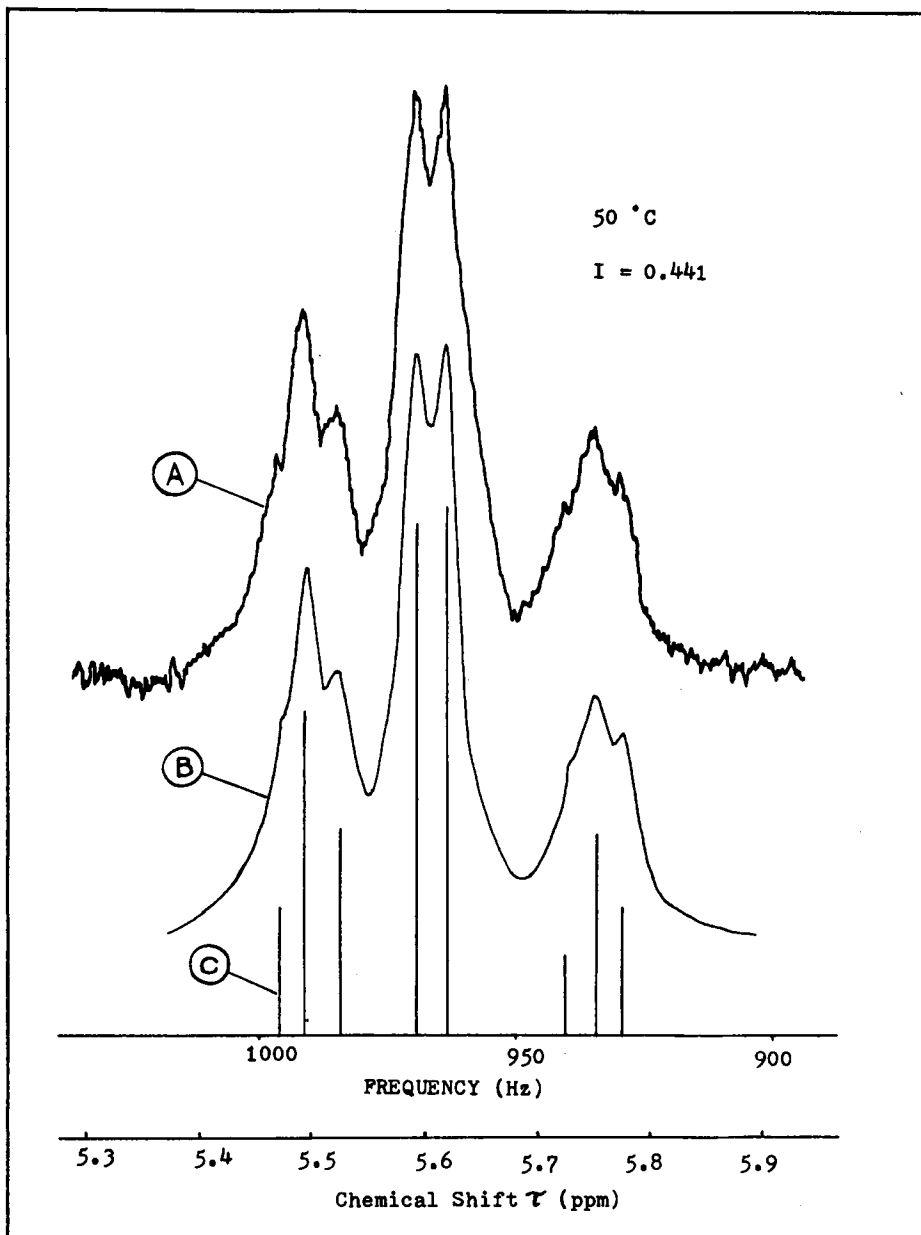


Fig. 2. 220-MHz NMR Spectrum of α -proton of PVC.

peak however is split into two peaks only rather than the possible four resonances. This implies some overlapping as shown in Table I.

The chemical shifts reported in Table I agree quite well with those reported by Cavalli et al.¹⁹ In addition, the three syndiotactic pentad resonances are clearly resolved and the corresponding chemical shifts are given. The heterotactic assignments reported before^{18,19} did not agree, however, with the measured spectrum. A different assignment had to be assumed, and the one given in Table I agreed with measurements. The higher-frequency peak is assigned to

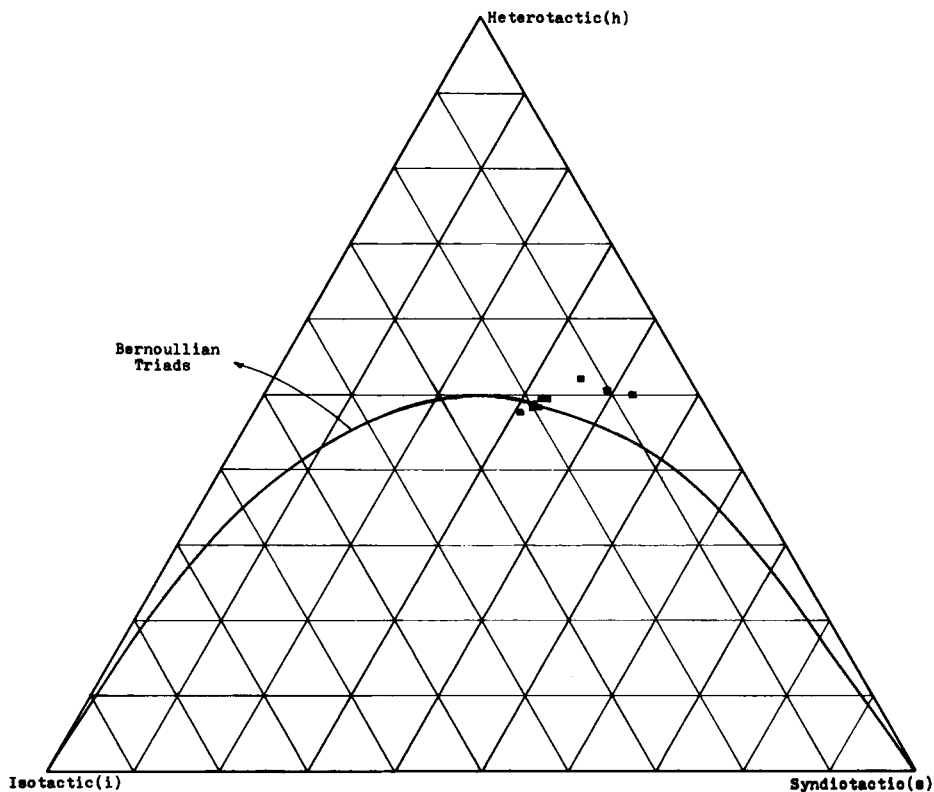


Fig. 3. Miller's diagram for triad tacticity data.

($ssii + isis$), while the lower-frequency peak is assigned to ($ssis + isii$) instead of^{18,19} ($ssii + isii$) and ($ssis + isis$), respectively.

Triad tacticity data were calculated from the pentad resonances as shown in Table I.

Table II lists the calculated triad tacticities for all the PVC samples prepared at different temperatures, including replicates at 70°C and -50°C. Diad tacticities were calculated from triads as shown above, eqs. (6) and (7), and are listed in Table II. The table also lists conditional probabilities calculated using eqs. (8) to (11), specific persistence ratios from eqs. (12) and (13), the parameters r_1 and r_2 from eqs. (14) and (15), and the ratio $G = r_1/r_2$.

As mentioned above, a test of Bernoullian statistics is that ρ_i , η_s , and G are all unity. Table II shows that this is probably the case for PVC polymerized at relatively higher temperatures, 30°C and above. Low-temperature PVC seems to deviate from that pattern.

Frisch et al.² and Miller²⁶ proposed that triad tacticities indicate Bernoullian statistics if they follow the relationship

$$4is = h^2.$$

When this is solved simultaneously with eq. (4) and the triad tacticities are plotted on triangular coordinates, the solid line in Figure 3 is obtained.

This provides a test for experimentally measured triads. As shown in the figure, the high-temperature PVC points lie very close to the Bernoullian curve.

TABLE II
 Tacticity Data and Conditional Probabilities

Polymerization temp., °C	$\frac{1000}{T}$, °K ⁻¹	S		I		s		h		i		$\frac{P(i\bar{i})}{P(is)}$		$P(i/s)$	ρ_i	η_s	G
		$P(s)$	$P(i)$	$P(ss)$	$P(ii)$	$P(si + is)$	$P(ii)$	$P(ii)$	$P(ii)$	$P(ii)$	$P(ii)$	$P(ii)$	$P(ii)$				
70	2.915	0.542	0.458	0.304	0.476	0.220	0.783	0.924	0.561	0.520	0.480	0.439	1.04	1.03	0.847		
70	2.915	0.544	0.456	0.306	0.476	0.218	0.778	0.916	0.563	0.522	0.478	0.437	1.04	1.03	0.849		
70	2.915	0.543	0.457	0.305	0.476	0.219	0.780	0.920	0.562	0.521	0.479	0.438	1.04	1.03	0.848		
70	2.915	0.544	0.456	0.306	0.476	0.218	0.778	0.916	0.563	0.522	0.478	0.437	1.04	1.03	0.849		
50	3.096	0.559	0.441	0.318	0.482	0.200	0.758	0.830	0.569	0.546	0.454	0.431	1.02	1.02	0.913		
45	3.145	0.565	0.435	0.321	0.488	0.191	0.760	0.783	0.568	0.561	0.439	0.432	1.01	1.01	0.971		
40	3.195	0.568	0.432	0.326	0.484	0.190	0.742	0.785	0.574	0.560	0.440	0.426	1.01	1.01	0.945		
35	3.247	0.570	0.430	0.322	0.496	0.182	0.770	0.784	0.565	0.577	0.423	0.435	0.988	0.991	1.05		
30	3.300	0.576	0.424	0.330	0.493	0.177	0.745	0.720	0.573	0.581	0.419	0.427	0.993	0.995	1.04		
-10	3.802	0.615	0.385	0.366	0.498	0.136	0.680	0.517	0.595	0.647	0.353	0.405	0.951	0.968	1.32		
-30	4.115	0.647	0.353	0.395	0.504	0.101	0.638	0.400	0.611	0.714	0.266	0.389	0.906	0.944	1.60		
-50	4.480	0.673	0.327	0.424	0.498	0.078	0.587	0.313	0.630	0.761	0.239	0.370	0.884	0.936	1.88		
-50	4.480	0.675	0.325	0.426	0.498	0.076	0.585	0.305	0.631	0.766	0.234	0.369	0.881	0.935	1.92		
-50	4.480	0.673	0.327	0.424	0.498	0.078	0.587	0.313	0.630	0.761	0.239	0.370	0.884	0.936	1.88		
-50	4.480	0.672	0.328	0.423	0.498	0.079	0.589	0.317	0.629	0.759	0.241	0.371	0.885	0.937	1.86		

The three separate points above and to the left of the curve are for PVC made at -10° , -30° , and -50°C with increasing syndiotacticities, respectively.

As shown in Table II for these samples, ρ_t , η_s , and G all indicate a tendency for more frequent switching between isotactic and syndiotactic placements than the Bernoullian case. PVC polymerized at low temperatures is known to have a high content of molecular aggregates.^{27,28} These are supermolecular structures made up of several molecules associated together.

The presence of these aggregates in dilute PVC solutions causes errors in experimental measurements such as light scattering, viscometry, and NMR. In order to obtain true results, the aggregates must be disintegrated (and not eliminated by filtration) into single molecules prior to any measurement.

In previous publications,^{27,28} a GPC study of these aggregates was performed and a heat treatment procedure was recommended to disintegrate the aggregates into single molecules. All PVC solutions used in this study for NMR analysis were prepared following that procedure. Accordingly, tacticity measurements in this work reflect true molecular properties.

The deviation from Bernoullian statistics at low polymerization temperatures is thus real. In fact, it is conceivable that this deviation plays a controlling role in the formation of the aggregates. A model of the aggregation process based on this hypothesis and previous results on conformational analysis in PVC will be presented in a later publication.

The ratio I/S varies with polymerization temperature according to the Arrhenius relationship

$$\frac{I}{S} = \frac{k_I}{k_S} = \exp \left\{ \frac{\Delta(\Delta S)_{s^I}}{R} - \frac{\Delta(\Delta H)_{s^I}}{RT} \right\}. \quad (18)$$

Thus, diad tacticities can be used to estimate the differential entropy and enthalpy changes $\Delta(\Delta S)_{s^I}$ and $\Delta(\Delta H)_{s^I}$, respectively, by plotting $\ln(I/S)$ versus $1/T$. From a statistical point of view, however, it was shown²⁹ that it is better to estimate the parameters using nonlinear regression rather than linear one, since the former gives a smaller variance. Accordingly, eq. (18) was used directly rather than its logarithmic transform.²⁹

Triad tacticities were similarly used to estimate the parameters $\Delta(\Delta S)_{ss^{st}}$, $\Delta(\Delta H)_{ss^{st}}$, $\Delta(\Delta S)_{is^{tt}}$, and $\Delta(\Delta H)_{is^{tt}}$ using eqs. (16) and (17). In this case also, it is better to use eqs. (16) and (17) directly rather than their logarithmic transforms for the following reason:

If a ratio is defined as γ , then

$$\text{var} \{ \ln \gamma \} = \gamma^{-2} \text{var} \{ \gamma \}.$$

Thus, $\text{var} \{ \gamma \}$ is smaller than $\text{var} \{ \ln \gamma \}$ only if γ is less than unity. Since r_1 and r_2 are ratios less than one, nonlinear regression was used. The routine employed in this work is the Marquardt method,³⁰ which is a combination of linearization and the steepest-descent method.

Tables III and IV show the analyses of variance for the nonlinear estimations of eqs. (16) and (17), respectively. Pure error sum-of-squares was obtained from replicates at 70°C and -50°C . In both cases, the ratio between the lack-of-fit and the pure error mean squares is less than the corresponding F value at 95% confidence level. This indicates the absence of lack-of-fit at that level.

TABLE III
Analysis of Variance for the Nonlinear Fit of Equation (16)

Polymerization temp., °C	$\frac{k_{st}}{k_{ss}}$	$\left(\frac{k_{st}}{k_{ss}}\right)_{\text{fitted}}$	Residuals
70	0.783	0.779	0.004
70	0.778	0.779	-0.001
70	0.780	0.779	0.001
70	0.778	0.779	-0.001
50	0.758	0.759	-0.001
45	0.760	0.763	-0.003
40	0.742	0.746	-0.004
35	0.770	0.768	0.002
30	0.745	0.743	0.002
-10	0.680	0.681	-0.001
-30	0.638	0.646	-0.008
-50	0.587	0.588	-0.001
-50	0.585	0.588	-0.003
-50	0.587	0.588	-0.001
-50	0.589	0.588	0.001

Source	Sum of squares SS	Degrees of freedom ν	Mean squares $MS = SS/\nu$	$\frac{(\text{L.O.F.})MS}{(\text{P.E.})MS}$	$F_{0.95}$ ($\nu_{\text{L.O.F.}}, \nu_{\text{P.E.}}$)
Residuals	130×10^{-6}	13	10×10^{-6}		
Pure error (P.E.)	25×10^{-6}	6	4.17×10^{-6}	3.6	4.21
Lack of fit (L.O.F.)	105×10^{-6}	7	15×10^{-6}		

TABLE IV
Analysis of Variance for the Nonlinear Fit of Equation (17)

Polymerization temp., °C	$\frac{k_{ii}}{k_{is}}$	$\left(\frac{k_{ii}}{k_{is}}\right)_{\text{fitted}}$	Residuals
70	0.924	0.920	0.004
70	0.916	0.920	-0.004
70	0.920	0.920	0.000
70	0.916	0.920	-0.004
50	0.830	0.822	0.008
45	0.783	0.791	-0.008
40	0.785	0.778	0.007
35	0.734	0.744	-0.010
30	0.720	0.709	0.011
-10	0.517	0.508	0.009
-30	0.400	0.400	0.000
-50	0.313	0.309	0.004
-50	0.305	0.309	-0.004
-50	0.313	0.309	0.004
-50	0.317	0.309	0.008

Source	Sum of squares SS	Degrees of freedom ν	Mean squares $MS = SS/\nu$	$\frac{(\text{L.O.F.})MS}{(\text{P.E.})MS}$	$F_{0.95}$ ($\nu_{\text{L.O.F.}}, \nu_{\text{P.E.}}$)
Residuals	639×10^{-6}	13	49.2×10^{-6}		
Pure error (P.E.)	120×10^{-6}	6	20×10^{-6}	3.71	4.21
Lack of fit (L.O.F.)	519×10^{-6}	7	74.1×10^{-6}		

TABLE V
Differential Enthalpy and Entropy Changes for Tactic Placements in PVC

	Present work	Pham et al. ²⁵
$\Delta(\Delta H)_{S^I}^a$	694 ± 34	560 ± 50
$\Delta(\Delta S)_{S^I}^a$	1.68 ± 0.13	1.2 ± 0.2
$\Delta(\Delta H)_{is^i}$	1399 ± 74	1300 ± 100
$\Delta(\Delta S)_{is^i}$	3.93 ± 0.14	4.8 ± 0.2
$\Delta(\Delta H)_{ss^i}$	341.2 ± 57	200 ± 100
$\Delta(\Delta S)_{ss^i}$	0.54 ± 0.07	0.6 ± 0.1

^a From previous publication.²⁹

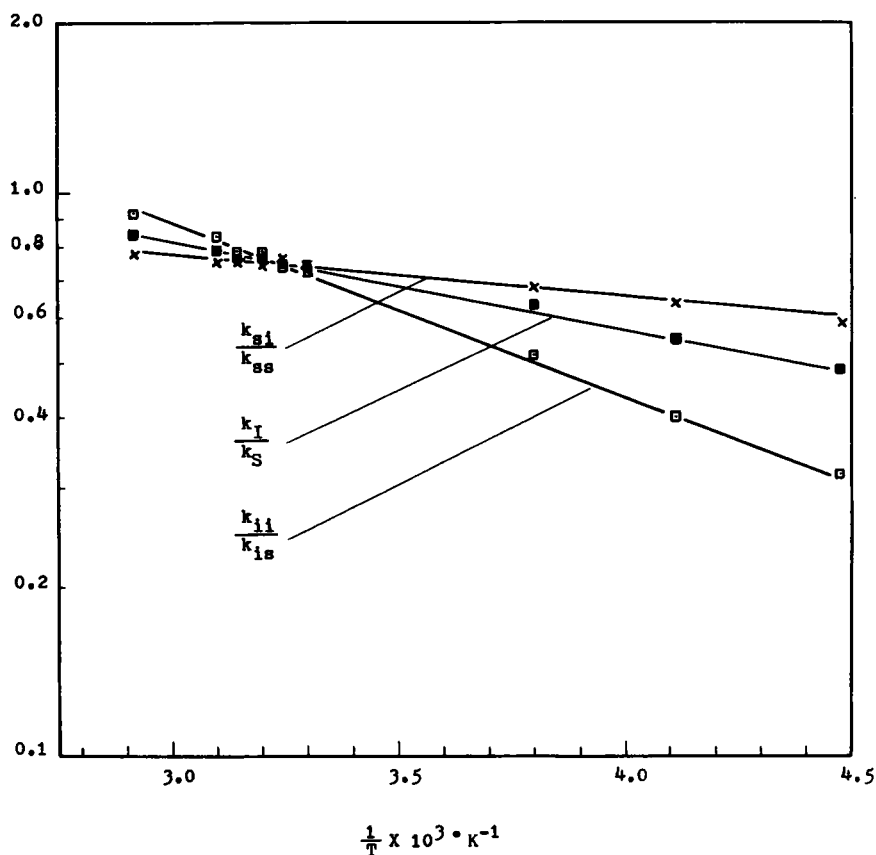


Fig. 4. Arrhenius plots for k_{SI}/k_{SS} , k_I/k_S , and k_{II}/k_{IS} .

Arrhenius plots for k_I/k_S , k_{SI}/k_{SS} , and k_{II}/k_{IS} are shown in Figure 4. The computed parameter values are listed in Table V along with the values reported by Pham et al.²⁵ These values suggest that the syndiotactic placement is always favored whether the chain end is syndiotactic or isotactic, with higher driving force [larger $\Delta(\Delta H)$ and $\Delta(\Delta S)$] in the latter case.

The relationship between the kinetic differential enthalpy change $\Delta(\Delta H)_{S^I}$ and the thermodynamic differential enthalpy change $\Delta(\Delta H^0)_{S^I}$ is given by³¹

$$\Delta(\Delta H)_{S^I} = \lambda \cdot \Delta(\Delta H^0)_{S^I}$$

where λ is a constant usually taken as 0.4. Using the above equation, $\Delta(\Delta H^0)_s^I$ was calculated to be

$$\Delta(\Delta H^0)_s^I = 1735 \pm 85 \text{ cal/mole.}$$

This value is in excellent agreement with Fordham et al.,^{32,33} who estimated that $\Delta(\Delta H^0)_s^I$ should be in the range of 1.4 to 1.9 kcal/mole.

Nomenclature

<i>s</i>	syndiotactic placement; also triad syndiotacticity
<i>i</i>	isotactic placement; also triad isotacticity
<i>h</i>	triad heterotacticity
<i>S</i>	diad syndiotacticity
<i>I</i>	diad isotacticity
<i>P</i>	normalized probability
<i>k</i>	reaction rate constant
<i>R</i>	universal gas constant
r_1, r_2	parameters defined by eqs. (14), (15)
<i>G</i>	ratio r_1/r_2
<i>T</i>	absolute temperature, °K
$\Delta(\Delta H)$	differential enthalpy change (kinetic)
$\Delta(\Delta H^0)$	differential enthalpy change (thermodynamic)
$\Delta(\Delta S)$	differential entropy change (kinetic)
var	variance

Greek Symbols

ρ, η	persistence ratios
τ, δ	chemical shifts, ppm

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