

Stereoregularity of PVC Studied by ^{13}C NMR

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Synopsis

The proton decoupled ^{13}C NMR spectra of PVC polymerized at various temperatures were obtained using a 150-MHz NMR spectrometer. Chemical shift changes induced by a solvent effect were utilized to allow the detection of the six possible tetrads. Eight of ten possible pentads were also observed. The relative areas of tetrads and triads indicate that the polymerization of PVC above -20°C is Bernoullian.

INTRODUCTION

The configuration of poly(vinyl chloride) (PVC) in solution has been studied extensively using proton and ^{13}C nuclear magnetic resonance (NMR).¹⁻¹¹ With carefully selected proton coupling constants, chemical shifts and line widths, the proton NMR spectra can be simulated and analyzed in terms of pentads for the α protons and tetrads for the β protons.⁴ On the other hand, it has been shown that triads and tetrads could be more precisely and directly measured by ^{13}C NMR.⁵⁻¹¹

The validity of Bernoulli trial statistics in describing the propagation mechanism of PVC polymerization under various temperatures has been tested by several workers^{1,5} using NMR. Proton NMR study¹ showed that the deviation appears for PVC polymerized below -10°C . In their ^{13}C NMR study, Pham et al.⁵ observed the deviation for temperatures lower than -30°C or higher than 25°C . The discrepancy may be due to the poor separation of the peaks.

From the study of model compounds, it was suggested^{12,13} that the observed relative chemical shifts of methylene carbons was a function of the population of gauche conformations in methylene tetrads. The distribution of the rotational conformations depends on configuration, temperature, and the nature of solvent, as demonstrated by Ando and his co-workers.⁸⁻¹⁰ Therefore the overlapping of the resonances can be removed by choosing a proper solvent.

The purpose of this work is to study the tacticity of the PVC polymerized at various temperatures by utilizing the solvent effect.

EXPERIMENTAL

The pulsed, proton decoupled ^{13}C FT-NMR spectra were obtained at 37.7 MHz using a Nicolet NTC-150 spectrometer. The instrument condition was spectral width, 1 kHz; acquisition time, 8.2 sec; 90° pulse width, 21 μsec ; 1024 transients; delay between transients, 9 sec.

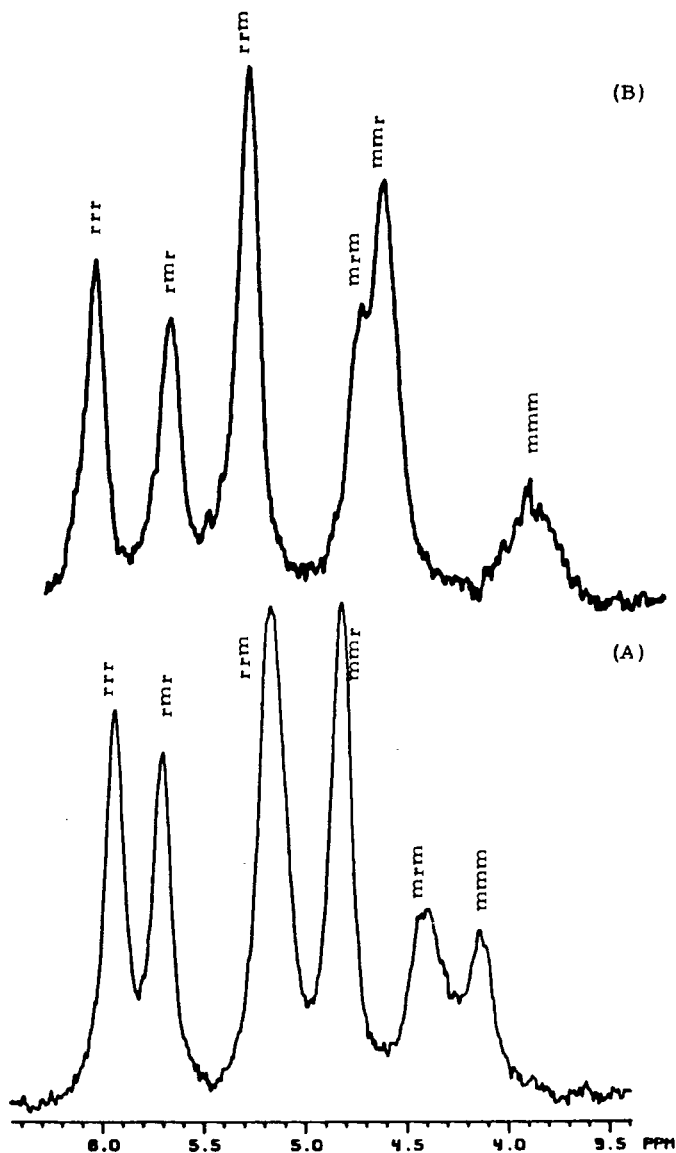


Fig. 1. ^{13}C NMR spectra of methylene carbon of PVC in *o*-dichlorobenzene at 100°C . (A) and (B) indicate the solution with and without DMSO, respectively. The chemical shifts are in ppm downfield from external DMSO.

The spin-lattice relaxation times T_1 of methylene and methyne carbons in PVC depend on the configurations and conformations.¹⁴ The relative peak areas of each configuration sequence will be unevenly suppressed if the improper delay between pulses is used. The typical value of T_1 for methylene and methyne carbon in PVC solution are 0.07 and 0.2 sec, respectively.¹⁴ Therefore, with delay time of 9 sec, which is more than ten times T_1 of either carbon, this kind of error is very unlikely.

The spectra were obtained using 20-mm sample tubes at 100°C . All chemical

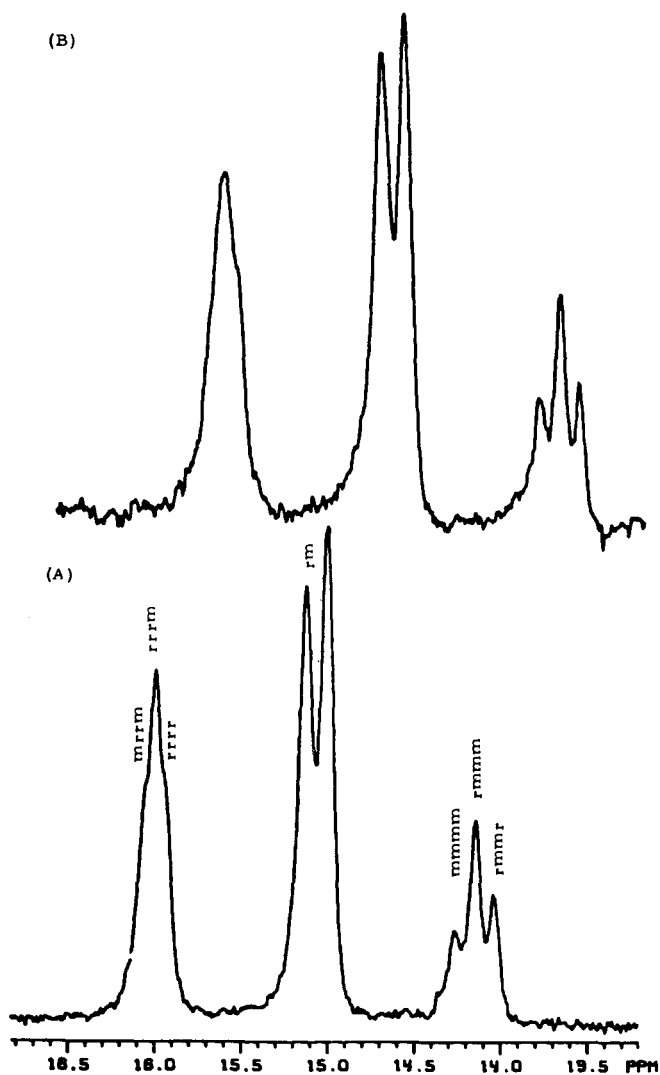


Fig. 2. ^{13}C NMR spectra of methyne carbon of PVC in *o*-dichlorobenzene at 100°C . (A) and (B) indicate the solution with and without DMSO, respectively.

shifts are relative to DMSO which is placed in a concentric tube. The PVC samples were obtained from B.F. Goodrich Chemical Co. The polymers were examined as a 5% w/v solution in a 1.4/19 mixture of DMSO and *o*-dichlorobenzene except for polymer polymerized at -20°C , which is in 2% solution. The infrared measurements were made on a Digilab FTS-14 spectrometer at a resolution of 4 cm^{-1} and 200 coadded scans.

All PVC solutions were prepared following the heat treatment recommended by Abdel-Alim and Hamielec¹⁵ in order to disintegrate the aggregates which may affect NMR measurements. The relative peak areas were measured with the curve analysis program provided by Nicolet.

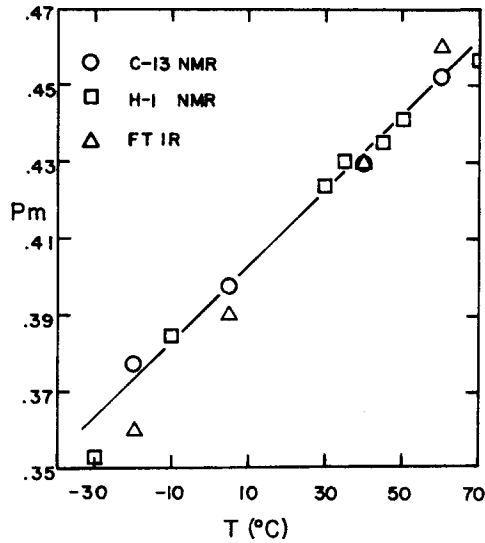


Fig. 3. P_m values of PVC as function of polymerization temperature.

RESULTS AND DISCUSSION

Figure 1 shows an example of the effect of DMSO on the high resolution ^{13}C spectra of methylene carbons of PVC polymerized at 60°C . (A) and (B) indicate solutions with and without DMSO, respectively. These two spectra clearly show the improvement in peak separation over the spectra previously reported^{5,6}

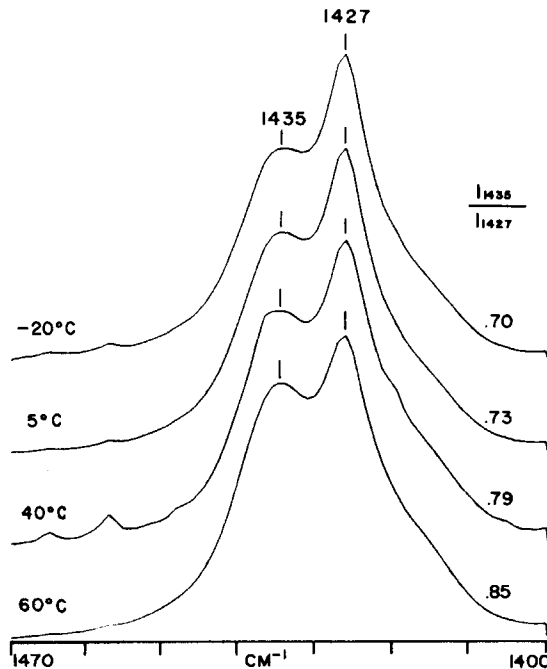


Fig. 4. Methylene deformation bands of PVC polymerized at various temperatures.

TABLE I
Effect of Polymerization Temperature on the Tacticity of Methylene Carbon in PVC

Assign- ment	60°C		40°C		5°C		-20°C	
	Ob- served	Calculated $P_m =$ 0.450	Ob- served	Calculated $P_m =$ 0.432	Ob- served	Calculated $P_m =$ 0.395	Ob- served	Calculated $P_m =$ 0.377
<i>rrm</i>	0.276	0.272	0.285	0.279	0.284	0.289	0.299	0.273
<i>mnr</i>	0.229	0.223	0.203	0.212	0.192	0.189	0.191	0.177
<i>rrr</i>	0.161	0.166	0.187	0.183	0.201	0.221	0.216	0.242
<i>rmr</i>	0.138	0.136	0.144	0.139	0.144	0.145	0.146	0.146
<i>mrm</i>	0.109	0.111	0.105	0.106	0.113	0.094	0.086	0.081
<i>mmm</i>	0.094	0.091	0.073	0.081	0.063	0.062	0.059	0.054

especially in Figure 1(A), where *mnr* and *mrm* resonances are well separated. The six well resolved peaks are directly attributed to the six possible tetrad configurations. After curve resolving, the relative area of those peaks are given in Table I. The assignment is based on the comparison of the observed areas with the calculated values from Bernoullian statistics.

Figure 2 shows the resonances of the methyne carbons where (A) and (B) indicate the same solutions as in Figure 1. Since there is no peak overlap among triads, the triad concentration can be easily obtained by integration as given in Table II.

The solvent effect as shown in Figures 1 and 2 has been studied by Ando et al.^{8,9} In their studies the roles of solvation, dielectric media, electron density distribution, and the probability of rotational isomeric states have been taken into consideration. Recently, Tonelli et al.¹⁷ have used γ effects and successfully predicted the chemical shift pattern of the methyne carbon. However, the prediction is not successful for methylene carbon because of complicated solvent-polymer interactions. In this article, the solvent effect was utilized to obtain well-separated peaks; therefore the relative population of the configurations can be determined more precisely.

From the methyne resonance, as shown in Figure 2, the P_m , probability of meso

TABLE II
Triad Assignments and Relative Areas for Methylene Carbon of PVC

Assignment	Bernoullian probability	Observed and calculated concentration			
		60°C	40°C	5°C	-20°C
<i>rr</i>	$(1 - P_m)^2$	0.307 (0.303) ^a	0.325 (0.333)	0.364 (0.366)	0.382 (0.388)
<i>rm</i>	$2P_m(1 - P_m)$	0.490 (0.495)	0.489 (0.491)	0.481 (0.478)	0.476 (0.470)
<i>mm</i>	P_m^2	0.203 (0.203)	0.186 (0.186)	0.156 (0.156)	0.142 (0.142)
P_m ^b		0.451	0.431	0.395	0.377
P_r ^b = 1 - P_m		0.550	0.568	0.605	0.623
ρ_m ^c = $P_m P_r / P_{rm}$		1.02	1.01	0.991	0.979
η_r ^c = $P_{rr} /$ P_r^2		1.01	0.999	0.992	0.984

^a Calculated Bernoullian concentration.

^b Probability of meso (*m*) and resmic (*r*) addition.

^c Persistence ratio.

addition can be obtained for each polymer. The results are shown in Table II and Figure 3. Figure 3 shows that ^{13}C NMR results are in good agreement with those obtained from proton NMR.¹ These P_m values then are used in the calculation of the Bernoullian tetrads concentration as given in Table I. The comparison of the experimental and calculated values indicates that propagation of vinyl chloride above -10°C seems to be Bernoullian in tacticity. The same conclusion can also be drawn from the calculation of the persistence ratios ρ_m and η_r , as listed in Table II.

Figure 3 also shows the comparison of the P_m values with those obtained from an IR study. In the IR spectra as shown in Figure 4, the CH_2 deformation bands at 1427 and 1435 cm^{-1} were assigned to the crystalline and amorphous phases, respectively.¹⁶ The intensity of 1435 and 1427 cm^{-1} bands indicate the relative degree of crystallinity. Following the procedure given by Germar et al.,¹⁸ the degree of syndiotacticity can be calculated using the relative crystallinity and ΔE , the energy difference between the two syndiotactic conformations gg and tt . The ΔE values used in this calculation are due to Nakajima et al.¹⁹ The IR results agree well with those calculated from ^{13}C NMR and proton NMR. The IR values given by Pham⁵ are generally higher than our results. This is not unexpected, as shown by the Tabb and Koenig study,²⁰ which found that the relative crystallinity of PVC is strongly dependent on the thermohistory of the film and the method of sample preparation. In our study, special precautions were taken to ensure that the films were prepared with the same thermohistory.

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References

1. A. H. Abdel-Alim, *J. Appl. Polym. Sci.*, **19**, 1227 (1975), and references cited therein.
2. A. M. Hassan, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 655 (1974).
3. L. Cavalli, G. C. Borsini, G. Carraro, and G. Confalonieri, *J. Polym. Sci. Part A-1*, **8**, 801 (1970).
4. F. Heatley and F. A. Bovey, *Macromolecules*, **2**, 241 (1969).
5. Q. T. Pham, J. L. Millan, and E. L. Madruga, *Makromol. Chem.*, **175**, 945 (1974).
6. C. J. Carman, *Macromolecules*, **6**, 725 (1973).
7. Y. Inoue, I. Ando, and A. Nishioka, *Polym. J.*, **3**, 246 (1972).
8. I. Ando, A. Nishioka, and T. Asakura, *Makromol. Chem.*, **176**, 411 (1975).
9. I. Ando, Y. Kato, and A. Nishioka, *Makromol. Chem.*, **177**, 2750 (1976).
10. I. Ando, Y. Kato, M. Kendo, and A. Nishioka, *Makromol. Chem.*, **178**, 803 (1977).
11. J. Schaefer, *Macromolecules*, **4**, 110 (1971).
12. C. J. Carman, A. R. Tarpley, and J. H. Goldstein, *J. Am. Chem. Soc.*, **93**, 2864 (1974).
13. E. F. Mooney and P. H. Winson, *Ann. Rev. NMR Spectrosc.*, **2**, 157 (1969).
14. F. C. Schilling, *Macromolecules*, **11**, 1290 (1978).
15. A. H. Abdel-Alim and A. E. Hamielec, *J. Appl. Polym. Sci.*, **16**, 1093 (1972); **17**, 3033 (1973).
16. J. L. Koenig and M. K. Antoon, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 1379 (1977).
17. A. E. Tonelli, F. C. Schilling, W. H. Starnes, L. Shepherd, and I. M. Plitz, *Macromolecules*, **12**, 78 (1979).
18. H. Germar, K. H. Hellwege, and U. Johnsen, *Makromol. Chem.*, **60**, 106 (1963).
19. A. Nakajima, H. Hamada, and S. Hayashi, *Makromol. Chem.*, **95**, 40 (1966).
20. D. L. Tabb and J. L. Koenig, *Macromolecules*, **8**, 929 (1975).

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