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# Contribution to the Solvent and Temperature Dependence of C-13 NMR Spectra from Poly(vinyl chloride)

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## Summary

Unique resolution is observed in C-13 nmr spectra of the methine carbon of poly(vinyl chloride) soluble in 1,4-dioxane.

## Introduction

C-13 nmr spectroscopy has been applied very successful to the determination of configurational monomer sequences in poly(vinyl chloride) (CARMAN et al.(1971), ANDO et al.(1976), STARNES et al.(1979)). Usually, spectroscopic investigations are performed in o-dichlorobenzene at 400 K which is near the thermal decomposition of the polymer.

## Results and Discussion

C-13 nmr spectra have been determined in numerous solvents at temperatures between 200 K and 470 K. The solvent list contains chloroalkanes, ethers, dimethylamides, ketones, chlorinated benzenes and others, e.g. nitrobenzene and esters of pthalic acid. Distinct spectra of the methine and methylene carbon with different resolution have been obtained and partially assigned. From a more practical point of view it is not necessary to apply high temperatures to observe all possible configurational pentad sequences. It is recommended to use chloroalkanes and ethers at temperatures below 375 K where thermal degradation is negligible during scanning times up to 6 h.

In dimethylsulfoxide at 398 K and dimethylformamide at 388 K nearly identical spectra are recorded. Spectra in solvent mixtures are mostly influenced by overlapping of resonance signals. As shown in fig.1 the resolution of the methine carbon in the -CHCl- group is sensitive to solvent changes even in solvents with similar dipole moments. This is different from the spectroscopic properties of the low molecular weight model compound, the methine carbon of which TONELLI (1979) found to be independent from solvent influences. Complete details will be given in a subsequent paper (ELGERT et al.(1981)).

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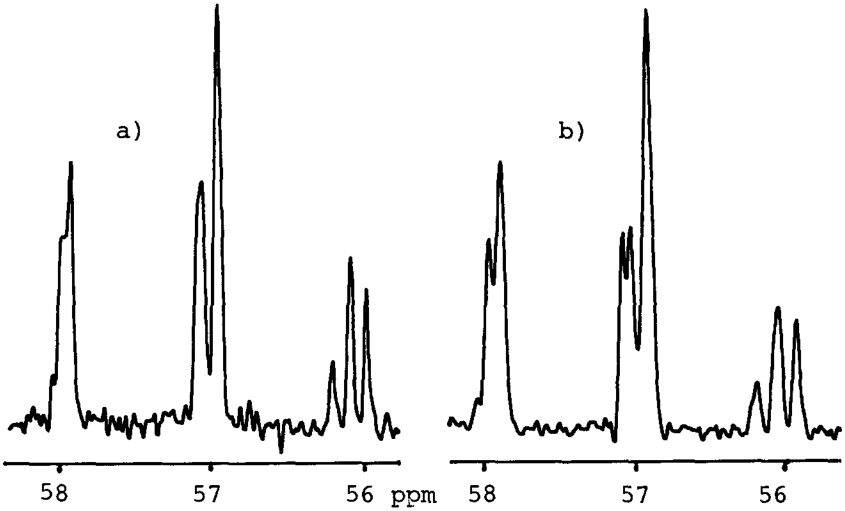

Figure 1 C-13 NMR Spectra of Poly(vinyl chloride)
a) solvent: 1,2-dichloroethane, $\mu = 5.7 \cdot 10^{-30}$ Cm
b) solvent: tetrahydrofurane, $\mu = 5.8 \cdot 10^{-30}$ Cm
temperature: 330 K; concentration: 10% (w/v); C-13 frequency: 67.9 MHz, Bruker WH 270; sweep: 6 kHz; pulse: 25 µsec; pulse delay: 10 sec; chemical shift in ppm, TMS = o ppm; dipole moments taken from McCLELLAN (1963)

C-13 nmr spectra of polymers are interpreted as the time average of solvent and temperature dependent populations of chain conformers generated by long- as well short-range interactions between polymer segments and solvent.

Unique resolution in C-13 spectra of poly(vinylchloride) is observed for the methine carbon of samples soluble in 1,4-dioxane at 370 K as shown in fig.2. The assignment of the spectrum in fig.2 has been made by comparison of experimental and calculated line intensities based on a Bernoullian distribution of configurational monomer sequences. From triad intensities Bernoullian statistic is confirmed by $d = 2 \cdot R(1-R)/MR = 0.98$.

In principle, in the case of Bernoullian statistic it is not possible by this way to assign resonance signals unambigously to sequences with equal numbers of M and R monomer placements, e.g. MMRR and MRMR. The assignment given in table 1 ( chemical shifts in ppm ) differs from calculations of TONELLI (1980). However, he predicted the chemical shift of the isotactic and syndiotactic heptades in a reverse order as given in fig.2 and table 1 (e.g. signals 11, 12, 13). These signals can be assigned unambigously from line intensities in the spectrum.

Table 1 Assignment of the C-13 NMR Spectrum

| Signal | Chemical Shift | Configurational Sequence | Sequence Distribution | |
|---|---|---|---|---|
| | | | calc. | exper. |
| 1 | 58.20 | R M R R M R | 0.020 | 0.023 |
| 2 | 58.11 | R M R R M M | 0.029 | 0.034 |
| 3 | 58.02 | M M R R M M | 0.104 | 0.103 |
| | | R R R R M M | | |
| | | R R R R M R | | |
| 4 | 57.94 | M R R R M M | 0.068 | 0.074 |
| | | M R R R M R | | |
| 5 | 57.83 | R R R R | 0.111 | 0.091 |
| 6 | 57.34 | M M M R M M | 0.035 | 0.037 |
| | | M M M R M R | | |
| 7 | 57.25 | R M M R M M | 0.136 | 0.114 |
| | | R M M R M R | | |
| | | M R M R M M | | |
| | | M R M R M R | | |
| 8 | 57.17 | R R M R M R | 0.068 | 0.073 |
| | | R R M R M M | | |
| 9 | 57.10 | M M R R | 0.100 | 0.087 |
| 10 | 57.00 | R M R R | 0.183 | 0.204 |
| 11 | 56.49 | R M M M M R | 0.011 | 0.011 |
| 12 | 56.43 | M M M M M R | 0.015 | 0.015 |
| 13 | 56.37 | M M M M M M | 0.004 | 0.004 |
| 14 | 56.26 | R M M M R R | 0.049 | 0.050 |
| | | R M M M R M | | |
| 15 | 56.20 | M M M M R R | 0.036 | 0.035 |
| | | M M M M R M | | |
| 16 | 56.04 | R M M R | 0.059 | 0.054 |
| 17 | 47.85 | R R R | 0.193 | 0.172 |
| 18 | 47.55 | R M R | 0.141 | 0.144 |
| 19 | 46.85 | R R M | 0.282 | 0.288 |
| 20 | 46.89 | M M R | 0.204 | 0.220 |
| 21 | 46.62 | M M R | | |
| 22 | 46.10 | M R M | 0.102 | 0.106 |
| 23 | 45.80 | M M M | 0.075 | 0.062 |

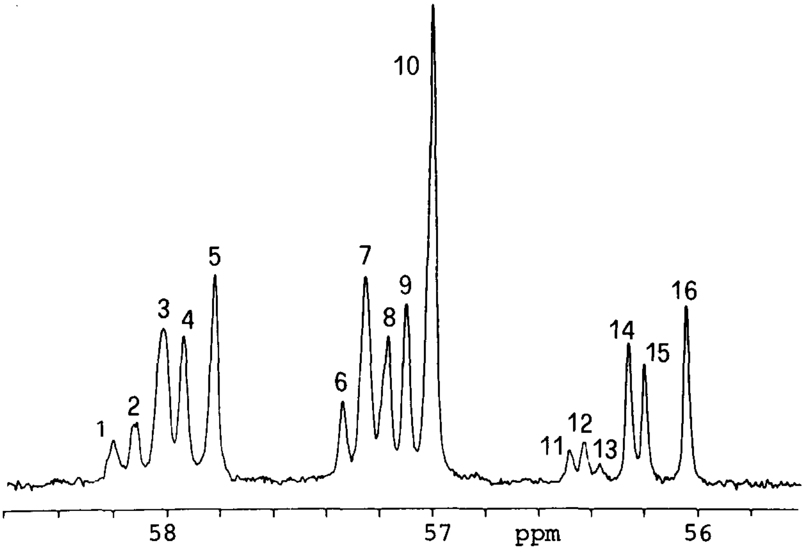

Figure 2 C-13 NMR Spectrum of Poly(vinyl chloride)

Resonance region of the methine carbon, -CHCl-group solvent: 1,4-dioxane-$d_8$; temperature: 370 K; C-13 frequency: 125.8 MHz, Bruker WH 500; concentration: 10% (w/v); chemical shifts in ppm, TMS = 0 ppm

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