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Carbon-13 NMR Investigation of Vinyl-chloride/Vinyl-acetate Copolymers

The Influence of Copolymerization on the Tacticity of PVC Sequences

K. Schlothauer and I. Alig

Department of Physics, Technical College Leuna-Merseburg, Leuna-Merseburg, German Democratic Republic

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SUMMARY

Copolymers of vinyl chloride with vinyl acetate have been studied by Carbon 13 NMR specroscopy to determine the influence of the copolymerization on the tacticity of PVC sequences. Diad and triad resonances have been assigned in terms of constitutional as well as of configurational sequences. The syntacticity of the PVC sequences appears to decrease with increasing comonomer content. This decrease might be caused by a steric hindrance which would favour a more atactic addition.

The influence of the copolymerization on the stereoregularity of vinyl chloride sequences has been previously studied for vinyl chloride (VC) vinyl acetate (VAc) copolymers by ROSEN and MARSHALL /1/.
The effect of incorporating VAc on the stereoregularity was measured by the ratio of the 635 cm^{-1} and 692 cm^{-1} infrared absorption bands and by means of X-ray powder diffraction patterns. The infrared absorption bands of PVC at 635 cm^{-1} was assigned to crystalline syndiotactic segments, the band at 692 cm^{-1} to noncrystalline atactic segments in the polymer chain.
As a result the authors /1/ found a decreasing D_{635}/D_{692} ratio for an increasing amount of VAc in the copolymer.
GUZMAN-PEROTE and MILLAN /2/ studied the tacticity of PVC sequences in copolymers of vinyl chloride (mole fraction higher than 0.9) with diethyl fumarate, isobutylene and vinyl bromide as a function of both the copolymer composition and the comonomer nature by the ratio of infrared absorption bands at 1428 cm^{-1} and 1434 cm^{-1}. According to GERMAR et al. /3/ they determined the i. r. absorbance ratio $A_{1428\ cm^{-1}}/A_{1434\ cm^{-1}}$ as a relative measure of the ratio syndio diads/iso diads. The number average weights of copolymers were determined by osmometry.
From the results it follows that the relative proportion of syndiotactic diads decreases as the comonomer content increases and that the dependence decreases from diethyl fumarate to vinyl bromide. Since the comonomer volume decreases in the same way, the tacticity decrease might be due to a steric hindrance which would prevent the syndiotactic structure from propagating during the co-

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polymerization. The steric hindrance increases with the increasing number of alternances. Both the comonomer volume and the number of alternances give rise to the same effect. On the basis of their experiments, the authors /2/ wasn't able to separate the effects, but the influence of the copolymerization on the tacticity of PVC sequences is established.

In the present work Carbon-13 NMR spectroscopy was used to determine the influence of vinyl acetate comonomer (mole fraction lower than 0.2) on the tacticity of vinyl chloride sequences.

Monomer placement assignments (diads, triads, tetrads) are made after observing a close conformity of methylene and methine carbon intensity distribution.

There is no peak overlap in the methine carbon resonances of vinyl chloride centered compositional triads (58.2-56.3 ppm) and their three components have been attributed to syndio-, hetero- and isotactic triads rr, rm+mr, mm, in the order of increasing field. Their integrated intensities are proportional to the corresponding tactic sequence concentrations, the propabilities (peak area divided by the total resonance area of the observed carbon) are denoted as Prr, Pmr and Pmm , where the heterotactic triad probabilities refer to the observed values (i. e., rm + mr, since these are indistinguisable) and

$$P_{rr} + P_{mr} + P_{mm} = 1 \qquad (1)$$

Triad data are necessary and sufficient to test for conformance to BERNOULLIAN statistics, but tetrad data are necessary to test first-order MARKOV statistics if it is found that the former treatment is inappropriate /4/.

The bad resolution of the methylene carbon resonances did not allow precise attributions of the tetrad stereo sequences rrr, rmr, mrr + rrm, mrm, rmm+mmr, mmm (47.8 ...45.2 ppm). From the following diad-triad relations /4/

$$\begin{aligned} P_r &= P_{rr} + P_{rm}/2 \\ P_m &= P_{mm} + P_{rm}/2 \qquad (2) \\ P_r &+ P_m = 1 \end{aligned}$$

we calculated the ratio of syndio- to isotactic diads P_r/P_m. For BERNOULLIAN statistics

$$\begin{aligned} P_{rr} &= P^2 \\ P_{rm} &= 2P_rP_m \qquad (3) \\ P_{mm} &= P_m^2 = (1 - P_r^2) \end{aligned}$$

and the persistance ratio p /5/

$$p = 2P_rP_m/P_{rm} \qquad (4)$$

is close to unity.
The ratio P_r/P_m, determined by Carbon-13 NMR spectroscopy, has a good correlation to the above i. r. absorbance ratio /5/. From methylene carbon compositional diads probabilities P_{AA}, P_{AB}, P_{BB} (A:VC, B:VAc, chemical shift 47.0, 43.4, 39.8 ppm) the composition sequence distribution parameters we calculated:
The average number of monomer sequence alternances per 100 monomer units (run number R as reported by HARWOOD /6/)

$$R = 100P_{AB} , \qquad (5)$$

the mole fraction P(A), P(B) of units A, B

$$\begin{aligned} P(A) &= P_{AA} + P_{AB}/2 \\ P(B) &= P_{BB} + P_{AB}/2 \qquad (6) \\ P(A) &+ P(B) = 1 \end{aligned}$$

the average block length in monomer units

$$\begin{aligned} l_A &= 1 + 2P_{AA}/P_{AB} \\ & \qquad\qquad\qquad (7) \\ l_B &= 1 + 2P_{BB}/P_{AB} \end{aligned}$$

and the compositional sequence persistance ratio, according to stereo sequence treament,

$$o = 2P(A)P(B)/P_{AB} \qquad (8)$$

Figure 1 shows the Carbon-13 NMR spectra of sample 4 (P(A) = 0.8, P(B) = 0.2) in the range 65 to 35 ppm.

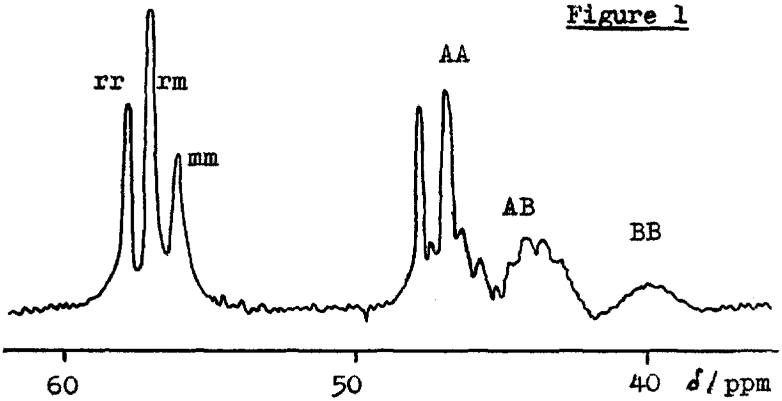


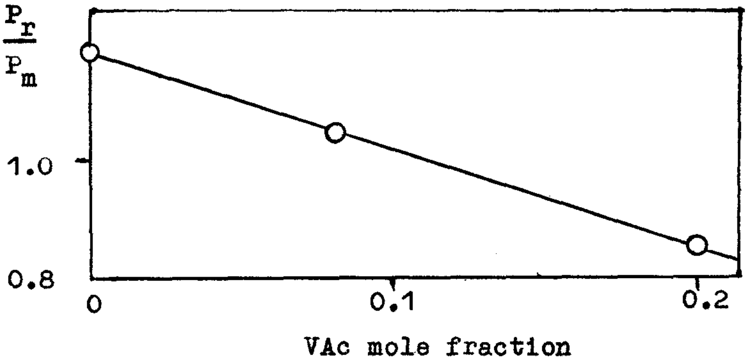
Figure 1

The results of stereosequence distribution and compositional sequence distribution analysis are summarized in the following table:

	Sample			
	1	2	3	4
P_{rr}	0.29	0.29	0.27	0.21
P_{rm}	0.50	0.44	0.47	0.49
P_{mm}	0.21	0.27	0.26	0.30
P_r	0.54	0.51	0.51	0.46
P_m	0.46	0.49	0.49	0.54
p	0.99	1.14	1.06	1.01
P_r/P_m	1.17	1.04	1.04	0.85
P_{AA}	1.0	0.87	0.86	0.67
P_{AB}	-	0.11	0.13	0.26
P_{BB}	-	0.02	0.01	0.07
P(A)	1.0	0.92	0.92	0.8
P(B)	0	0.08	0.08	0.2
R	-	11	13	26
o	-	1.3	1.13	1.23
l_A	-	16.8	14.2	6.2
l_B	-	1.4	1.2	1.5

As expected from /2/ we found that the relative proportion of syndiotactic diads decreases as the comonomer content increases, s. Figure 2.

Figure 2: Tacticity versus vinyl acetate content



For all samples the persistance ratios for stereosequence distribution and compositional sequence distribution are closed to unity. Only sample 2 has a small deviation from BERNOULLIAN statistics.

Carbon-13 NMR spectra were recorded at 22.635 MHz on a Bruker HX 90 spectrometer with B-NC 12 NMR Fourier transform accessory. Typical conditions were as follows: 3..5 . 10^4 scans, 4.5 µs pulse width (lower than 90° flip angle), 0.9 s aquisition time, 4.5 kHz sweep width, 4 K data points for the real spectrum, broad band proton decoupling, 5..10 Vol. % polymer in THF - solution, 60 °C probe temperature and internal HMDS as reference.
The samples are products of Buna factories.

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