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Sequence Analysis of Head-Head Vinyl Homopolymers by ^{13}C NMR Spectroscopy

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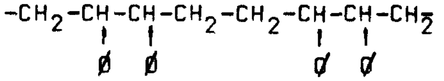
Several papers have recently dealt with the synthesis, properties and spectra of head-head(H-H) polymers (WEILL AND VOGL 1978 b). It has been suggested that in H-H vinyl homopolymers, the nmr signals of the tail-tail methylene carbons would be the most useful for the study of configurational sequences (WEILL AND VOGL 1978 a).



$$-CH_2-\underset{\phi}{CH}-\underset{\phi}{CH}-CH_2-CH_2-\underset{\phi}{CH}-\underset{\phi}{CH}-CH_2-$$

H-H Polystyrene

The ^{13}C NMR spectrum of H-H polystyrene was analysed assuming a tetrad chemical shift sensitivity for the tail-tail methylene carbons. Six tetrad placements were envisioned and the observed spectrum was interpreted as arising out of a total of six signals (four of equal intensity and two of twice the intensity when Pm = 0.5, Pm being the probability of 'meso' addition).

However, theoretically one must expect a total of eight signals from the six possible tetrads for the methylene carbons. While the symmetric tetrads (mMm, rMr, rRr, mRm,) shall give a total of four signals (one each), the unsymmetric tetrads(mMr,mRr)

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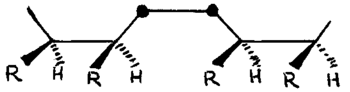
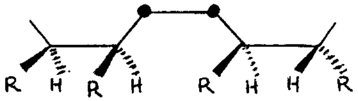
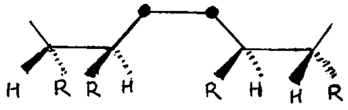
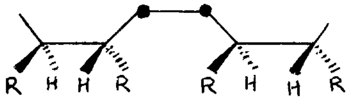
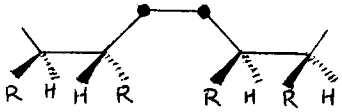
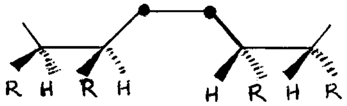
SCHEME

TETRAD PLACEMENTS IN H-H VINYL HOMOPOLYMERS

Polymer Segment	Tetrad[a]	No. of signals[b]	Probability
	mMm	1	${}^{H}\mathrm{Pm}^{2}\ {}^{T}\mathrm{Pm}$
	mMr	2	$2\,{}^{H}\mathrm{Pm}(1-{}^{H}\mathrm{Pm})\,{}^{T}\mathrm{Pm}$
	rMr	1	${}^{T}\mathrm{Pm}(1-{}^{H}\mathrm{Pm})^{2}$
	rRr	1	$(1-{}^{H}\mathrm{Pm})^{2}(1-{}^{T}\mathrm{Pm})$
	rRm	2	$2\,{}^{H}\mathrm{Pm}(1-{}^{H}\mathrm{Pm})$ $(1-{}^{T}\mathrm{Pm})$
	mRm	1	${}^{H}\mathrm{Pm}^{2}(1-{}^{T}\mathrm{Pm})$

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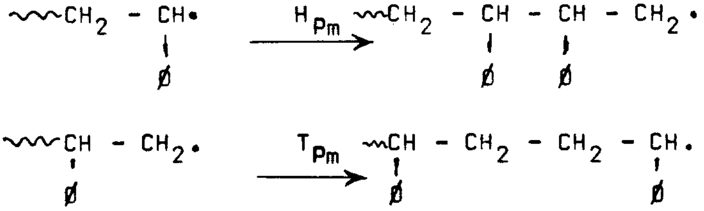
[a] 1,2 configurations are denoted by m (meso) and r (racemic) and 1,4 configurations by M(meso) and R (racemic); A different notation was employed by Weill and Vogl. A polymer segment - R - R - O - O - R - R - was designated mmm: but strictly speaking it must be rrr;

[b] As usual it is assumed that the different conformations possible for a given configurational sequence can be attained and no restriction of rotation of bonds exists.

shall also give four signals (two each) making a total of eight signals (SCHEME). The observed spectrum seems to be in agreement with this argument. Hence in H-H polymers the number of expected signals will not be equal to the number of n-ads for a given configurational sequence (RANDALL 1977).

By considering the following imaginary propagation steps for a H-H vinyl homopolymer, Bernoulli probabilities of various tetrads could be calculated.



$$\sim CH_2-\underset{\phi}{CH}\cdot \xrightarrow{^{H}P_m} \sim CH_2-\underset{\phi}{CH}-\underset{\phi}{CH}-CH_2\cdot$$

$$\sim\underset{\phi}{CH}-CH_2\cdot \xrightarrow{^{T}P_m} \sim\underset{\phi}{CH}-CH_2-CH_2-\underset{\phi}{CH}\cdot$$

^{H}Pm and ^{T}Pm are the probabilities of meso addition, of a monomer 'head - on' and 'tail-on' respectively. Assuming $^{T}Pm = 0.5$, we arrive at identical results with those of Weill and Vogl. When $^{T}Pm = {}^{H}Pm = 0.5$, eight signals of equal intensity would be obtained.

REFERENCES

RANDALL, J.C.: Polymer sequence determination - Carbon - 13 NMR Method, New York, San Francisco, London: Academic Press 1977.

WEILL, G, and VOGL, O. : Polymer Bulletin, 1, 181 (1978 a).

WEILL, G, and VOGL, O. : Polymer Bulletin, 1, 191 (1978 b).

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