The large difference in the number of active sites for styrene (0.1%) and ethene (60% of titanium atoms) found with this catalyst strongly suggests that the reactivity with ethene must depend heavily upon the breaking-up of the performed catalyst particles into very small pieces indeed. Only thus can the very high site concentration be generated for ethene, and the lower site counts for other monomers may be explained on the basis that encapsulation of catalyst particles within growing polymer particles is faster than diffusion — with concomitant disruption of the inorganic matrix — of these larger molecules into the catalyst particles.

A Referee suggests that, alternatively, it may be that the different monomers are directly involved somehow in the formation of active sites, other than by their simple consumption, and that this involvement causes the different numbers of active sites via differing reactivities of monomers. We cannot, however, see how to distinguish these possibilities with presently available data.

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^{13}C nuclear magnetic resonance spectroscopy of polyvinylferrocene

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INTRODUCTION

Many studies have shown that ^{13}C n.m.r. is a useful tool for detecting and measuring the distributions of stereochemical configurations that can occur in polymers. Monomer placement assignments (triad, tetrad, pentad, etc.) are generally made after observing a close conformity of a methylene or methine intensity distribution with either Markovian or Bernoullian statistics.

We report in this note the stereochemical configuration of polyvinylferrocene by means of a ^{13}C n.m.r. study showing the assignment of the peaks arising from tetrad and hexad configurations.

EXPERIMENTAL

Polyvinylferrocene was prepared with butyllithium in tetrahydrofuran at 20°C[1-2]. The ^{13}C n.m.r. spectra were recorded at 25.033 MHz at approximately 120°C on a Jeol J NM PS 100. The polyvinylferrocene sample was dissolved in *ortho*(1,2-)dichlorobenzene and mono-bromo-perdeuterobenzene was added to the mixture to maintain a lock signal at 120°C.

Polyvinylferrocene spectra were accumulated with pulse spacings of 0.82 s. The spectra were ^1H noise decoupled and obtained after accumulation of 20000 transients.

RESULTS AND DISCUSSION

The point of most interest is the methylene carbon resonance (*Figure 1*) in which nine methylene resonances are present.

This observation is in itself interesting since a ^{13}C n.m.r. sensitivity to just tetrad sequences would have produced six resonances while a complete hexad sensitivity would have produced twenty resonances. Combinations of tetrad and hexad resonances are possible that will produce

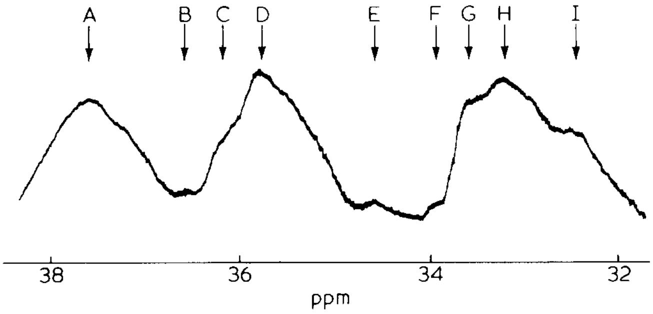

Figure 1 The methylene region of a ^{13}C n.m.r. spectrum for polyvinylferrocence at 25.033 MHz and 120°C. The ppm values are relative to TMS

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Table 1 Calculated and observed methylene intensities for polyvinylferrocene using a one-parameter Markov—model

CH_2	TMS ppm	Observed relative intensities (obtained from curve-fitting using Gaussian peak shape)		Calculated relative intensities (P_m = 0.33)		Assignment	
A	37.62	0.16		0.15		rmr	
B	36.56	0.04	−0.34	0.03	−0.30	mrrrm	−rrr
C	36.23	0.10		0.13		mrrrr	
D	35.85	0.20		0.14		rrrrr	
E	34.64	0.02		0.07		mrm	
F	33.97	0.01		0.04		mmm	
G	33.57	0.16		0.15		mmr	
H	33.28	0.19		0.13		rmrrr	−mrr
I	32.50	0.12		0.16		mmrrr mmrrm rmrrm	

nine peaks but require overlap among the various tetrad and hexad resonances.

It is possible to make CH_2 assignments in polyvinylferrocene if the methylene resonance intensity distribution conforms to a one-parameter statistical model. Bovey[3] has given the following tetrad relationships for a one-parameter Bernoullian statistical calculation:

$$\mathrm{mmm}=P_{\mathrm{m}}3$$

$$\mathrm{mmr}=2P_{\mathrm{m}}2(1-P_{\mathrm{m}})$$

$$\mathrm{rmr}=P_{\mathrm{m}}(1-P_{\mathrm{m}})^2$$

$$\mathrm{mrm}=P_{\mathrm{m}}2(1-P_{\mathrm{m}})$$

$$\mathrm{mrr}=2P_{\mathrm{m}}(1-P_{\mathrm{m}})^2$$

$$\mathrm{rrr}=(1-P_{\mathrm{m}})^3$$

where P_{m} is the probability for a meso addition.

The chemical shifts and relative intensities of resonances A–I are given in *Table 1* with the calculated intensities using a P_{m} value obtained from the relative intensity of the mmm tetrad. The assignments presented in *Table 1* were obtained by matching the calculated relative intensities with the closest observed relative intensity.

Resonances B–D were assigned to hexad sequences since the sum of B–D corresponded to the calculated rrr tetrad relative intensity.

We note the preference for racemic over meso additions for the polyvinylferrocene examined in this study. This suggests that the propagation involves a freely dissociated anionic endgroup producing a syndiotactic polymer because electrostatic or steric interactions are generally repulsive, that is, the syndiotactic form is the most thermodynamically stable configuration for the attainment of minimum steric and polar repulsions. This supports the one-parameter statistical model.

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Applicability of the Moseley equation to the determination of the degree of orientation of fibres made of crystalline polymers by the sonic method

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Sonic velocity measurements have been used in the determination of the molecular orientation of polymer fibres. Moseley[1], who suggested this method, started by assuming that the degree of crystallinity of the polymer did not affect the sonic velocity and the sonic modulus to any important degree, if measurements were made at temperatures below T_g. It follows that:

$$\alpha=1-c_u^2/c^2 \qquad (1)$$

where α is the orientation factor (degree of orientation) defined by Hermans[2] as $\alpha=(1/2)(3\overline{\cos^2\varphi}-1)$, c_u and c are the sonic velocity values in the isotropic and measured fibre, respectively, and $\overline{\cos^2\varphi}$ is the mean square value of the cosine of an angle between the axes of linear macromolecular chains and the fibre axis. Samuels[3] used basic arguments formulated by Moseley and derived an equation in which the effect of crystallinity on the fibre modulus was considered. (The fibre modulus is a function of the specific mass, ρ, and of the sonic velocity: $E=\rho c^2$.)

$$\frac{3}{2}\left(\Delta\frac{1}{E}\right)=\frac{\beta\alpha_c}{E^0_{t,a}}+\frac{(1-\beta)\alpha_a}{E^0_{t,a}} \qquad (2)$$

where $\Delta(1/E)=1/E_{u(\beta)}-1/E$; $E_{u(\beta)}$ is the modulus of elasticity of the isotropic fibre with degree of crystallinity (volume fraction of the crystalline phase) β; E is the modulus of the measured sample; α_c and α_a are the degrees of orientation of the crystalline and amorphous phases, respectively; and $E_{t,c}$ and $E_{t,a}$ are the transverse moduli of elasticity of the hypothetical, ideally-oriented, crystalline and amorphous fibres, respectively.

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