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.

REFERENCES

1 Fitzgerald, W. P. Jr. *Ph.D. Thesis* Purdu University, West Lafayette, Indiana, 1963
2 Haies, G. F. and Young, F. N. *Polymer* 1977, **18**, 1286
3 Bovey, F. A. 'Polymer Conformation and Configuration' Academic Press, New York, 1969, Chs 1 and 2

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:

$$\alpha=1-c_u^2/c^2 \tag{1}$$

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: $E=\rho c^2$.)

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

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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Here, we derive a relationship between equations (1) and (2), define the difference between the degree of overall orientation determined according to Moseley and Samuels, and discuss conditions under which the effect of crystallinity in the determination of the degree of orientation by the sonic method can be neglected.

The overall orientation, α, in two-phase model of crystalline polymer is defined[4] as:

$$\alpha = \beta\alpha_c + (1-\beta)\alpha_a \tag{3}$$

α_a is calculated from equation (2) and substituted into equation (3). The overall degree of orientation thus calculated is denoted as α^S, while α^M stands for α determined according to Moseley from equation (1). Hence:

$$\alpha_a = \frac{1}{1-\beta}\left[\frac{3}{2}\left(\Delta\frac{1}{E}\right)E^0_{t,a} - \frac{E^0_{t,a}}{E^0_{t,c}}\beta\alpha_c\right] \tag{4}$$

and

$$\alpha^S = \frac{3}{2}E^0_{t,a}\left(\Delta\frac{1}{E}\right) + \beta\alpha_c\left(1 - \frac{E^0_{t,a}}{E^0_{t,c}}\right) \tag{5}$$

For the isotropic fibre it holds that[3]:

$$\frac{3}{2}\frac{1}{E_{u(\beta)}} = \frac{\beta}{E^0_{t,c}} + \frac{1-\beta}{E^0_{t,a}} \tag{6}$$

whence:

$$\tfrac{3}{2}E^0_{t,a} = E_{u(\beta=0)} \tag{7}$$

and:

$$\frac{1}{E_{u(\beta)}} = k\beta + q \tag{8}$$

where $k = (2/3)(1/E^0_{t,c} - 1/E^0_{t,a})$ and $q = 1/E_{u(\beta=0)}$. By substituting equations (7) and (8) into equation (5) and noting the definition of $\Delta(1/E)$, we obtain:

$$\alpha^S = E_{u(\beta=0)}k\beta + 1 - \frac{E_{u(\beta=0)}}{E} + \beta\alpha_c\left(1 - \frac{E^0_{t,a}}{E^0_{t,c}}\right) \tag{9}$$

From equation (1) and from the known relationship $E = c^2$, it follows that:

$$1 - \frac{c_u^2}{c^2} = 1 - \frac{\rho E_{u(\beta=0)}}{\rho_u E} \tag{10}$$

where ρ_u is the specific mass of the isotropic amorphous fibre. Hence:

$$\alpha^M + \frac{E_{u(\beta=0)}}{E}\left(\frac{\rho}{\rho_u} - 1\right) = 1 - \frac{E_{u(\beta=0)}}{E} \tag{11}$$

Equation (11) is substituted into equation (9):

$$\alpha^S = \alpha^M + \frac{E_{u(\beta=0)}}{E}\left(\frac{\rho}{\rho_u} - 1\right) + E_{u(\beta=0)}k\beta + \beta\alpha_c\left(1 - \frac{E^0_{t,a}}{E^0_{t,c}}\right) \tag{12}$$

It also follows from equation (6) that $3E^0_{t,a}/2 = E_{u(\beta=0)}$ and $3E^0_{t,c}/2 = E_{u(\beta=0)}$, so that:

$$1 - \frac{E^0_{t,a}}{E^0_{t,c}} = 1 - \frac{E_{u(\beta=0)}}{E_{u(\beta=1)}} \tag{13}$$

Finally, by combining equations (8), (13) and (12) we obtain:

$$\alpha^S = \alpha^M + \frac{E_{u(\beta=0)}}{E}\left(\frac{\rho}{\rho_u} - 1\right) + E_{u(\beta=0)}k\beta(1-\alpha_c) \tag{14}$$

This equation may be rearranged to:

$$\alpha^S = \alpha^M - E_{u(\beta=0)}\left[|k|\beta(1-\alpha_c) - \frac{\left(\frac{\rho}{\rho_u} - 1\right)}{E}\right] \tag{15}$$

bearing in mind that, according to equation (6), k is always negative. Equation (15) gives a quantitative description of the effect of crystallinity on the average degree of overall orientation determined by the sonic method and defines the difference in its value calculated according to Samuels and Moseley. The equation contains all factors in which the effect of crystallinity is reflected. It is clear that for an amorphous polymer ($\beta = 0$ and $\rho = \rho_u$) no difference exists between α^S and α^M, if, of course, the effect of orientation of the amorphous polymer on its specific mass is neglected. This, however, represents another inaccuracy of the Moseley equation, which does not take into account that the sonic velocity is also a function of the specific mass. It can be proved, however, that the expression $(\rho/\rho_u - 1)$ may assume a value of the order of 10^{-3}, so that it may be neglected. In this case, the difference between α^S and α^M is mainly a function of the degree of crystallinity, of the extent of dependence of $E_{u(\beta)}$ on the degree of crystallinity defined by the parameter k and $E_{u(\beta=0)}$, and of the degree of orientation of the crystalline phase. At higher degrees of orientation of the crystalline phase, the vector of transverse sonic velocity becomes less operative which reduces the difference between sonic velocity in the crystalline and amorphous (similarly oriented) phases. As a result, equation (15) offers the possibility of an estimating of the applicability of the Moseley equation to the given polymer fibre.

REFERENCES

1 Moseley, W. W. Jr. *J. Appl. Polym. Sci.* 1960, **3**, 266

2 Hermans, P. H. 'Physics and Chemistry of Cellulose Fibers', Elsevier, New York, 1949, Ch 5

3 Samuels, R. H. *J. Polym. Sci.* (*A*) 1965, **3**, 1741

4 Samuels, R. J. 'Structured Polymer Properties', Wiley, New York, 1949, p 20