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NMR PENTAD RELATIONSHIPS

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ABSTRACT

Modern NMR apparatus can now resolve polyolefin compositional sequences of up to five consecutive monomer units (pentads). The relationships among these pentads and their predicted frequencies for different kinetic models are presented here.

DISCUSSION

In all cases, these relationships are extrapolations of earlier published work with shorter sequences. Derivation of the present equations is straightforward but tedious. The previous work should be consulted for basic equations and nomenclature. Except where specifically noted, the nomenclature and methods of Frisch et al [1] and Ross [5] are used.

Pentad Interrelationships are listed in Table I.

Kinetic Models

- Bernoullian pentads are designated PB (n)

Coefficients given in Tables II, III, IV refer to the following equations:

- First Order Markovian:

$$PF(n) = FF(n)/(a+b)$$

TABLE I

NECESSARY RELATIONSHIPS AMONG PENTADS

SUM = 1

(mmmrm) + (mmmrr) = (mmmmr) + 2[(rmmmr)]

(mmmrm) + (rmmrm) = (mmrmr) + 2[(mmrmm)]

(mmmrr) + (rmmrr) = (mmrrm) + (mmrrr)

(mmrmr) + 2[(rmrmr)] = (mrmrr) + 2[(mrmrm)]

(rmrrm) + (rmrrr) = (mrmrr) + 2[(rrmrr)]

(mmrrr) + (rmrrr) = (mrrrr) + 2[(mrrrm)]

(mmmm) = (mmmmm) + 1/2[(mmmmr)]

(mmmr) = (rmmmr) + 1/2[(mmmmr) + (mmmrm) + (mmmrr)]

(rmmr) = 1/2[(rmmrm) + (rmmrr)]

(mmrm) = (mmrmm) + 1/2[(mmmrm) + (rmmrm) + (mmrmr)]

(mmrr) = 1/2[(mmmrr) + (rmmrr) + (mmrrm) + (mmrrr)]

(rmrm) = (mrmrm) + (rmrmr) + 1/2[(mrmrr) + (mmrmr)]

(rmrr) = (rrmrr) + 1/2[(rmrrr) + (rmrrm) + (mrmrr)]

(mrrm) = 1/2[(rmrrm) + (mmrrm)]

(mrrr) = (mrrrm) + 1/2[(mrrrr) + (rmrrr) +m (mmrrr)]

(rrrr) = (rrrrr) + 1/2[(rrrrm)]

where $a = P_{m/r} = (mr)/[2(mm) + (mr)]$ (change in nomenclature from [2],[3])
$b = P_{r/m} = (mr)/[2(rr) + (mr)]$

- Second Order Markovian:

$$PS(n) = \frac{FS(n)}{\left(\bar{\alpha}\bar{\beta} + 2\bar{\alpha}\delta + \gamma\delta\right)}$$

- Dual Site or Modified Coleman – Fox [4],[3]

$$PD(n) = \frac{F_1D(n) + F_2D(n)A}{F_3D(n)}$$

TABLE II

MARKOVIAN PENTAD FACTORS

N	Config.	PB(n)	FF(n)	FS(n)
1	(mmmmm)	m^5	$a(1-b)^4$	$\alpha^3\gamma\delta$
2	(mmmmr)	$2m^4r$	$2ab(1-b)^3$	$2\alpha^2\bar{\alpha}\gamma\delta$
3	(rmmmr)	m^3r^2	$ab^2(1-b)^2$	$\alpha\bar{\alpha}^2\gamma\delta$
4	(mmmrm)	$2m^4r$	$2a^2b(1-b)^2$	$2\alpha\bar{\alpha}\beta\gamma\delta$
5	(mmmrr)	$2m^3r^2$	$2ab(1-a)(1-b)^2$	$2\alpha\bar{\alpha}\bar{\beta}\gamma\delta$
6	(rmmrm)	$2m^3r^2$	$2a^2b^2(1-b)$	$2\bar{\alpha}^2\beta\gamma\delta$
7	(rmmrr)	$2m^2r^3$	$2ab^2(1-a)(1-b)$	$2\bar{\alpha}^2\bar{\beta}\gamma\delta$
8	(mrmrm)	m^3r^2	a^3b^2	$\bar{\alpha}\beta^2\bar{\gamma}\delta$
9	(mrmrr)	$2m^2r^3$	$2a^2b^2(1-a)$	$2\bar{\alpha}\beta\bar{\beta}\bar{\gamma}\delta$
10	(rrmrr)	mr^4	$ab^2(1-a)^2$	$\bar{\alpha}\bar{\beta}^2\bar{\gamma}\delta$
11	(mmrmm)	m^4r	$a^2b(1-b)^2$	$\bar{\alpha}\beta\gamma^2\delta$
12	(mmrmr)	$2m^3r^2$	$2a^2b^2(1-b)$	$2\bar{\alpha}\beta\gamma\bar{\gamma}\delta$
13	(rmrmr)	m^2r^3	a^2b^3	$\bar{\alpha}\beta\bar{\gamma}^2\delta$
14	(mmrrm)	$2m^3r^2$	$2a^2b(1-a)(1-b)$	$2\bar{\alpha}\bar{\beta}\gamma\delta^2$
15	(mmrrr)	$2m^2r^3$	$2ab(1-a)^2(1-b)$	$2\bar{\alpha}\bar{\beta}\gamma\delta\bar{\delta}$
16	(rmrrm)	$2m^2r^3$	$2a^2b^2(1-a)$	$2\bar{\alpha}\bar{\beta}\bar{\gamma}\delta^2$
17	(rmrrr)	$2mr^4$	$2ab^2(1-a)^2$	$2\bar{\alpha}\bar{\beta}\bar{\gamma}\delta\bar{\delta}$
18	(mrrrm)	m^2r^3	$a^2b(1-a)^2$	$\bar{\alpha}\bar{\beta}\delta^2\bar{\delta}$
19	(mrrrr)	$2mr^4$	$2ab(1-a)^3$	$2\bar{\alpha}\bar{\beta}\delta\bar{\delta}^2$
20	(rrrrr)	r^5	$b(1-a)^4$	$\bar{\alpha}\bar{\beta}\bar{\delta}^3$

TABLE III

DUAL SITE OR MODIFIED COLEMAN – FOX PENTAD FACTORS

n	F_1D	$F_2D(n)$	$F_3D(n)$
1	$(mmmm)^2$	M^3	(mmm)
2	(mmmm)(mmmr)	$-2M^3$	(mmm)
3	$(mmmr)^2$	$4M^3$	4(mmm)
4	(mmmr)(mmrm)	$4M^2R$	(mmr)
5	(mmmr)(mmrr)	$-4M^2R$	(mmr)
6	2(rmmr)(mmrm)	$-4M^2R$	(mmr)
7	2(rmmr)(mmrr)	$4M^2R$	(mmr)
8	$(mmmr)^2$	$4MR^2$	4(rmr)
9	(mmmr)(rmrr)	$-4MR^2$	2(rmr)
10	$(rmmr)^2$	$4MR^2$	4(rmr)
11	$(mmrm)^2$	$4M^2R$	4(mrm)
12	(mmrm)(mrmr)	$-4M^2R$	2(mrm)
13	$(rmrm)^2$	$4M^2R$	4(mrm)
14	2(mmrr)(mrrm)	$4MR^2$	(mrr)
15	2(mmrr)(mrrr)	$-4MR^2$	(mrr)
16	(rmrr)(mrrm)	$-4MR^2$	(mrr)
17	(rmrr)(mrrr)	$4MR^2$	(mrr)
18	$(mrrr)^2$	$4R^3$	4(rrr)
19	(mrrr)(rrrr)	$-2R^3$	(rrr)
20	$(rrrr)^2$	R^3	(rrr)

TABLE IV

NON-HOMOGENEOUS PENTAD FACTORS

n	$F_1N(n)$	$F_2N(n)$	$F_3N(n)$	$F_4N(n)$
1	$10m^3$	$10m^2$	5m	1
2	$4m^2(3-5m)$	$4m(2-5m)$	$2(1-5m)$	–2
3	$m(3-12m+10m^2)$	$1-8m+10m^2$	$-2+5m$	1
4	$F_1N(2)$	$F_2N(2)$	$F_3N(2)$	–2
5	$2F_1N(3)$	$F_2N(3)$	$2F_3N(3)$	2
6	$2F_1N(3)$	$2F_2N(3)$	$2F_3N(3)$	2
7	$2(1-9m+18m^2-10m^3)$	$2(-3+12m-10m^2)$	$2(3-5m)$	–2
8	$F_1N(3)$	$F_2N(3)$	$F_3N(3)$	1
9	$F_1N(7)$	$F_2N(7)$	$F_3N(7)$	–2
10	$2(-2+9m-12m^2+5m^3)$	$2(3-8m+5m^2)$	$-4+5m$	1
11	$1/2\ F_1N(2)$	$1/2\ F_2N(2)$	$1/2\ F_3N(2)$	–1
12	$2F_1N(3)$	$2F_2N(3)$	$2F_3N(3)$	2
13	$1/2\ F_1N(7)$	$1/2\ F_2N(7)$	$1/2\ F_3N(7)$	–1
14	$2F_1N(3)$	$2F_2N(3)$	$2F_3N(3)$	2
15	$F_1N(7)$	$F_2N(7)$	$F_3N(7)$	–2
16	$F_1N(7)$	$F_2N(7)$	$F_3N(7)$	–2
17	$2F_1N(10)$	$2F_2N(10)$	$2F_3N(10)$	2
18	$1/2\ F_1N(7)$	$1/2\ F_2N(7)$	$1/2\ F_3N(7)$	–1
19	$2F_1N(10)$	$2F_2N(10)$	$2F_3N(10)$	2
20	$10(1-m)^3$	$-10(1-m)^2$	$5(1-m)$	–1

- Non Homogeneous [5]

$$PN(n) = PB(n) + F_1N(n)\chi_2 + F_2N(n)\chi_3 + F_3N(n)\chi_4 + F_4N(n)\chi_5$$

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