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Copolymerization of Propene and 5-Vinyl-2-Norbornene: A Simple Route to Polar Poly(propylene)s

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1-a Varying $[VNB]_0$: full polymerization data for **1**/$[Ph_3C][B(C_6F_5)_4]/AlBu^i_3$

Table 1. Influence of VNB feed concentration on the copolymerization of P and VNB with **1**/$[Ph_3C][B(C_6F_5)_4]/AlBu^i_3$.[a)]

Run	**1** [μmol]	VNB in feed [mol-%]	t [min]	Yield [g]	Prod.[b)]	VNB in copol. [mol-%]	$\bar{M}_w$ [$g{\cdot}mol^{-1}$]	$\bar{M}_w / \bar{M}_n$
1	10	-	10	14.56	8750	-	32000	2.0
2	10	3	10	0.61	366	3.7	31500	1.9
3	10	5	20	1.14	342	6.3	30500	2.1
4	30	10	20	2.03	203	12.5	25500	2.2
5	30	20	20	1.92	192	28.2	21000	2.2
6	30	30	30	1.69	113	37.1	10500	1.9
7	30	40	30	1.40	93	40.3	10500	2.7
8	30	50	30	1.08	72	41.0	14000	3.9

[a)] Polymerizations carried out in 100 ml of toluene at T = 20 °C ± 1°C under 1 bar of propene, with **1**/B/Al = 1:1:150.

[b)] Productivity in $kg_{pol}{\cdot}(mol\ Zr{\cdot}h{\cdot}bar)^{-1}$.

1-b Temperature influence: full polymerization data for 1/$[Ph_3C][B(C_6F_5)_4]/AlBu^i_3$

Table 2. Influence of the temperature on P/VNB copolymerizations with **1**/$[Ph_3C][B(C_6F_5)_4]/AlBu^i_3$.[a)]

Run	Temp. [°C]	P[b)] [$mol\cdot L^{-1}$]	VNB in feed [mol-%]	*t* [min]	Yield [g]	Prod.[c)]	VNB in copol. [mol-%]	$\overline{M}_w$ [$g\cdot mol^{-1}$]	$\overline{M}_w$ / $\overline{M}_n$
9	0	1.278	3	20	0.39	117	8.5	52000	2.7
10	10	0.930	3	10	0.26	156	6.0	-	-
11	20	0.710	3	10	0.61	366	3.7	17500	1.9
12	30	0.540	3	10	1.19	714	1.9	-	-
13	40	0.430	3	10	1.23	738	1.4	-	-
14	50	0.327	3	10	4.83	2898	traces	12000	1.9

[a)] Polymerizations carried out in 100 ml of toluene under 1 bar of propene, with 10 μmol of **1** and **1**/B/Al = 1:150.

[b)] Concentration of propene in $mol\cdot L^{-1}$

[c)] Productivity in $kg_{pol}\cdot(mol\ Zr\cdot h\cdot bar)^{-1}$.

1-c Varying $[VNB]_0$: full polymerization data for $2/[Ph_3C][B(C_6F_5)_4]/AlBu^i_3$

Table 3. Influence of VNB feed concentration on the copolymerization of P and VNB with **2**/$[Ph_3C][B(C_6F_5)_4]/AlBu^i_3$.[a)]

Run	**2** [μmol]	VNB in feed [mol-%]	*t* [min]	Yield [g]	Prod.[b)]	VNB in copol. [mol-%]	$\bar{M}_w$ [g·mol^{-1}]	$\bar{M}_w / \bar{M}_n$
15	10	-	10	10.22	6130	-	75000	1.9
16	10	1	10	1.77	1062	1.5	-	-
17	10	3	10	0.67	402	2.5	16000	2.3
18	10	5	10	0.46	276	3.8	-	-
19	10	7	10	0.33	198	5.5	5000	3.3
20	10	9	10	0.28	168	6.1	4000	3.0
21	30	30	30	1.15	77	18.8	-	-
22	30	40	60	1.69	56	29.7	-	-
23	30	50	60	0.59	20	34.3	-	-

[a)] Polymerizations carried out in 100 ml of toluene at *T* = 20 °C ± 1°C under 1 bar of propene, with **2**/B/Al = 1:1:150.

[b)] Productivity in $kg_{pol}\cdot(mol\ Zr\cdot h\cdot bar)^{-1}$.

1-d Full polymerization data for 3/MAO

Table 4. P/VNB copolymerization data with **3**/MAO.

Run	**3** [μmol]	*T* [°C]	VNB in feed [mol-%]	*t* [min]	Yield [g]	Prod.[a]	VNB in copol. [mol-%]	$\overline{M}_w$ [g·mol^{-1}]	$\overline{M}_w / \overline{M}_n$
24 [b]	7.5	20	-	3	2.64	7040	-	-	-
25 [b]	30	20	10	60	0.20	6.7	3.6	-	-
26 [b]	30	20	20	60	0.17	5.7	8.8	-	-
27 [b]	30	20	40	60	0.07	2.3	17.6	-	-
28 [b]	30	20	50	60	0.06	2.0	20.0	-	-
29 [c]	7.5	60	5	60	3.00	400	0.9	22500	2.2
30 [c]	7.5	60	9	5	0.35	560	1.6	15600	2.3
31 [c]	7.5	60	9	60	1.27	169	1.9	19000	2.1
32 [c]	7.5	60	33	60	0.39	52	8.9	7200	2.3

[a] Productivity in kg_{pol}·(mol Zr·h·bar)$^{-1}$.

[b] Polymerizations in 100 ml of toluene, with MAO/**3** = 1000:1.

[c] Polymerizations in 250 ml of toluene, with MAO/**3** = 5000:1.

1-e FTIR spectra of PP and poly(P-co-VNB)

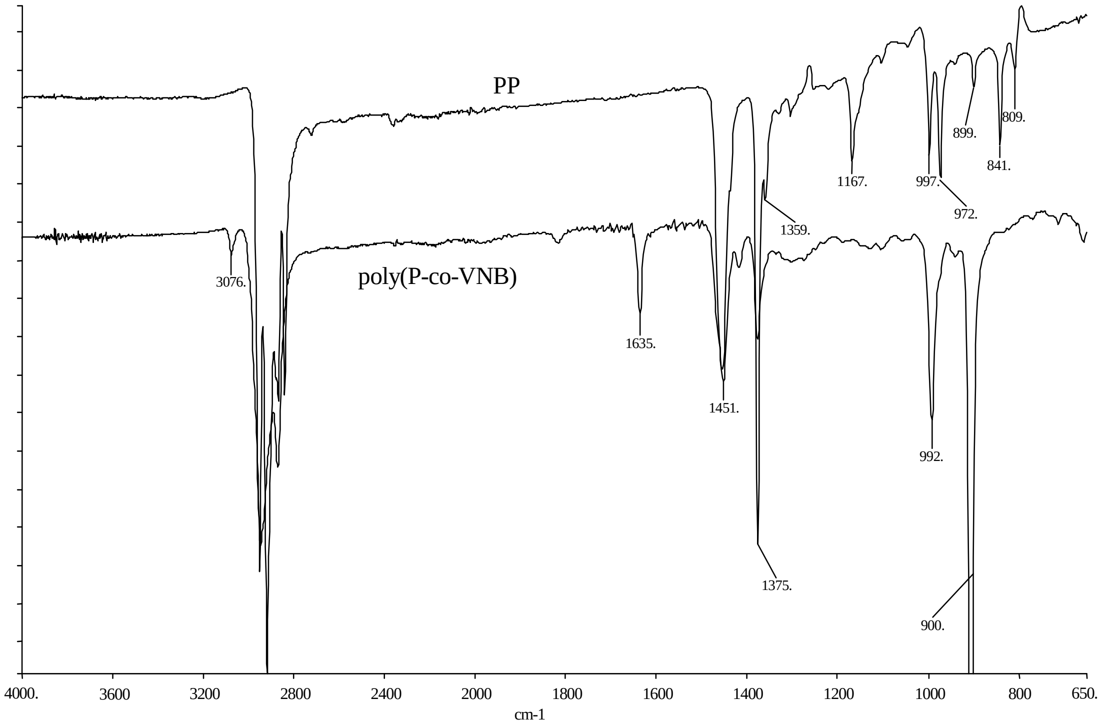


Figure 1. FTIR spectra of polypropene (top) and poly(P-co-VNB) (bottom).

1-f FTIR spectra of poly(P-co-VNB) and its ester and epoxy derivatives

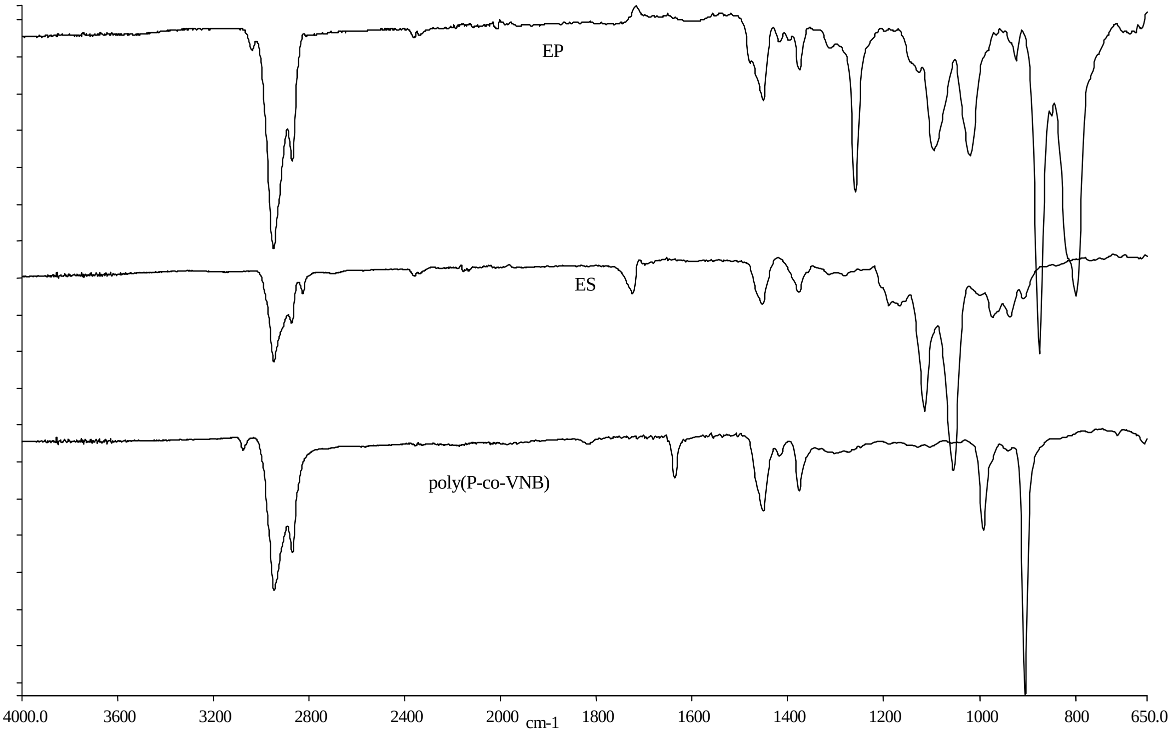


Figure 2. FTIR spectra of poly(P-co-VNB) (bottom), and its ester (center) and epoxide (top) derivatives.

1-g NMR spectra of ester- (ES, top half) and epoxy-functionalized (EP, bottom half) derivatives of poly(P-co-VNB)

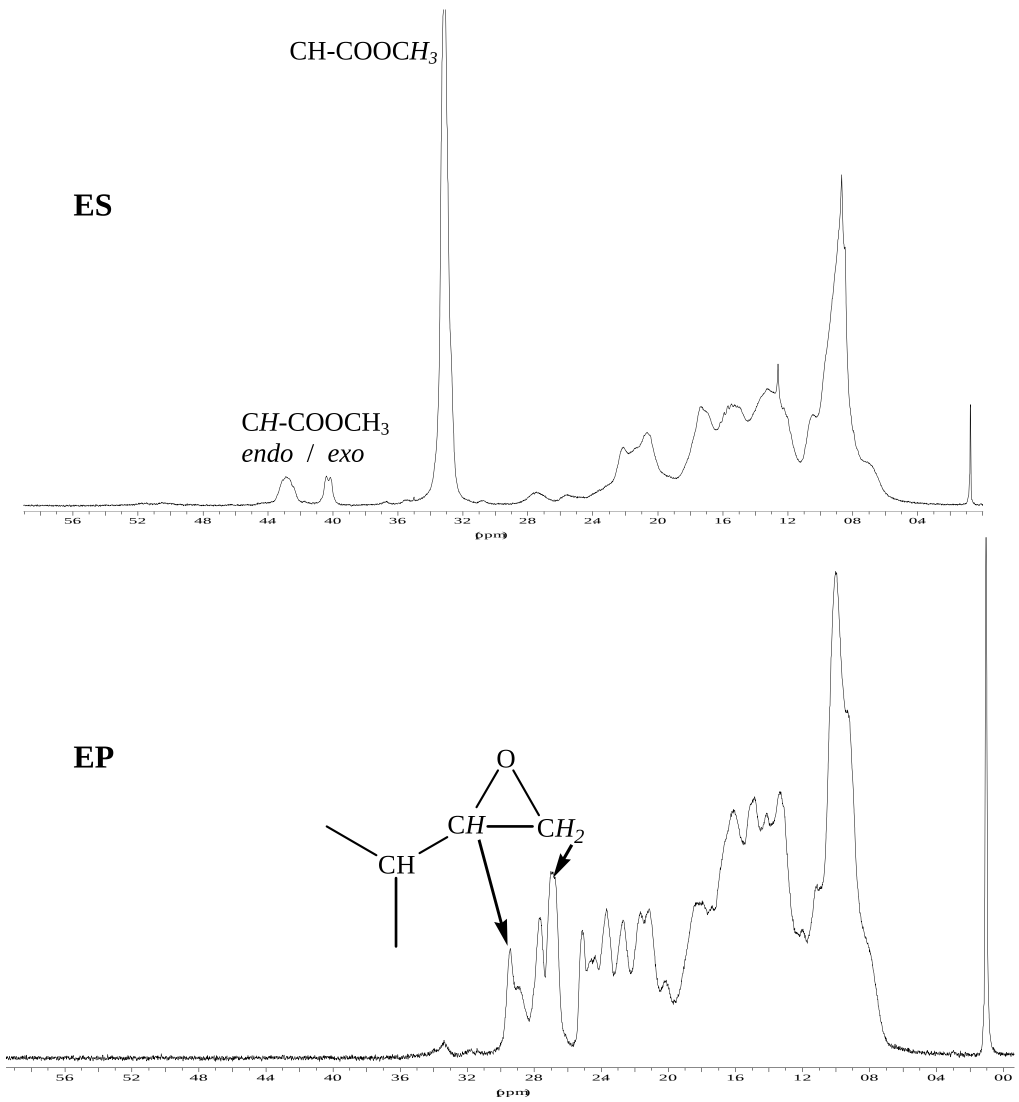


Figure 3. ^{1}H NMR spectra ($CDCl_3$, 60 °C) of ester- (**ES**, top half) and epoxy-functionalized (**EP**, bottom half) derivatives of poly(P-co-VNB).

1-h Finemann-Ross determination of reactivity ratios for $AlBu^{i}_{3}$/1/[Ph_3C][$B(C_6F_5)_4$]

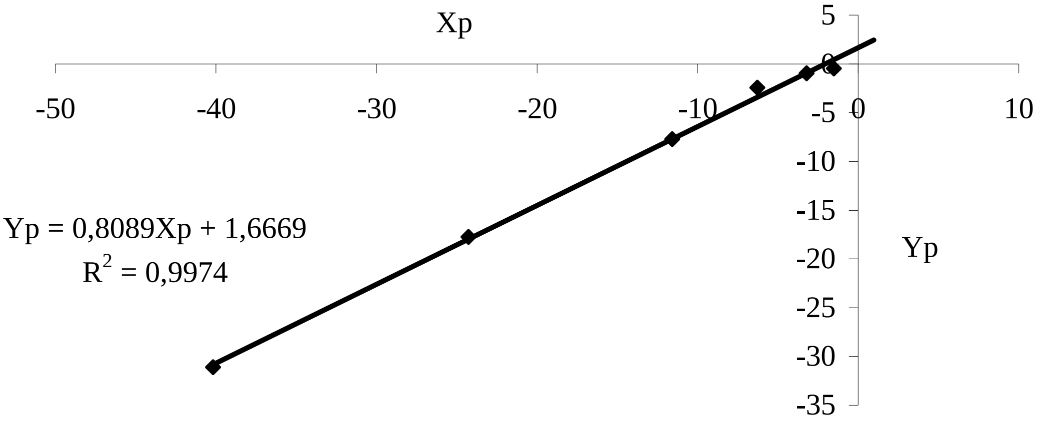
f_p	f_{vnb}	F_p	F_{vnb}	X_p	Y_p	X_{vnb}	Y_{vnb}
0.970	0.030	0.963	0.037	-40.177	-31.091	-0.025	0.774
0.950	0.050	0.937	0.063	-24.272	-17.722	-0.041	0.730
0.900	0.100	0.875	0.125	-11.571	-7.714	-0.086	0.667
0.800	0.200	0.718	0.282	-6.284	-2.429	-0.159	0.386
0.700	0.300	0.629	0.371	-3.211	-0.957	-0.311	0.298
0.600	0.400	0.597	0.403	-1.519	-0.487	-0.658	0.321

f_i = molar fraction of monomer *i* in the feed ratio

F_i = molar fraction of the monomer *i* in the polymer

$X_p = [f_p^2 \cdot (F_p - 1)]/[(1-f_p)^2 \cdot F_p]$ $Y_p = [f_p \cdot (1-2 \cdot F_p)]/[(1-f_p) \cdot F_p]$

$X_v = [f_{vnb}^2 \cdot (F_{vnb} - 1)]/[(1-f_{vnb})^2 \cdot F_{vnb}]$ $Y_{vnb} = [f_{vnb} \cdot (1-2 \cdot F_{vnb})]/[(1-f_{vnb}) \cdot F_{vnb}]$

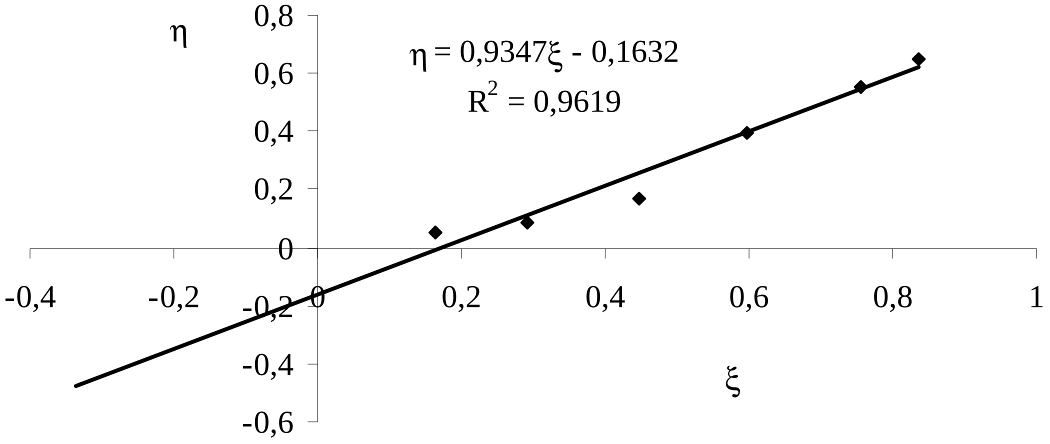


1-i Kelen-Tüdos determination of reactivity ratios for $AlBu^i_3$/1/$[Ph_3C][B(C_6F_5)_4]$

f_p	F_p	x	y	G	F	α	η	ξ
0.970	0.963	32.333	26.027	31.091	40.167	7.811	0.648	0.837
0.950	0.937	19.000	14.873	17.722	24.272	7.811	0.552	0.756
0.900	0.875	9.000	7.000	7.714	11.571	7.811	0.398	0.597
0.800	0.718	4.000	2.546	2.429	6.284	7.811	0.172	0.446
0.700	0.629	2.333	1.695	0.956	3.211	7.811	0.087	0.291
0.600	0.597	1.500	1.481	0.487	1.519	7.811	0.052	0.163

$x = f_p/(1-f_p)$, $y = F_p/(1-F_p)$, $G = x(y-1)/y$, $F = x^2/y$,

$\alpha = (F_{min} \cdot F_{max})^{1/2}$, $\eta = G/(\alpha+F)$, $\xi = F/(\alpha+F)$.



1-j Finemann-Ross determination of reactivity ratios for $AlBu^{i}_{3}$/2/$[Ph_3C][B(C_6F_5)_4]$

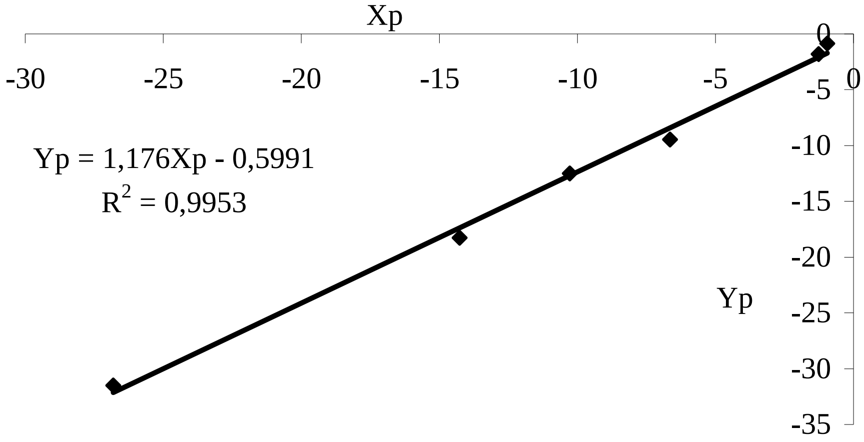
f_p	f_{vnb}	F_p	F_{vnb}	X_p	Y_p	X_{vnb}	Y_{vnb}
0.970	0.030	0.975	0.025	-26,806	-31,504	-0,037	1,175
0.950	0.050	0.962	0.038	-14,260	-18,249	-0,070	1,280
0.930	0.070	0.945	0.055	-10,273	-12,512	-0,097	1,218
0.910	0.090	0.939	0.061	-6,641	-9,454	-0,150	1,.423
0.700	0.300	0.812	0.188	-1,260	-1,793	-0,793	1,422
0.600	0.400	0.703	0.297	-0,950	-0,866	-1,052	0,911

f_i = molar fraction of monomer *i* in the feed ratio

F_i = molar fraction of the monomer *i* in the polymer

$X_p = [f_p^2 \cdot (F_p-1)]/[(1-f_p)^2 \cdot F_p]$ $Y_p = [f_p \cdot (1-2 \cdot F_p)]/[(1-f_p) \cdot F_p]$

$X_v = [f_{vnb}^2 \cdot (F_{vnb}-1)]/[(1-f_{vnb})^2 \cdot F_{vnb}]$ $Y_{vnb} = [f_{vnb} \cdot (1-2 \cdot F_{vnb})]/[(1-f_{vnb}) \cdot F_{vnb}]$

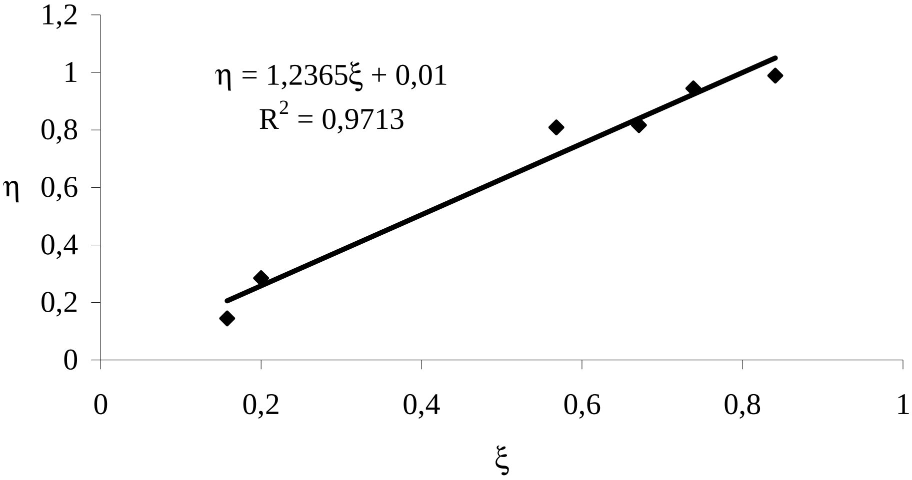


1-k Kelen-Tüdos determination of reactivity ratios for $AlBu^i_3$/2/[Ph_3C][$B(C_6F_5)_4$]

f_p	F_p	$x =$ $f_p/(1-f_{p)}$	$y =$ $F_p/(1-F_p)$	$G =$ $x(y-1)/y$	$F =$ x^2/y	$\alpha =$ $(F_m \cdot F_M)^{1/2}$	$\eta =$ $G/(\alpha+F)$	$\xi=$ $F/(\alpha+F)$
0.970	0.975	32.333	39.000	31.504	26.806	5.046	0.989	0.841
0.950	0.962	19.000	25.316	18.249	14.260	5.046	0.945	0.739
0.930	0.945	13.286	17.182	12.513	10.273	5.046	0.817	0.671
0.910	0.939	10.111	15.393	9.454	6.641	5.046	0.809	0.568
0.700	0.812	2.333	4.319	1.793	1.260	5.046	0.284	0.200
0.600	0.703	1.500	2.367	0.866	0.950	5.046	0.144	0.158

$x = f_p/(1-f_{p)}$, $y = F_p/(1-F_p)$, $G = x(y-1)/y$, $F = x^2/y$,

$\alpha = (F_{min} \cdot F_{max})^{1/2}$, $\eta = G/(\alpha+F)$, $\xi= F/(\alpha+F)$.



1-l Finemann-Ross determination of reactivity ratios for 3/MAO

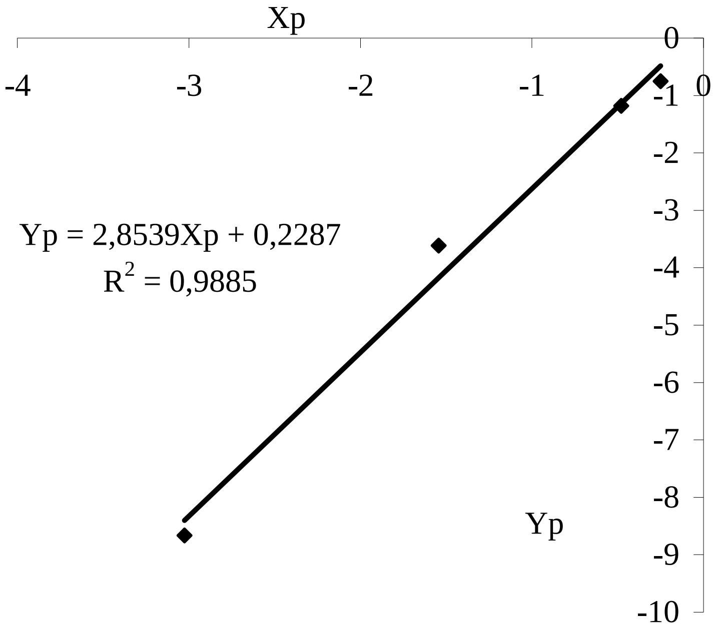
f_p	f_{vnb}	F_p	F_{vnb}	X_p	Y_p
0.900	0.100	0.964	0.036	-3.025	-8.664
0.800	0.200	0.912	0.088	-1.544	-3.614
0.600	0.400	0.824	0.176	-0.480	-1.180
0.500	0.500	0.800	0.200	-0.250	-0.750

f_i = molar fraction of monomer *i* in the feed ratio

F_i = molar fraction of the monomer *i* in the polymer

$X_p = [f_p^2 \cdot (F_p - 1)]/[(1-f_p)^2 \cdot F_p]$ $\quad$ $Y_p = [f_p \cdot (1 - 2 \cdot F_p)]/[(1-f_p) \cdot F_p]$

$X_v = [f_{vnb}^2 \cdot (F_{vnb} - 1)]/[(1-f_{vnb})^2 \cdot F_{vnb}]$ $\quad$ $Y_{vnb} = [f_{vnb} \cdot (1 - 2 \cdot F_{vnb})]/[(1-f_{vnb}) \cdot F_{vnb}]$



1-m Kelen-Tüdos determination of reactivity ratios for 3/MAO

f_p	F_p	$x =$	$y =$	$G =$	$F =$	$\alpha =$	$\eta =$	$\xi =$
		$f_p/(1-f_p)$	$F_p/(1-F_p)$	$x(y-1)/y$	x^2/y	$(F_m \cdot F_M)^{1/2}$	$G/(\alpha+F)$	$F/(\alpha+F)$
0.900	0.964	9	26.778	8.664	3.025	0.870	2.224	0.777
0.800	0.912	4	10.364	3.614	1.544	0.870	1.497	0.640
0.600	0.824	1.5	4.682	1.180	0.480	0.870	0.874	0.355
0.500	0.800	1	4	0.750	0.250	0.870	0.670	0.223

$x = f_p/(1-f_p)$, $y = F_p/(1-F_p)$, $G = x(y-1)/y$, $F = x^2/y$,

$\alpha = (F_{min} \cdot F_{max})^{1/2}$, $\eta = G/(\alpha+F)$, $\xi = F/(\alpha+F)$.