Polymer Bulletin 23, 127–131 (1990)

Polymer Bulletin

On the intermolecular and intramolecular branching distribution in ethylene/α-olefin copolymers*

Jianguo Wang, Deren Pang, and Baotong Huang**

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin 130022, People's Republic of China

SUMMARY

For the complex phenomena of comonomer distribution in ethylene/α-olefin copolymers prepared on heterogeneous Ziegler-Natta catalysts, a branch distribution function P(b) was proposed to quantify the intermolecular branch distribution (InterBD). P(b) values calculated from solvents extraction fractions were found to correspond to the alleged sequence length distribution represented by $r_1 \cdot r_2$ as determined from ^{13}C NMR data. The InterBD is attributed to thermodynamically-controlled polymerization processes due to the presence of multiple active centers. Literature data also showed a decrease in reactivity parameter $r_1 \cdot r_2$ with increasing comonomer ratio. A diffusion-controlled model is suggested for the intramolecular branch distribution (IntraBD).

INTRODUCTION

For linear low density polyethylene (LLDPE), the important member of industrial polyethylenes, the physical properties are dictated by the variation in several structural parameters of these ethylene/α-olefin copolymers. The branch-chain length is defined by the comonomer used, and the level of branching is measurable (IR or NMR method) and is controllable by the dosage of the comonomer. The structural factor that affects much the physical properties of LLDPE but is elusive to be trackled is the distribution of the branches among and within the macromolecules.

The value of the product of the reactivity ratios, $r_1 \cdot r_2$, nominally correlating the comonomer distribution in the chain (>1, blocky; ~1, random; <1, alternating) is now known to be but a gross manifestation of the effect of the existing multiple active centers on heterogeneous Ziegler-Natta catalysts (1-5). Multiplicity of the active centers together with unrevealed kinetic details lead to an unknown mode of the intermolecular and intramolecular branch distribution in LLDPE copolymers.

In the present work, attempt has been made to clarify the nature and mechanism of the intermolecular branch distribution (InterBD) and intramolecular branch distribution (IntraBD) of LLDPE, and a function to quantify the InterBD is proposed.

---

*Supported by the Chinese Petrochemical Corporation (SINOPEC)

**To whom correspondence should be addressed

EXPERIMENTAL

Ethylene/butene-1 copolymers were prepared by bubbling the gaseous monomer mixture through hexane solvent. Catalysts used were heterogeneous $MgCl_2/SiO_2$-supported $TiCl_4$ catalysts prepared in this laboratory (6) activated by Et_3Al.

Extraction of the gross copolymers by respective solvents was carried out in Soxhlet extractors at boiling temperature of the solvent used. Recovery and drying of the extrated fractions were in usual manner.

Calculation of the number of branches by counting the concentration of the end CH_3-group was by IR technique and ^{13}C NMR method according to (3). The $r_1 . r_2$ values were evaluated from ^{13}C NMR data of the gross copolymers using the relationship (7):

$$r_1 \cdot r_2 = 1 + f(x+1) - (f+1)(x+1)^{\frac{1}{2}} \qquad (1)$$

where $f = E/B$ and $x = (BBB+BBE)/EBE$.

RESULTS AND DISCUSSION

Intermolecular Branch Distribution (InterBD)

Thanks to the fractionation techniques, including the recently developed TREF (temperature rising elution fractionation) technique, more light has been shed on the intermolecular branching distribution (InterBD) by studing (^{13}C NMR) composition of the individual fractions. The consensus is that fractions of ethylene/butene-1 (E/B, or C_2/C_4) copolymers (or with other comonomer) differ appreciably in r_1 and r_2 values and thus in $r_1 \cdot r_2$ values and comonomer distribution, substantiating the existence of multiple active centers.

Usami asserted on the basis of studies (SEC, ^{13}C NMR, DSC and FTIR) on preparative TREF fractions, that there was intermolecularly a bimodal short-chain branching distribution formed on the two kinds of active centers (1) in E/B and E/hexene-1 copolymers. Most TREF fractions, lower in MW, had an alternating enchainment ($r_1 \cdot r_2 = 0.5-0.6$) and fractions separated at higher temperature with higher MW had less and random branching ($r_1 \cdot r_2 = 1$). Other workers, working either on solvents extraction (2,3) or TREF (4,5) fractions, claimed rather the presence of multiple active centers. Kuroda (2) found different r_1 and r_2 values for each of five ethylene/butene-1 copolymer fractions. Nowlin et al obtained fractions (1-25mol% hexene) with r_1 values ranging from 4 to 200, confirming the differing relative activites of ethylene and hexene at different active centers on $Ti/Mg(SiO_2)$ catalysts (3). Kimura recognized earlier different Tm of samples at even the same butene-content and deduced from ^{13}C NMR tetrad analysis that the origin of the difference in Tm was due to the mode of butene distribution along the polymer chain (4). Mirabella and Ford attributed the broad and multimodal Tm envelop of LLDPE to a broad and multiple short-chain branching distribution which originated from heterogeneous comonomer incorporation (5).

In this work, to quantify the InterBD in LLDPE, a branch distribution function is suggested:

$$P(b) = \bar{b}_w / \bar{b}_n \text{ , in which } \bar{b}_w = \quad b_i^2 \cdot w_i \; / \quad b_i \cdot w_i \qquad (2)$$

where $\bar{b}_w$ is the weight-average and $\bar{b}_n$ the number-average of branching, and w_i the weight-fraction and b_i the degree of branching in mol% in fractionated fractions. The expression $P(b) = \bar{b}_w / \bar{b}_n$ bears exactly the same formal resemblance to that for molecular weight distribution, and the meaning attached to it is comprehensible accordingly.

Table 1 gives the fractionation data of seven E/B copolymers and the $r_1 \cdot r_2$ values of the gross copolymers. Each copolymer was extracted successively with pentane, hexane, heptane and octane. The weight fraction (w_i) and degree of brabching (b_i) as determined by IR method of the successive soluble fractions as well as of the octane-insoluble residue were used to calculate the weight-average branching ($\bar{b}_w$). From $\bar{b}_w$ and $\bar{b}_n$ the distribution function P(b) was calculated.

Table 1 Solvent Extration and ^{13}C NMR Data of Ethylene/Butene-1 Copolymers

Cat. no.	$r_1 \cdot r_2$		Pentane soluble	Hexane soluble	Heptane soluble	Octane soluble	Octane insoluble	$\bar{b}_n$	$\bar{b}_w$	P(b)
S1	3.44	w_i(wt%)	2.6	1.8	7.0	29.9	58.7	4.0	7.2	1.80
		b_i(mol%)	18.7	13.7	11.6	3.5	2.4			
S2	3.64	w_i(wt%)	5.4	3.7	13.1	32.0	45.7	4.5	8.1	1.80
		b_i(mol%)	16.3	11.6	9.5	3.1	2.1			
S3	3.36	w_i(wt%)	3.0	2.7	10.3	31.5	47.5	4.6	8.3	1.81
		b_i(mol%)	18.4	14.7	11.8	3.8	2.6			
S4	2.97	w_i(wt%)	5.6	5.1	13.3	36.8	39.2	5.4	9.1	1.69
		b_i(mol%)	19.5	11.8	9.9	3.6	2.7			
S5	1.71	w_i(wt%)	4.1	3.9	14.2	39.5	37.3	6.1	9.9	1.62
		b_i(mol%)	22.3	14.4	11.9	4.4	3.2			
S6	1.43	w_i(wt%)	5.7	5.6	21.3	36.6	30.8	7.4	11.7	1.58
		b_i(mol%)	27.9	15.0	11.1	4.4	3.3			
S7	1.29	w_i(wt%)	5.9	9.8	32.1	34.0	18.2	9.6	14.7	1.53
		b_i(mol%)	32.4	16.3	11.2	5.6	3.3			

Linearity of P(b) with $r_1 \cdot r_2$ values of the samples is shown in Fig. 1, depicting the correspondence between the proposed branching distribution function and the commonly used parameter describing the mode of gross comonomer distribution. The quantified P(b) values for InterBD are founded on fractionated samples, thus obliterating the inexplicability of $r_1 \cdot r_2$ values derived from a gross copolymer.

Fractionation seperates a PE copolymer sample into fractions according to difference in crystallinity. Crystallinity originates from long ethylene sequences featuring the relative reactivity of ethylene to the comonomer and the nature of the active centers. The origin of InterBD is thus attributed to thermodynamically-controlled polymerization processes involving multiple active centers, each contributing a different $r_1 \cdot r_2$.

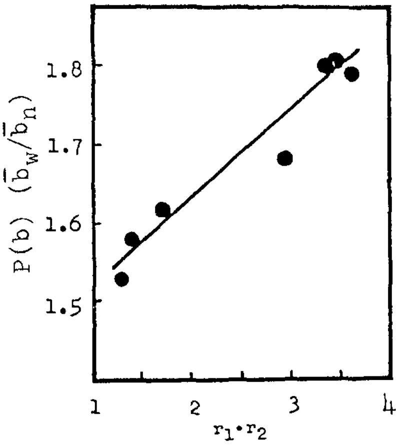

Fig. 1 The branch distribution function P(b) vs. $r_1 \cdot r_2$.

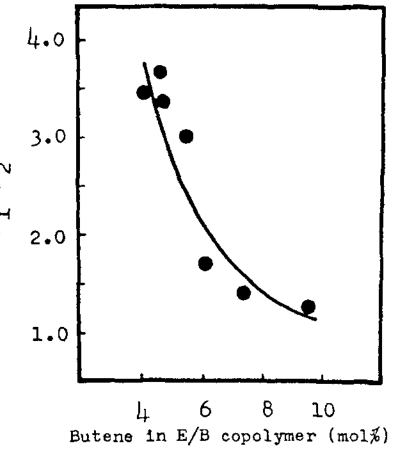

Fig. 2 $r_1 \cdot r_2$ vs. composition of ethylene/butene-1 copolymers prepared with different catalysts of Table 1.

Intramolecular Branch Distribution (Intra BD)

The fact that decrease in value of the kinetic parameter $r_1 \cdot r_2$ of the seven LLDPE samples with increasing incorporated butene-1 in the copolymer (Fig. 2), irrespective of the seven different catalysts used (see Table 1), is contradictory to the classical thermodynamics of copolymerization and suggests a changing kinetics during the course of copolymerization.

Search of literature data revealed that in copolymers of C_2/C_3 and C_2/C_4 polymerized with heterogeneous Ti-based catalysts (in one case Cr), decrease in $r_1 \cdot r_2$ values with increasing comonomer ratio is a rule rather than an isolated case (Fig. 3a,4), all following the same trend as with our seven samples (also compared in Fig. 4).

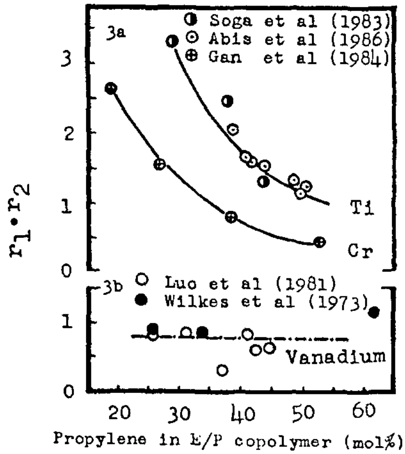

Fig. 3 $r_1 \cdot r_2$ vs composition of ethylene/propylene copolymers.

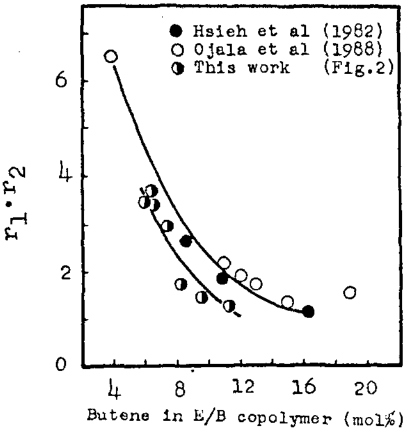

Fig. 4 $r_1 \cdot r_2$ vs. composition of ethylene/butene-1 copolymers.

It is reasoned that the changing copolymerization kinetics might have come into play as a result of fluctuation in comonomer concentrations on the catalyst surface near the reactive sites. For example, fast consumption of the more reactive ethylene will leave behind an increasing concentration of the bulkier, slower-diffusing comonomer butene-1 and, consequently, an enrichment in butene leads to a subsequent richer butene enchainment. Thus, the IntraBD can best be visualized in terms of a diffusion-controlled kinetic process, which originates from fluctuation of the monomer ratio around the active centers. The result is the changing of a copolymerization with longer ethylene blocks ($r_1 \cdot r_2 > 1$ at higher E) to one richer in random and alternating disposition (lowering of $r_1 \cdot r_2$ at higher comonomer concentration).

Supporting evidence for this diffusion-controlled model is provided by the absence of such a variation in $r_1 \cdot r_2$ values with soluble vanadium catalyst (Fig. 3b). Even though E/P copolymers showed heterogeneity in composition on fractionation for the sake of the presence of multiple active centers (8), since no heterogeneous surface is involved, there is no problem in fluctuation in comonomer consumption due to diffusion processes.

REFERENCE

1. Usami, T., Gotoh, Y., Takayama, S., Macromolecules, 19, 2722(1986).
2. Kuroda, N., Nishikitani, Y., Matsuura, K., Miyoshi, M., Makromol. Chem., 188, 1897(1987).
3. Nowlin, T. E., Kissin, Y. V., Wagner, K. P., J. Polym. Sci.: Part A : Polym. Chem., 26, 755(1988).
4. Kimura, K., Shigemura, T., Yuasa. S., J. Appl. Polym. Sci., 29, 3161(1984).
5. Mirabella,Jr.,F. M., Ford, E. A., J. Polym. Sci.: Part B: Polym. Phys., 25, 777(1987).
6. Wang, J. G., Pang, D. R., Huang, B. T., Polymer Symposium, Chinese Chemical Society, Chengdu, 1989; to be published.
7. Carman, C. J., Wilkes, C. E., Rubber Chem. Technol., 44, 781 (1971).
8. Baldwin, F. P., Ver Strate, G., Rubber Chem. Technol., 45, 709(1972).

Accepted November 25, 1989 S