An Analytical Method for Long-Chain Branching in Free-Radical Polymerization of Ethylene

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ABSTRACT

Quantitative measurements on long-chain branching in polyethylene have not been established. This paper presents a method available for calculating the degree of long-chain branching and the exponent α in the hydrodynamic relation $g = G^{\alpha}$ (where g is the ratio of the intrinsic viscosities of branched and linear molecules at the same molecular weight, and G is the corresponding ratio of mean square radii of gyration), by means of polymerization parameters, size exclusion chromatography, viscosity measurement, and amount of total unsaturation. The calculation based on our experimental data shows the following, in radical polymerization of ethylene. (1) With reaction pressure and temperature varied, the degree of long-chain branching was 0.5 to 3.7 per 1000 carbons. (2) As for the rate constant for long-chain branching, the activation energy $E_{trp} - E_{p}$, and the activation volume $\Delta V_{trp}^{*} - \Delta V_{p}^{*}$ were 4.1 kcal/mol and 20 cc/mol, respectively. (3) The value of the exponent α, which is considered to represent the type of branching, was independent of reaction pressure and decreased with an increase of reaction temperature, and it was between 0.9 to 1.5, centering around 1.1. The validity of these values in (1), (2), and (3) and the type of branching are discussed.

INTRODUCTION

The degree, type, and distribution of long-chain branching in poly-
ethylene are important factors in determination of the viscoelastic
properties in the melt and morphological properties of the polymer.
In measuring long-chain branching, such methods as gel permeation
chromatography (or more correctly, size exclusion chromatography),
viscosity measurements, and carbon-13 Fourier transform nuclear
magnetic resonance spectroscopy have been used [6, 22]. In particu-
lar, size exclusion chromatography (SEC) coupled with automatic
viscometry or low-angle laser light scattering (LALLS) measurements
appears to be the most promising method [6, 22].

Unfortunately, however, despite the considerable effort that has
been expended on studying branching in polyethylene, it can hardly
be claimed that it is at present possible to determine the degree of
long-chain branching in this polymer unambiguously [3, 6]. This is
because there has been no established theory with respect to the
hydrodynamic relation between g and G for the randomly branched
polymer, where g is the ratio of the intrinsic viscosity of branched
polymer to that of linear at the same molecular weight, and G is the
corresponding ratio of mean square radii of gyration [6].

The molecular weight distribution in free-radical polyethylene is
usually broad; this is attributed to the presence of long-chain branches
in polymer molecules [1-5]. Thus the author attempts a reverse
approach to obtain long-chain branches from molecular weight dis-
tribution in the free-radical polymerization of ethylene. The previous
paper [8] suggested the method of obtaining the rate constant for long-
chain branching from average molecular weight and polymerization
parameters, using Mullikin and Mortimer's probabilistic model [4, 7].

The present paper, further advancing this method [8] and Drott
and Mendelson's method [9, 11], proposes a method for calculating
the hydrodynamic relation and degree of long-chain branching in
radical polymerization by means of size exclusion chromatography,
viscosity measurement, and polymerization parameters.

Moreover, an attempt is made to determine the hydrodynamic
relation and degree of long-chain branching in radical polymeriza-
tion of ethylene from our experimental data. Lastly, by discussing
the pressure and temperature dependence of the hydrodynamic rela-
tion, we presume the type of long-chain branching in radical poly-
ethylene.

METHOD OF CALCULATION FOR
LONG-CHAIN BRANCHING

Since 1953 a great deal of work has been directed to the estimation
of long-chain branching (LCB) in low-density polyethylene (LDPE).
The more important studies are listed in Table 1 in roughly chronological

TABLE 1. Studies of LCB on LDPE

Authors	Refs.	Method	Exponent α (-)	LCB (per 1000 CH_2)
Billmeyer	16	$[\eta]$, $\overline{M}_w$	3/2	0.12–1.02
Moore et al.	31	$[\eta]$, S_0	3/2	
Guillet	32	$[\eta]$, S_0	3/2	0.41–1.02
Mendelson and Drott	33	$[\eta]$, $\overline{M}_w$	1/2	1.96–7.70
Yamaguchi et al.	34	$[\eta]$, S_0	3/2	
Drott and Mendelson	11	GPC, $[\eta]$	1/2	1.96–7.7
Völker and Luig	29	$[\eta]$, $\overline{M}_w$	1.3	0.07–0.15
Cote and Shida	14	SEC, $[\eta]$	4/3	0.84–4.48
Otocka et al.	35	SEC, $[\eta]$	1/2	2.24–12.88
Miltz and Ram	25	SEC, $[\eta]$	1/2	4.48–7.56
Bovey et al.	30	C-13 NMR	-	0.8, 1.0
Bohdanecký	24	$[\eta]$	0.8, 1.0	1.96, 3.36
Axelson et al.	22	SEC, LALLS	1/2	0.5–1.5

order [6]. Nearly all the studies listed in Table 1 use intrinsic viscosity as one of the quantities measured. So it can be said that the evaluation of LCB depends, for the most part, on how to assume the hydrodynamic relation between g and G, where g is the ratio of the intrinsic viscosities of the branched and linear molecules at the same molecular weight and G is the corresponding ratio of mean square radii of gyration. For theta conditions it has become customary to formulate the relation between g and G as

$$g = G^{\alpha} \tag{1}$$

where the exponent α is variously reported (cf. Table 1), but at present it is not known reliably.

In 1970 Drott and Mendelson suggested a convenient method for SEC-$[\eta]$ analysis [9, 11]: they obtained the degree of LCB per molecular weight, λ, and average molecular weights, M_n and M_w, on the assumption that λ is independent of molecular weight and that a certain value is substituted for the exponent α (for which the value

3/2 and 1/2 are most frequently substituted). In 1979 Yamamoto et al. derived a method of calculating the rate constant for long-chain branch formation, by means of polymerization parameters and average degrees of polymerization (X_n and X_w) [8], using Mullikin and Mortimer's probabilistic model [4, 7]. From the rate constant, the degree of LCB per molecular weight can be readily obtained. Accordingly, if we stand on the assumption that λ is independent of molecular weight and that a certain value is substituted for the exponent α, then we have two methods available for obtaining the degree of long-chain branching: Drott et al.'s method by means of SEC and $[\eta]$ [9, 11], and Yamamoto et al.'s by means of average degrees of polymerization, total unsaturation, and polymerization parameters.

Then by connecting the two methods, the present paper suggests a method for obtaining both the exponent α and degree of long-chain branching on the assumption of constant λ and a continuous perfectly stirred tank reactor.

Assumptions and Definitions

The same assumptions made in Drott and Mendelson's method are retained [9, 11]: the long-chain branching density is independent of molecular weight. As for the intrinsic viscosity of linear molecules, the well-known Mark-Houwink equation is assumed to hold. Size exclusion chromatography (SEC or GPC) is divided into fractions small enough to show a monodisperse system.

The same basic process assumptions made by Mullikin and Mortimer are retained: the reactor is a well-stirred reactor with continuous feed and discharge [4, 7]. The elementary reactions are assumed to be the following six kinds of reactions: propagation, termination, chain transfer to transfer agent, chain transfer to monomer, chain transfer to polymer (long-chain branch formation), and total β-scission. Intramolecular hydrogen transfer (short-chain branch formation) can be neglected because it does not contribute to molecular weight distribution. The rate for long-chain branch formation is assumed to be proportional to the molecular weight of a polymer.

Hydrodynamic parameters are $[\eta]$, intrinsic viscosity (dL/g); $\langle S^2 \rangle$, mean square radius of gyration; g, the ratio of the intrinsic viscosity of a branched molecule to that of a linear polymer having the same molecular weight, defined as

$$g = [\eta]_{br}/[\eta]_{lin} \tag{2}$$

where br and lin represent branched and linear molecules, respectively; and G, the corresponding ratio of mean square radii of gyration, defined as

$$G = \langle S^2 \rangle_{br} / \langle S^2 \rangle_{lin} \tag{3}$$

SEC parameters are v, elution volume; and w, weight fraction. In order to show the i-th fraction of SEC, the index i is added to each parameter, where i = 1, 2, . . ., n (n is the number of total fractions).

Molecular parameters are M, molecular weight; M_n, number-average molecular weight; M_w, weight-average molecular weight; X_n, number-average degree of polymerization; X_w, weight-average degree of polymerization; λ, degree of long-chain branching per molecular weight (long-chain branching density); m, degree of long-chain branching per molecule; LCB, degree of long-chain branching per a monomer; U, amount of total unsaturation; and M*, molecular weight of monomer.

Kinetic parameters (all in L/mol·s) are K_p, rate constant for propagation; K_{trp}, rate constant for chain transfer to a polymer; and K_{trs}, rate constant for chain transfer to a transfer agent.

Reaction parameters are T, reaction temperature (°K); T_0, feed gas temperature (°K); P, reaction pressure (kg/cm²); F_g, feed monomer amount (mol/h); F_s, feed transfer agent amount (mol/h); F_i, feed initiator amount (mol/h); and X, conversion.

Formulation

First, for K_{trp}/K_p, the rate constant for LCB formation, and second, for the exponent α in Eq. (1), an appropriate initial value is set up.

As suggested by Drott and Mendelson [9, 11], hydrodynamic volume, M[η], which was introduced by Benoit [10], can be related to elution volume v in SEC as follows:

$$M[\eta] = 10^{Av+B} \tag{4}$$

where the constants A and B can be obtained from the calibration curve (based on the results of Loy [12]).

Now we set up appropriate initial values for the intrinsic viscosities of individual eluted species at volumes v_i, where i = 1, 2, . . ., n: $[\eta]_1, [\eta]_2, . . ., [\eta]_n$. From Eq. (4), for the i-th fraction, we have

$$M_i = (10^{Av_i+B}) / [\eta]_i \tag{5}$$

From the initially set value K_{trp}/K_p, kinetically we have

$$LCB = K_{trp}X/K_p(1 - X) \tag{6}$$

thus, if X is given, obtaining

$$\lambda = LCB/M* \tag{7}$$

By using M_i in Eq. (5) and λ in Eq. (7), we can obtain m_i (i = 1, 2, . . ., n) as follows:

$$m_i = \lambda M_i \tag{8}$$

Zimm and Stockmayer have derived an equation relating G and m for randomly branched polymer having trifunctional branch points for monodisperse system [13]:

$$G = \left[(1 + m/7)^{\frac{1}{2}} + 4m/9\pi \right]^{-\frac{1}{2}} \tag{9}$$

Putting Eq. (8) in Eq. (9), we have

$$G_i = \left[(1 + m_i/7)^{\frac{1}{2}} + 4m_i/9\pi \right]^{-\frac{1}{2}} \tag{10}$$

where i = 1, 2, . . ., n.
As for the intrinsic viscosity of linear molecules, the well-known Mark-Houwink equation holds:

$$[\eta]_{lin} = KM_{lin}^a \tag{11}$$

where K and a are Mark-Houwink constants. From Eqs. (1) and (11), we can readily derive

$$[\eta]_{br} = KM_{br}^a G^\alpha \tag{12}$$

Setting Eqs. (5) and (10) in Eq. (12), we have

$$[\eta]_i = KM_i^a G_i^\alpha \tag{13}$$

where i = 1, 2, . . ., n.

At this stage, $[\eta]_i$ is computed by an iterative process of Eqs. (5)-(13). The initially set values $[\eta]_i$ are iteratively varied until they come to be consistent with $[\eta]_i$ obtained from Eq. (13) with certain accuracy.

The intrinsic viscosity of whole polymer is given by

$$[\eta] = \sum_i [\eta]_i w_i / \sum_i w_i \tag{14}$$

So, by putting $[\eta]_i$ calculated by the first iterative process and w_i obtained from SEC, in Eq. (14), $[\eta]$ of the whole polymer can be calculated.

Here, the secondary iterative process is carried out until the calculated $[\eta]$ from Eqs. (14) agrees with the experimentally obtained viscosity when the initially set value of the exponent α is iteratively varied.

Then, using M_i obtained from the calculation result mentioned above, M_n and M_w are obtained from

$$M_n = 1 / \sum_i (W_i/M_i) \tag{15}$$

$$M_w = \sum_i (W_i M_i) \tag{16}$$

From the M_n and M_w, X_n and X_w are given by

$$X_n = M_n/M^* \tag{17}$$

$$X_w = M_w/M^* \tag{18}$$

So, from the equation presented in the previous paper [8], we can obtain K_{trp}/K_p by means of the X_n and X_w, the total unsaturation, and the polymerization parameters as follows:

$$K_{trp}/K_p = (1 - 1/X_n - \sqrt{1 - 1/X_n^2 + 2X_n - 2X_w/X_n^2})$$

$$(1 - X)[1 + C_s F_s/F_g(1 - X) + U/500 + F_i/F_g X]/$$

$$[(1 + 1/X_n + \sqrt{1 - 1/X_n^2 + 2X_n - 2X_w/X_n^2})X] \tag{19}$$

where

$$C_s = K_{trs}/K_p \qquad (20)$$

Lastly, the exponent α, λ, M_n, M_w, and K_{trp}/K_p are determined by an iterative process in which the initially set value of K_{trp}/K_p is iteratively varied until it agrees with the K_{trp}/K_p obtained in Eq. (19) with certain accuracy.

EXPERIMENTAL

In order to calculate α, λ, M_n, M_w, and K_{trp}/K_p by use of the method described in the preceding section, we measured SEC, $[\eta]$, total unsaturation per 1000 CH_2, and reaction parameters (T, T_0, P, F_g, F_s, F_i, and X) by experiment.

Reaction Conditions

The samples were obtained by our continuous well-stirred tank reactor (V = 1.466 L, L/D = 5). The stirring speed and the feed gas amount were kept constant at 1500 rpm and 1537 mol/h, respectively. n-Hexane was used as the chain transfer agent.

Two series of polymerization were carried out in order to investigate the dependence of α, λ, M_n, M_w, and K_{trp}/K_p on pressure and temperature. In one series, the reaction temperature was kept constant and the reaction pressure was varied. In the other series the temperature was varied and the pressure was kept constant. The reaction pressure ranged from 1800 to 3000 kg/cm^2 (at 230°C), and the reaction temperature ranged from 175 to 275°C (at 2400 kg/cm^2). Within the above ranges of pressure and temperature, the contribution of the termination reaction to the number-average molecular weight is considered to be negligibly small.[15].

Tert-butylperoxy isobutyrate as initiator was used in almost all the runs. However, at extremely high or extremely low temperatures, tert-butylperoxy isopropyl and tert-butylperoxy pivalate, respectively, were used. Further detailed conditions are shown in Table 2.

Molecular Analysis

SEC and intrinsic viscosity were measured for each sample. The SEC measurements were performed on a Waters Model 200 GPC under the following conditions: column combination, four mixed gel columns

TABLE 2. Reaction Conditions

Run no.	Reaction pressure P (kg/cm^2)	Reaction temperature T (°C)	Feed gas temperature T_0 (°C)	Gas feed F_g (mol/h)	Solvent feed F_s (mol/h)	Initiator feed F_i (mol/h)	Conversion X (%)
1	3000	230.5	70.2	1537	41.19	1.734×10^{-3}	14.13
2	2700	230.4	70.8	1537	35.74	2.366×10^{-3}	14.07
3	2400	230.3	70.3	1537	33.83	3.323×10^{-3}	14.11
4	2000	229.2	70.5	1537	32.44	5.203×10^{-3}	14.00
5	1800	230.3	69.9	1537	26.09	9.314×10^{-3}	14.14
6	2400	256.0	70.0	1537	23.59	4.558×10^{-3}	16.32
7	2400	231.2	70.0	1537	36.98	3.073×10^{-3}	14.21
8	2400	215.0	70.8	1537	47.48	2.213×10^{-3}	12.77
9	2400	201.6	70.6	1537	53.16	1.582×10^{-3}	11.64
10	2400	174.8	70.6	1537	63.54	4.79×10^{-3}	9.35

TABLE 3. Molecular Structures

Run no.	$[\eta]$	Total unsaturation per 1000 CH₂
1	0.77	0.31
2	0.81	0.30
3	0.79	0.31
4	0.82	0.34
5	0.74	0.37
6	0.76	0.43
7	0.77	0.30
8	0.78	0.26
9	0.78	0.21
10	0.76	0.28

GMF (made by Toyo Soda Co.); solvent, o-chlorobenzene; flow rate, 1 mL/min; temperature, 140°C; input-solution concentration, 4 mg/mL; and injection time, 2 min. A linear calibration curve for SEC was used on the basis of the results of Loy [12]. The calibration was performed by use of Pressure Chemical's monodisperse polystyrene.

The viscosity measurements were performed on an automatic viscometer under the following conditions: capillary diameter, 0.420 mm; capillary length, 100 mm; upper bulb volume, 3.0 cc; lower bulb volume, 2.0 cc; and temperature, 130.00 ± 0.01°C. The kinetic energy correction was performed by the use of pure benzene [23].

The total unsaturation per 1000 CH₂ of any sample was obtained by summing the contents of $\diagdown$C=C, $\diagdown$C=C$\diagdown$, and $\diagup$C=C per 1000 CH₂. The content of these three was determined by analyzing the IR spectra at 966, 905, and 888 cm^{-1}, respectively, obtained on a Type 403-G made by Nippon Bunko Co. The data on $[\eta]$ and the total unsaturation of the samples in each run are shown in Table 3.

RESULTS AND DISCUSSION

α, λ, M_n, M_w, and K_{trp}/K_p were calculated from the method mentioned above by using the experimental data shown in Tables 2 and 3 and the SEC data of the samples corresponding to each run in Table 2. In order to calculate α, λ, M_n, M_w, and K_{trp}/K_p in the triple iterative process, a computer program was written in ASCII Fortran and it requires about 2 s of UNIVAC 1100/81 run time.

TABLE 4. Calculation Results

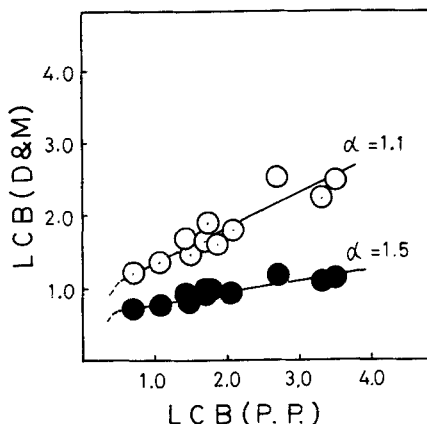| Run no.	P (kg/cm)	T (°C)	α (-)	$\lambda \times 10^4$	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	$K_{trp}/K_p \times 10^2$
1	3000	230.5	1.19	1.01	2.33	1.30	1.72
2	2700	230.4	1.08	1.20	2.38	1.51	2.06
3	2400	230.3	1.14	1.23	2.54	1.71	2.09
4	2000	229.2	1.04	1.46	2.57	1.94	2.51
5	1800	230.3	1.08	1.91	2.65	2.47	3.25
6	2400	256.0	0.94	2.37	2.20	2.03	3.41
7	2400	231.2	1.14	1.30	2.52	1.77	2.20
8	2400	215.0	1.10	1.02	2.15	1.17	1.96
9	2400	201.6	1.26	0.736	2.26	1.07	1.57
10	2400	174.8	1.52	0.486	2.26	0.838	1.32

FIG. 1. Comparison between LCB (present paper) and LCB (Drott and Mendelson) per 1000 CH_2.

In this calculation, g in good solvents is assumed to be equal to that in theta solvent, and a C_s value obtained from the following equation [8] was used:

$$C_s = 0.22 \exp \{ - 2300/1.987T + 0.24P/84.78T \}$$

The correction for SCB had so little effect on α, λ, M_n, M_w, and K_{trp}/K_p that it was neglected in order to simplify the calculation.

The calculation results of α, λ, M_n, M_w, and K_{trp}/K_p are shown in Table 4.

With respect to the samples used here, the relation between LCB obtained by Drott and Meldelson's method and LCB by the present papers is illustrated in Fig. 1 (in the former method, α was assumed to be 1.5 and 1.1). Figure 1 shows that LCB per 1000 CH_2 (Drott and Mendelson) and LCB per 1000 CH_2 (present paper), for the most part, agree with each other in their order, though the degrees of LCB (present paper) lie in a range broader than those of LCB (Drott and Mendelson):

0.5 < LCB (present paper) < 3.5
0.6 < LCB (Drott and Mendelson) < 1.2 (at α = 1.5)
1.1 < LCB (Drott and Mendelson) < 2.6 (at α = 1.1)

As is known from Table 1, the degrees of LCB of LDPE reported by other investigators are between 0.1 and 13 per 1000 CH_2. The degrees of LCB (present paper) are included within the range.
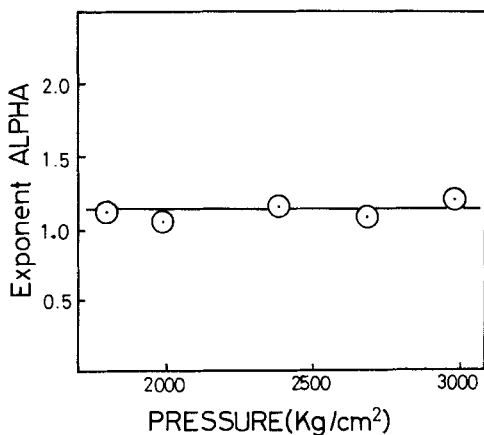
FIG. 2. Pressure dependence of exponent α.

As for K_{trp}/K_p, from its dependence on pressure and temperature (in Table 4), the activation energy, E_a, and the activation volume, ΔV^*, were determined to be 4.1 kcal/mol and 20.0 cc/mol, respectively. The values are very close to those obtained in the previous paper [8] (where E_a and ΔV^* were 3.6 kcal/mol and 24.1 cc/mol, respectively). They are therefore considered to be reasonable.

The exponent α obtained in the present paper lays between 0.9 and 1.5, being centered at 1.1 (Table 4). The values between 0.5 and 1.5 are currently used for LDPE (Table 1), where ours are included. The values reported by other investigators who performed detailed studies on α in LDPE are as follows: Cote and Shida [14], 4/3; Ham et al. [27], 1.0 ± 0.2; Moore and Millns [28], 1.2; Völker and Luig [29], 1.3; and Bohdanecký [24], 0.8 and 1.0. All of these values are in good agreement with ours.

For LCB, K_{trp}/K_p, and α, our values are considered to be valid, so our method is verified.

Now we discuss the pressure and temperature dependence of α. The pressure dependence of α, with the reaction temperature kept constant at 230°C, is illustrated in Fig. 2. Figure 2 shows that the value of α is independent of the reaction pressure, lying around 1.1. In contrast, the temperature dependence of α, with the reaction pressure kept constant at 2400 kg/cm^2, is illustrated in Fig. 3. Figure 3 shows that the value of α decreases linearly from 1.5 to 0.9 as the reaction temperature increases from 180 to 260°C.

What do these results imply? No adequate theory on the meaning of α is available for random branched polymer, but α is considered
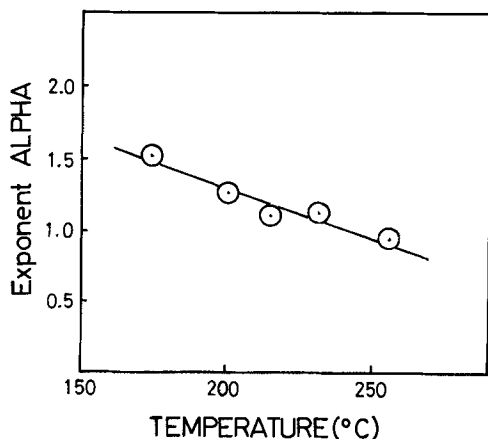
FIG. 3.   Temperature dependence of exponent α.

to be closely related to the type of branching. The values 3/2 and
1/2 are most frequently substituted for α. The former is considered
to be adequate for comblike molecules with short lateral chains [26].
The latter has been theoretically found to be satisfactory for certain
types of starlike branching [17]. Zimm and Kilb [17] suggested
that it might also be used as an approximation for other starlike
structures and for randomly branched ones. Experimental investi-
gations carried out with well-defined model polymers (polystylene
and polybutadiene) have shown that this approximation holds for
starlike branched structures at low degrees of branching only [18,
19], while higher α values are to be used at higher degrees [20].
Berry and Cassasa suggested for star-and-comb type polymers that
$\alpha = 1/2 + \lambda$, where λ is the material fraction in the backbone of the
molecule [21]. That is, α becomes 1/2 at $\lambda = 0$ (starlike branching),
approaching 3/2 at $\lambda \rightarrow 1$ (comblike branching with short lateral chains).
      Therefore the calculation results (Figs. 2 and 3) based on our
experimental data may lead to the suggestion that the branching
structure in LDPE might be intermediate, presumably a ramified
structure between starlike structure and comblike one. Small pointed
out that for the type of branching present in LDPE, presumably lead-
ing to ramified structures, if g is represented as a power of G, the
best value of the exponent is somewhere between 1.0 and 1.3 [6].
This is in fair agreement with our results.
      Moreover, Figs. 2 and 3 may be considered to suggest that the
branching structure is independent of reaction pressure in free-
radical polymerization of ethylene, but it depends on reaction tem-
perature. As a polymerization parameter with the same behavior,
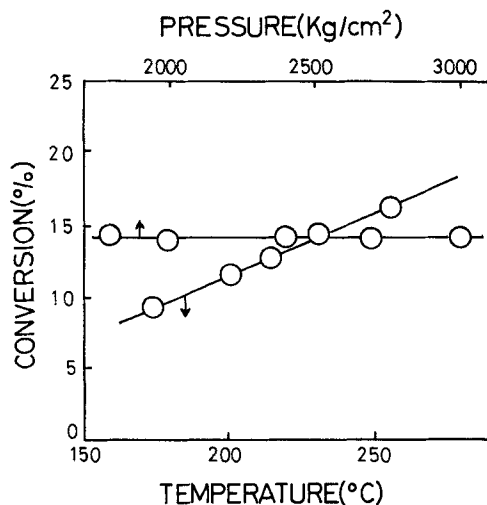the conversion can be noted (Fig. 4). Therefore, from Figs. 2, 3, and

FIG. 4. Pressure and temperature dependence of conversion.

4, α, which is considered to represent the branching structure, may be interpreted as a parameter which depends on polymer concentration in the reactor. At lower polymer concentrations, polymers with $\alpha \simeq 1.5$ (maybe comblike ramified structures) may much produced, but, as the polymer concentration increases, polymers with $\alpha \to 0.5$ (starlike ramified structures) may much produced.

This may possibly be explained in terms of the following hypothesis: As the polymer concentration increases, diffusion of polymer radicals is controlled, thus creating a condition which produces a starlike ramified molecule rather than a comblike one.

We could obtain valid values for LCB, K_{trp} and α, and in addition the pressure and temperature dependence of α could be favorably interpreted. These prove that our method is reasonable, although it rests on the important assumptions that the reactor is perfectly stirred and that λ is constant, both of which may not actually apply. They also prove the validity of Mullikin and Mortimer's probabilistic model and Drott and Mendelson's method. Henceforth, measurements based on other approaches such as C-13 NMR and SEC-LALLS will be necessary for each fraction of the samples we used in this work.

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REFERENCES

[1] J. K. Beasley, J. Am. Chem. Soc., 75, 6123 (1953).
[2] L. Nicolas, J. Chim. Phys., 55, 185 (1958).
[3] P. Ehrlich and C. A. Mortimer, Adv. Polym. Sci., 7, 386, 448 (1970).
[4] R. V. Mullikin and G. A. Mortimer, J. Macromol. Sci.–Chem., A4, 1495 (1970).
[5] P. A. Small, Polymer, 13, 536 (1972).
[6] P. A. Small, Adv. Polym. Sci., 18, 1 (1975).
[7] R. V. Mullikin and G. A. Mortimer, J. Macromol. Sci.–Chem., A6, 1301 (1972).
[8] K. Yamamoto and M. Sugimoto, Ibid., A13(8), 1067 (1979).
[9] E. E. Drott and R. A. Mendelson, J. Polym. Sci., A-2, 8, 1361 (1970).
[10] H. C. Benoit, Z. Grubisic, P. Rempp, D. Decker, and J. G. Zilliox, J. Chim. Phys., 63, 1507 (1966).
[11] E. E. Drott and R. A. Mendelson, J. Polym. Sci., A-2, 8, 1373 (1970).
[12] B. R. Loy, J. Polym. Sci., Polym. Chem. Ed., 14, 2321 (1976).
[13] B. H. Zimm and W. H. Stockmayer, J. Chem. Phys., 17, 1301 (1949).
[14] J. A. Cote and M. Shida, J. Polym. Sci., A2(9), 421 (1971).
[15] Th. J. Van der Molen, IUPAC-Conference Budapest, 1969, Preprint 777.
[16] F. W. Billmeyer, J. Am. Chem. Soc., 75, 6118 (1953).
[17] B. H. Zimm and R. W. Kilb, J. Polym. Sci., 37, 19 (1959).
[18] M. Morton, T. E. Helminiak, S. D. Gadkary, and F. Bueche, Ibid., 57, 471 (1962).
[19] T. Altares, D. P. Wyman, V. R. Allen, and K. Meyersen, Ibid., A3, 4131 (1965).
[20] H. Eschwey, M. L. Hellensleben, and W. Burchard, Angew. Chem. Int. Ed., 13, 412 (1974).
[21] G. C. Berry and E. F. Casassa, Macromol. Rev., 4, 1 (1970).
[22] D. E. Axelson and W. C. Knapp, J. Appl. Polym. Sci., 25, 119 (1980).
[23] L. H. Cragg and H. Van Oene, Can. J. Chem., 39, 203 (1961).
[24] M. Bohdanecky, Macromolecules, 10(5), 971 (1977).
[25] J. Miltz and A. Ram, Polymer, 12, 685 (1971).
[26] G. C. Berry, J. Polym. Sci., Part A-2, 9, 687 (1971).
[27] T. Ham, K. Yamaguchi, and T. Suzuki, Macromol. Chem., 155, 282 (1972).
[28] W. R. A. D. Moore and W. Millns, Br. Polym. J., 1, 81 (1969).
[29] H. Völker and F. J. Luig, Angew. Macromol. Chem., 12, 43 (1970).

[30] F. A. Bovey, F. C. Schilling, F. L. McCrackin, and H. L. Wagner, Macromolecules, 9, 76 (1976).
[31] L. D. Moore, G. R. Greear, and J. O. Sharp, J. Polym. Sci., 59, 339 (1962).
[32] J. E. Guillet, Ibid., A1, 2869 (1963).
[33] R. A. Mendelson and E. E. Drott, Ibid., B6, 795 (1968).
[34] K. Yamaguchi, M. Kawagucki, M. Kishi, N. Aki, and K. Sawanishi, Kobunshi Kagaku, 26, 522 (1969).
[35] E. P. Otocka, R. J. Roe, and M. Muglia, Prepr., Am. Chem. Soc., Polym. Div., 12, 685 (1971).