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Rate Constant for Long-Chain Branch Formation in Free-Radical Polymerization of Ethylene

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ABSTRACT

Quantitative measurements on the rate constant for long-chain branching in radical polymerization of ethylene have not yet been cited. This paper presents a convenient method of calculating the ratio of the rate constant for long-chain branching to that for propagation, by means of polymerization parameters, average degrees of polymerization (\bar{X}_n and \bar{X}_w), and amount of total unsaturation. The results of calculation based on our experimental data show that the activation energy $E_{trp} - E_p$, and the activation volume $\Delta V_{trp}^* - \Delta V_p^*$, were 3.6 kcal/mole and 24 cc/mole, respectively, in radical polymerization of ethylene. The validity of these values is discussed.

INTRODUCTION

The molecular weight distribution in free-radical polyethylene is usually broad; this is attributed to the presence of long-chain branches in polymer molecules [1-4]. It has been considered by a number of

authors that long-chain branching probably arises from the abstraction by a growing radical of any hydrogen atom at sites (chain transfer to polymer), followed by monomer addition to the new radical. The rate constant for chain transfer to a polymer has already been used in recent papers of Chen et al. and Agrawal and Han regarding the computer model for their high-pressure polyethylene reactor [8, 9]. Unfortunately, however, as pointed out by Ehrlich and Mortimer [3], quantitative measurements on the rate constant for chain transfer to a polymer and its dependence on pressure and temperature has not yet been cited.

In this paper, we attempt to derive a method of expressing K_{trp}/K_p by means of polymerization parameters, average degrees of polymerization, and total unsaturation, using Mullikin and Mortimer's probabilistic model [4].

An attempt is made, further, to determine the dependence on pressure and temperature of K_{trp}/K_p from our experimental data.

METHOD OF CALCULATION FOR K_{trp}/K_p

In 1970, Mullikin and Mortimer suggested a method of calculating number-average degree of polymerization X_n and weight-average degree of polymerization X_w by using a probabilistic model [4]. Such a model was further studied, and the validity of the above calculation method was shown by Small in 1972 by use of a generating function method [5]. Moreover, in order to take account of the time dependence of branching probability and the distribution of residence time in a continuous reactor, Mullikin and Mortimer extended their own model and suggested an improved method of calculating degrees of polymerization (X_n and X_w), using a nonuniform probability of branching [6]. Small confirmed the above method, again using the generating-function method [7]. However, as pointed out by Mullikin and Mortimer [6], the results of calculation show the predictions of the two mathematical models are similar, and both models fit published data on polyethylene equally well.

Thus, on the assumption of constant branching probability [4], the present paper suggests the calculation method for K_{trp}/K_p .

Assumptions and Definitions

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]. The elementary reactions are assumed to be

the following seven 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 can be neglected because it does not contribute to the molecular weight distribution.

Kinetic parameters (all in liters/mole-sec) are K_p , rate constant for propagation; K_t , rate constant for termination; K_{td} , rate constant for disproportionation termination; K_{trs} , rate constant for chain transfer to a transfer agent; K_{trm} , rate constant for chain transfer to a monomer; K_{trp} , rate constant for chain transfer to a polymer; K_β is the rate constant for total β -scission (sec^{-1}); and $2fk_d[I]$ is the rate of initiation of new polymer chains by initiator radicals (mole/liter-sec). $[M]$, $[S]$, $[P]$, and $[R]$ are concentration of monomer, chain transfer agent, polymer and free radical, respectively, all in mole/liter.

Reaction parameters are T , reaction temperature ($^\circ\text{K}$); T_0 , feed gas temperature ($^\circ\text{K}$); P , reaction pressure (kg/cm^2); τ , mean residence time (sec); F_g , feed monomer amount (mole/hr); F_s , feed transfer agent amount (mole/hr); F_i , feed initiator amount (mole/hr); X , conversion; V , volume of reactor (liters).

Molecular parameters are X_n , the number average degree of polymerization; X_w , weight-average degree of polymerization; $Q = X_w/X_n$; and (U) , total unsaturation per 1000 CH_2 . p is the probability of chain propagation and b denotes the probability of long-chain branching. p and b are defined as kinetically expressed as: $p = \text{rate of propagation}/\text{rate of total reactions of radicals which contribute to MWD}$; and $b = \text{rate of long-chain branching}/\text{rate of total reactions of radicals which contribute to MWD}$.

Formulation

p and b are kinetically formulated on the basis of above definitions as follows:

$$p = K_p [R] [M] / D \quad (1)$$

$$b = K_{trp} [R] [P] / D \quad (2)$$

where

$$D = K_p [R][M] + K_{trs} [R][S] + K_{trm} [R][M] + K_{trp} [R][P] + K_B [R] + K_t [R]^2 + [R]/\tau \quad (3)$$

Putting

$$K_t [R]^2 + [R]/\tau = 2fK_d [I]$$

in Eq. (3) at steady state, we have

$$D = K_p [R][M] + K_{trs} [R][S] + K_{trm} [R][M] + K_{trp} [R][P] + K_B [R] + 2fK_d [I] \quad (4)$$

The kinetic parameters are written in terms of polymerization parameters as Eqs. (5)-(8):

$$[M] = F_g (1 - X) \tau / v \quad (5)$$

$$[S] = F_s (\tau / v) \quad (6)$$

$$[P] = F_p X (\tau / v) \quad (7)$$

Assuming that $f = 1$ and $[I]/\tau = 0$, we have

$$fK_d [I] / K_p [R][M] = F_i / X F_g \quad (8)$$

Moreover, total unsaturation is kinetically expressed as:

$$U = 500K_B [R] + K_{trm} [R][M] + K_{td} [R]^2 / K_p [R][M] \quad (9)$$

If both the numerator and the denominator of Eq. (2) are divided by $K_p [R][M]$, then, by using Eqs. (5)-(9), b can be expressed in terms of reaction parameters and total amount of unsaturation, as in Eq. (10).

$$b = [K_{\text{trp}}X/K_p(1-X)]/[1 + C_s F_s/F_g(1-X) + K_{\text{trp}}X/K_p(1-X) + U/500 + F_i/XF_g] \quad (10)$$

where

$$C_s = K_{\text{trs}}/K_p$$

So, we can obtain K_{trp}/K_p from Eq. (10) as follows:

$$K_{\text{trp}}/K_p = b(1-X)[1 + C_s F_s/F_g(1-X) + U/500 + F_i/XF_g]/[(1-b)X] \quad (11)$$

In the meantime, as Mullikin and Mortimer and Small reported [4, 5], X_n and X_w are expressed as:

$$X_n = 1/(1-p-b) \quad (12)$$

$$X_w = (1-p^2 - b^2)/(1-p-b)^2 \quad (13)$$

Then, solving Eqs. (12) and (13) with respect to p and b , we have

$$p = (1-A + \sqrt{1-A^2 + 2A - 2B})/2 \quad (14)$$

$$b = (1-A - \sqrt{1-A^2 + 2A - 2B})/2 \quad (15)$$

where

$$A = 1/X_n$$

and

$$B = A^2 X_w$$

Therefore, if Eq. (15) is set in Eq. (11), we can calculate K_{trp}/K_p from reaction parameters (F_g , F_s , X , F_i , and C_s), X_n , X_w , and total unsaturation per 1000 CH_2 .

$$K_{\text{trp}}/K_p = (1 - 1/X_n - \sqrt{1 - 1/X_n^2 + 2/X_n - 2X_w/X_n^2}) (1 - X) \\ [1 + C_s F_s/F_g (1 - X) + U/500 + F_i/F_g X] / \\ [(1 + 1/X_n + \sqrt{1 - 1/X_n^2 + 2/X_n - 2X_w/X_n^2}) X] \quad (16)$$

EXPERIMENTAL

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

Reaction Conditions

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

Two series of polymerizations were carried out in order to investigate the dependence on pressure and temperature: in one series, reaction temperature was kept constant and reaction temperature was varied; in the other series, temperature was varied and pressure was kept constant. The reaction pressure ranged from 1800 to 3000 kg/cm^2 (at 230°C), and reaction temperature from 175°C to 275°C (at 2400 kg/cm^2). Within the above ranges of pressure and temperature, the contribution of termination reaction to number-average molecular weight is considered to be negligibly small [18].

Tert-butylperoxy isobutyrate as initiator was used in almost all the runs, but at extremely high or extremely low temperature, tert-butylperoxy isopropyl and tert-butylperoxy pivalate, respectively, were used. Further detailed conditions are shown in Table 1.

Molecular Analysis

As for each sample, M_n and M_w were obtained on the basis of the combination of GPC and intrinsic viscosity measurements [10-12]. The GPC measurements were performed on a Waters Model 200

TABLE 1. Reaction Conditions

Run no.	Reaction pressure P (kg/cm ²)	Reaction temperature T (°C)	Feed gas temperature T ₀ (°C)	Gas feed F _g (mole/hr)	Solvent feed F _s (mole/hr)	Initiator feed F _i (mole/hr)	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

under following conditions: column combination, four mixed gel columns GMF (made by Toyo Soda Co., Ltd.); solvent, o-chlorobenzene; flow rate, 1 ml/min; temperature, 140°C; input-solution concentration, 4 mg/ml; injection time, 2 min. A linear calibration curve for GPC was used on the basis of the results of Loy [12].

The total unsaturation per 1000 CH₂ of any sample was obtained by summing the contents of >C=C, >C=C< and >C=C per 1000 CH₂. The content of these three was determined by analyzing IR spectra at 966 cm⁻¹, 905 cm⁻¹, and 888 cm⁻¹, respectively, obtained on a Type 403-G made by Nippon Bunko Co., Ltd. The detailed data on molecular structures of the samples in each experimental run are shown in Table 2.

RESULTS AND DISCUSSION

K_{trp}/K_p was calculated from Eq. (16) by using the experimental data shown in Tables 1 and 2. In this calculation, a C_s value obtained from the following equation [21] was used:

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

The calculation results of K_{trp}/K_p are given in Table 3.

The relation between $\ln(K_{trp}/K_p)$ and the reciprocal of reaction temperature $1/T$ and the relation between $\ln(K_{trp}/K_p)$ and the reaction pressure P are illustrated in Figs. 1 and 2, respectively. The plots in Figs. 1 and 2 were found to be linear.

By means of the multiple regression analysis, the dependence on pressure and temperature of K_{trp}/K_p is expressed in Eq. (17):

$$K_{trp}/K_p = 3.1155 \exp \{-3562/1.9872T - 24.07P/84.07T\} \quad (17)$$

where the multiple regression coefficient $R^2 = 0.935$.

From Eq. (17), we obtained 3.6 kcal/mole, 24 cc/mole, and 3.1155, as the activation energy $E_{trp} - E_p$, the activation volume, $\Delta V_{trp}^* - \Delta V_p^*$, and the frequency factor, respectively.

The activation energy for ethyl radical addition to ethylene E_p was reported as 6.9 kcal/mole [20]. Moreover, the estimated value of E_p and ΔV_p^* in polymerization of ethylene were reported as 7-8 kcal/mole [3, 8, 9] and as -23 cc/mole [19], respectively.

TABLE 2. Molecular Structures

Run no.	$M_n \times 10^4$	$M_w \times 10^4$	Q	$[\eta]$	Total unsaturation per 1000 CH ₂
1	2.27	13.9	6.1	0.77	0.31
2	2.28	16.6	7.3	0.81	0.30
3	2.46	18.7	7.6	0.79	0.31
4	2.46	22.8	9.3	0.82	0.34
5	2.52	29.9	11.9	0.74	0.37
6	2.07	24.6	11.9	0.76	0.43
7	2.43	19.7	8.1	0.77	0.30
8	2.09	13.0	6.2	0.78	0.26
9	2.21	11.3	5.1	0.78	0.21
10	2.21	8.5	3.8	0.76	0.28

Therefore, if these values are adopted, we can estimate the values of E_{trp} and ΔV_{trp}^* to be 10.5-11.6 kcal/mole and 1 cc/mole, respectively.

The validity of values obtained will be investigated in succession.

E_{trp}

The activation energy for hydrogen abstraction from $CH_3(CH_2)_5CH_3$ by methyl radical and by ethyl radical was reported as 9.20 kcal/mole [14], and 10.6 and 11.6 kcal/mole [14, 20], respectively.

The activation energy for chain transfer to a transfer agent in polymerization of ethylene, $E_{trs} - E_p$, was reported as 4.2 kcal/mole for propane [22], and as 2.3 kcal/mole for n-hexane [21].

The activation energy for intramolecular hydrogen transfer in free-radical polymerization of ethylene, $E_b - E_p$ (where b refers to the short-chain branching reaction), was reported as 5.0 kcal/mole [17], 6.0 kcal/mole [16], and 2 to 3 kcal/mole [15].

As for E_{trp} , the value obtained in our study is found to be in fair

TABLE 3. Calculation Results

Run no.	P (kg/cm)	$1/T$ (deg^{-1}) $\times 10^{-3}$	X_n	X_w	K_{trp}/K_p	$\ln(K_{\text{trp}}/K_p)$
1	3000	1.99	810.7	4964	0.015578	-4.162
2	2700	1.99	814.3	5929	0.019989	-3.913
3	2400	1.99	878.6	6679	0.019581	-3.933
4	2000	1.99	878.6	8143	0.025685	-3.662
5	1800	1.99	900.0	10679	0.033731	-3.389
6	2400	1.89	739.3	8786	0.034846	-3.356
7	2400	1.98	867.9	7036	0.021446	-3.842
8	2400	2.05	746.4	4643	0.019481	-3.938
9	2400	2.11	789.3	4035	0.015070	-4.195
10	2400	2.32	789.3	2964	0.010840	-4.525

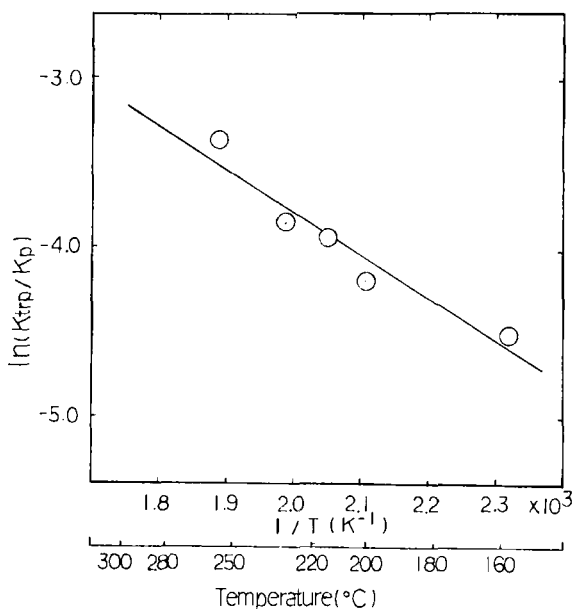


FIG. 1. Logarithm of calculated K_{trp}/K_p vs. temperature at 2400 kg/cm^2 .

agreement with the activation energy for hydrogen abstraction by the radicals mentioned above.

ΔV_{trp}^*

A mean value of activation volume for typical transfer agents in free-radical polymerization of ethylene, $\Delta V_{trs}^* - \Delta V_p^*$, was reported as +3 cc/mole [23, 21]. On the assumption that $\Delta V_p^* = -23$ cc/mole, ΔV_{trs}^* is roughly estimated to be -20 cc/mole.

The value $\Delta V_b^* - \Delta V_p^*$ was reported as 24 cc/mole [19, 23]. On the assumption that $\Delta V_p^* = -23$ cc/mole, ΔV_b^* is roughly estimated to be 1 cc/mole.

From the above, it can be noticed that the value we estimated, ΔV_{trp}^* , is much more similar to ΔV_b^* than to ΔV_{trs}^* . This means that the chain transfer to a polymer is hardly dependent on pressure, as well as on intramolecular hydrogen abstraction.

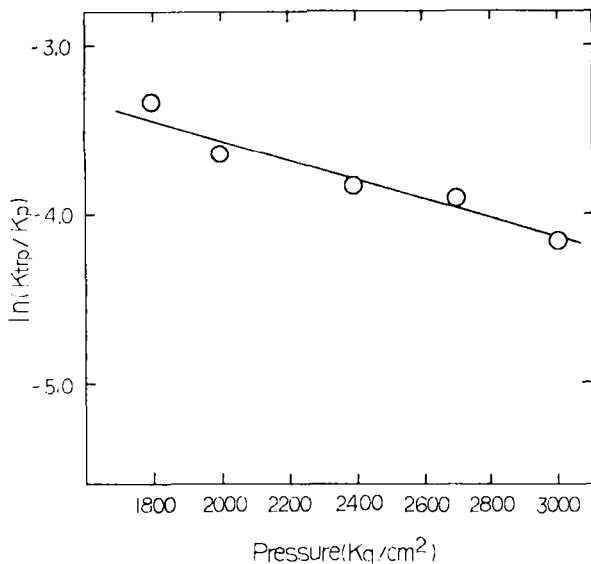


FIG. 2. Logarithm of calculated K_{trp}/K_p vs. pressure at 230°C.

Comparison with Literature Data

Lastly, as for K_{trp} , the comparison of our value with other authors' should be discussed, but, as few papers concerning K_{trp} have been published to date, it must be limited to discussion of the values used by a few authors in their computer models of tubular reactors.

Chen et al. [8] used 9 kcal/mole as the value of E_{trp} at 2000 kg/cm² in the computer model of their tubular high-pressure polyethylene reactor.

S. Agrawal and Han [9] used 12 kcal/mole and 0 cc/mole as the values of E_{trp} and ΔV_{trp}^* respectively, in their computer model.

According to Small [24], Jackson obtained estimates of K_{trp}/K_p by choosing the value so as to fit MWD, thus finding K_{trp}/K_p to be about 4.0×10^{-3} at 200°C and 2000 atm.

Our values are in fair agreement with those of the above-mentioned authors.

We could obtain an extremely valid value of kinetic factors of K_{trp}/K_p . This proves that our method is reasonable, although our

model described here rests on an important assumption that the reactor is perfectly stirred, which may actually not apply. We think this fact also proves the validity of Mullikin and Mortimer's probabilistic model.

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