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Formation of High Polymers on Solid Surfaces I. Theoretical Study of Mechanisms

ALFRED CLARK AND GRANT C. BAILEY

From the Phillips Petroleum Company, Bartlesville, Oklahoma

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Four models are set up for polymerization on solid surfaces. In two of the models, it is assumed that all adsorption sites have the same adsorption energy. The first of these (Rideal mechanism) assumes that polymerization occurs by reaction of monomer in the gas phase with adsorbed monomer or adsorbed, growing polymer chains. The second model (Langmuir-Hinshelwood mechanism) assumes that polymerization occurs by reaction of an adsorbed monomer molecule with an adjacently adsorbed monomer molecule or growing polymer chain. The other two models are the counterparts of the first two with a variation of adsorption energies among the sites.

With all adsorption sites of equal energy, it is shown that in both mechanisms there is a unique weight average molecular weight for each number average molecular weight. Weight average–number average molecular weight ratio, $(\bar{W}/\bar{N})$, a measure of the broadness of molecular weight distribution, is shown to be in the range, $1 \leqslant \bar{W}/\bar{N} \leqslant 2$, for all values of velocity constants and pressure. In the Rideal mechanism, number and weight average molecular weights and rates of reaction increase without limit as pressure is increased. In the Langmuir-Hinshelwood mechanism, molecular weights and rates approach a maximum value asympotically as pressure is increased.

With a distribution of adsorption energies, weight average–number average molecular weight ratios $(\bar{W}/\bar{N})$ can have values far in excess of 2 for both mechanisms. Molecular weights and rates of reaction again level out with increasing pressure for the Langmuir-Hinshelwood mechanism, and increase without restriction in the Rideal mechanism.

I. Introduction

The discoveries that certain solid catalysts (*1–3*) can produce high polymers from olefins and diolefins have sparked a great deal of theoretical and experimental work on the nature of the reactions. In this paper the objectives are to derive expressions for the following quantities: (1) number average molecular weights, (2) weight average molecular weights, (3) weight average-number average molecular weight ratios, and (4) rates of polymerization. These quantities are derived as functions of velocity constants (adsorption, reaction, and desorption), pressure, and temperature. Four possible models are set up and, in the following paper, compared with the results of experiments on the polymerization of ethylene in the presence of chromium oxide-silica-alumina catalyst.

In all four models, the polymerization process is restricted to reaction of monomer with itself and with growing polymer chains. Also, the density of adsorption sites is assumed constant over the catalyst surface.

In two of the models, it is assumed that all adsorption sites have the same adsorption energy. The first of these assumes that polymerization occurs by reaction of monomer in the gas phase with adsorbed monomer or with adsorbed, growing polymer chains. This will be referred to as the Rideal mechanism (*4*). The second model

assumes that polymerization occurs by reaction of an adsorbed monomer molecule with an adjacently adsorbed monomer molecule or growing polymer chain. It will be referred to as the Langmuir-Hinshelwood mechanism (*5*, *6*).

The other two models are the counterparts of the first two with an exponential distribution of adsorption energies among the sites.

Some simplifications in the kinetics have been made in order to make the calculations tractable. These simplifications affect the magnitude of the results, but not the general character of the relationships. Conclusions in this paper have been limited to those which depend only on the general character of the relationships.

II. Definitions of Number Average and Weight Average Molecular Weight

Number and weight average molecular weight are defined respectively as follows:

$$\bar{N} = M_1 \frac{\Sigma n N_n}{\Sigma N_n}$$

$$\bar{W} = M_1 \frac{\Sigma n^2 N_n}{\Sigma n N_n}$$

where N_n is the number of molecules containing n monomer units, M_1 is the molecular weight of monomer, and $\bar{N}$ and $\bar{W}$ are the number and weight average molecular weights respectively. The summations extend over all polymer species from $n = 2$ to ∞.

For each model, the three quantities, ΣN_n, $\Sigma n N_n$, and $\Sigma n^2 N_n$ will be evaluated explicitly.

III. Derivation of Equations for Energetically Homogeneous Surfaces

A. Rideal Mechanism

The term ΣN_n is regarded as the number of molecules of polymer desorbed per unit catalyst surface per second. It can be expressed as:

$$\Sigma N_n = k_d N_0 \sum_{n=2}^{\infty} \theta_n \qquad (1)$$

where k_d, the desorption velocity constant, is the number of polymer molecules desorbed per second from one site, N_0 is the total number of sites per unit catalyst surface, and θ_n is the fraction of sites covered with n-mer (a polymer chain of n monomer units). It is assumed that k_d is independent of n.

Similarly,

$$\Sigma n N_n = k_d N_0 \sum_{n=2}^{\infty} n\theta_n \qquad (2)$$

$$\Sigma n^2 N_n = k_d N_0 \sum_{n=2}^{\infty} n^2 \theta_n \qquad (3)$$

The terms, $\Sigma_{n=2}^{\infty}\theta_n$, $\Sigma_{n=2}^{\infty} n\theta_n$, and $\Sigma_{n=2}^{\infty} n^2\theta_n$ are evaluated explicitly as follows:

At steady state conditions, a balance for adsorbed n-mer gives:

$$k_r P\theta_{n-1} - k_r P\theta_n - k_d\theta_n = 0$$

where k_r (assumed independent of n) is the reaction velocity constant for the reaction of gas phase monomer with adsorbed n-mer, and P is the gas-phase pressure of monomer.

Using balances of this type for various values of n, it can be shown that $\Sigma_{n=1}^{\infty}\theta_n$ is an infinite geometric series whose sum is:

$$\sum_{n=1}^{\infty} \theta_n = \frac{(k_r P + k_d)\theta_1}{k_d}$$

Therefore,

$$\sum_{n=2}^{\infty} \theta_n = \frac{k_r P\theta_1}{k_d}$$

$$\sum_{n=2}^{\infty} n\theta_n = \frac{k_r P\theta_1(k_r P + 2k_d)}{k_d^2}$$

$$\sum_{n=2}^{\infty} n^2\theta_n = \frac{k_r P\theta_1(2k_r^2P^2 + 5k_r P k_d + 4k_d^2}{k_d^3}$$

The term θ_1 is evaluated explicitly from the balance of adsorbed monomer:

$$k_a P\left(1 - \sum_{n=1}^{\infty} \theta_n\right) - k_r P\theta_1 - k_d\theta_1 = 0$$

where k_a is the adsorption velocity constant of monomer, and the term in parentheses is the fraction of unoccupied sites.

The final expressions for ΣN_n, ΣnN_n, and Σn^2N_n are:

$$\Sigma N_n = k_a k_d k_r P^2 N_0/(k_a P + k_d)(k_r P + k_d)$$

$$\Sigma nN_n = k_a k_r P^2 N_0(k_r P + 2k_d)/(k_a P + k_d)(k_r P + k_d)$$

$$\Sigma n^2N_n = k_a k_r P^2 N_0(2k_r^2P^2 + 5k_r P k_d + 4k_d^2)/k_d(k_a P + k_d)(k_r P + k_d)$$

Expressions for number average molecular weight, weight average molecular weight, weight average-number average ratio, and rate of polymerization are now easily obtained:

$$\bar{N}/M_1 = (k_r P/k_d) + 2 = r + 2, \quad r = k_r P/k_d \quad (4)$$

$$\bar{W}/M_1 = (2r^2 + 5r + 4)/(r + 2) \quad (5)$$

$$\bar{W}/N = (2r^2 + 5r + 4)/(r + 2)^2 \quad (6)$$

$$\bar{R} = N_0 k_a P^2 k_r (k_r P + 2k_d)/(k_a P + k_d)(k_r P + k_d) = \Sigma nN_n \quad (7)$$

where the rate of polymerization, $\bar{R}$, is expressed as total number of monomer units in the polymer that is desorbed from unit catalyst surface per second.

B. Langmuir-Hinshelwood Mechanism

The procedure is nearly identical with that for the Rideal mechanism. The same implicit equations for ΣN_n, ΣnN_n, and Σn^2N_n hold, namely, Eqs. (1), (2), and (3). In determining the expressions for $\Sigma\theta_n$, $\Sigma n\theta_n$ and $\Sigma n^2\theta_n$, the same material balance procedure is employed except that pressure, P, is now replaced by $\theta_1 N_0$. These quantities now become:

$$\sum_{n=2}^{\infty} \theta_n = K_r\theta_1^2/k_d$$

$$\sum_{n=2}^{\infty} n\theta_n = K_r\theta_1^2(K_r\theta_1 + 2k_d)/k_d^2$$

$$\sum_{n=2}^{\infty} n^2\theta_n = K_r\theta_1^2(2K_r^2\theta_1^2 + 5K_r k_d\theta_1 + 4k_d^2)/k_d^3$$

where $K_r = k_r N_0$.

Expressions for ΣN_n, ΣnN_n, and Σn^2N_n, in terms of θ_1, then become:

$$\Sigma N_n = N_0 K_r \theta_1^2$$

$$\Sigma nN_n = N_0 K_r \theta_1^2(K_r\theta_1 + 2k_d)/k_d \quad (8)$$

$$\Sigma n^2N_n = N_0 K_r \theta_1^2(2K_r^2\theta_1^2 + 5K_r k_d\theta_1 + 4k_d^2)/k_d^3 \quad (9)$$

Expressions for number and weight average molecular weight, weight-number average ratio, and rate of polymerization become:

$$\bar{N}/M_1 = R_L + 2, \qquad R_L = K_r\theta_1/k_d \quad (10)$$

$$\bar{W}/M_1 = (2R_L^2 + 5R_L + 4)/(R_L + 2)$$

$$\bar{W}/N = (2R_L^2 + 5R_L + 4)/(R_L + 2)^2 \quad (11)$$

$$\bar{R} = N_0 K_r \theta_1^2(K_r\theta_1 + 2k_d)/k_d = \Sigma nN_n \quad (12)$$

A monomer material balance calculation carried out using the same principles as for the Rideal case leads to the steady state equation,

$$b^2\theta_1^3 + cb\theta_1^2 + 2b\theta_1^2 + c\theta_1 + \theta_1 - c = 0 \quad (13)$$

where $b = K_r/k_d$ and $c = k_a P/k_d$. This equation is difficult to solve for θ_1, with unevaluated parameters c and b. If the expression for θ_1 obtained from Eq. (10) (with $R_L = b\theta_1$) is substituted in Eq. (13), the following expression is obtained:

$$(\bar{N}/M_1)^3 + (c - 4)(\bar{N}/M_1)^2 + (5 - 3c)(\bar{N}/M_1) + 2c - cb - 2 = 0 \quad (14)$$

The properties of this equation will be discussed in a later section.

IV. Derivation of Equations for Energetically Heterogeneous Surfaces

A. Rideal Mechanism

The general expressions for ΣN_n, ΣnN_n, and Σn^2N_n are the same as in the preceding case for the Rideal mechanism except that they must be integrated over the adsorption energy Q, since the energy is variable.

$$\Sigma N_n = \int_0^{\infty} N_0 k_d(Q) \sum_{n=2}^{\infty} \theta_n(Q) F(Q) dQ \quad (15)$$

$$\Sigma nN_n = \int_0^\infty N_0 k_d(Q) \sum_{n=2}^{\infty} n\theta_n(Q)F(Q)dQ \tag{16}$$

$$\Sigma n^2N_n = \int_0^\infty N_0 k_d(Q) \sum_{n=2}^{\infty} n^2\theta_n(Q)F(Q)dQ \tag{17}$$

where all terms except N_0 are now functions of Q, and $F(Q)\,dQ$ is the fraction of sites with adsorption energy between Q and $Q + dQ$. If the distribution of adsorption energies is taken to be exponential, then:

$$F(Q)dQ = Ce^{-cQ}dQ$$

where C is a constant that describes the exact nature of the distribution function. An exponential distribution was selected because experimental evidence on the adsorption of ammonia on chromium oxide-silica-alumina polymerization catalysts indicates such a distribution of adsorption energies. However, the conclusions which will be drawn from the present work are not limited to an exponential distribution; they apply to any distribution which decreases monotonically with coverage.

The desorption velocity constant, k_d (Q), is put into the Arrhenius form, B exp $(-Q/RT)$. The pre-exponential factor B is assumed constant in these calculations; and Q is assumed numerically equal to the adsorption energy, which is tantamount to assuming a negligible activation energy of adsorption.

The substitutions for $F(Q)dQ$ and k_d are placed in Eqs. (15), (16), and (17). The explicit expressions for θ_1, $\Sigma\theta_n$, $\Sigma n\theta_n$, and $\Sigma n^2\theta_n$ are the same as in the equations for the homogeneous-site case of the Rideal mechanism. After considerable algebra, involving separation by partial fractions, the expressions for number average molecular weight, weight average molecular weight, weight average–number average ratio, and rate of polymerization become: [see Eq. (18)], where $Z = \exp(-Q/RT)$, $s = B/k_aP$, $q = B/k_rP$, and $p = RTC$, and the constant in the expression for rate is $k_r spPN_0/s - q$. The expressions are integrated. A value of p is selected and each of the quantities $\bar{N}$, $\bar{W}$, $\bar{W}/\bar{N}$, and $\bar{R}$ may be plotted against $1/q = k_rP/B$ to give a family of curves each representing a different value of the parameter $q/s = k_a/k_r$. In this way the general behavior according to the Rideal mechanism can be determined.

It will be observed in Eq. (18) that $\bar{W}$ becomes infinite for $p \leqslant 1$, when the integration is between the limits $Z = 0$ to $Z = 1$ ($Q = \infty$ to $Q = 0$). Under these conditions, it is necessary to know the finite upper limit of $Q(Z > 0)$. The lower limit of Z is then a function of temperature ($Z = \exp(-Q/RT)$).

B. *Langmuir-Hinshelwood Mechanism*

In this case, not only does k_d vary with Q, but also k_r. Interaction is restricted to pairs of sites acting independently. All possible combinations of paired energies are con-

$$\frac{\bar{N}}{M_1} = \frac{\left[\frac{s-q}{s}\int_0^1 \frac{Z^{p-1}}{1+sZ}dZ + \int_0^1 \frac{Z^{p-1}}{1+qZ}dZ\right]}{\left[\int_0^1 \frac{Z^{p-1}}{1+qZ}dZ - \int_0^1 \frac{Z^{p-1}}{1+sZ}dZ\right]}$$

$$\frac{\bar{W}}{M_1} = \frac{\left[\frac{2(s-q)}{q^2}\int_0^1 Z^{p-2}dZ + \frac{5sq-4q^2-2s^2}{q^2}\int_0^1 \frac{Z^{p-1}}{1+sZ}dZ + \int_0^1 \frac{Z^{p-1}}{1+qZ}dZ\right]}{\left[\frac{(s-q)}{s}\int_0^1 \frac{Z^{p-1}}{1+sZ}dZ + \int_0^1 \frac{Z^{p-1}}{1+qZ}dZ\right]} \tag{18}$$

$$\frac{\bar{W}}{\bar{N}} = \frac{\left[\frac{2(s-q)}{q^2}\int_0^1 Z^{p-2}dZ + \frac{5sq-4q^2-2s^2}{q^2}\int_0^1 \frac{Z^{p-1}}{1+sZ}dZ + \int_0^1 \frac{Z^{p-1}}{1+qZ}\right]\left[\int_0^1 \frac{Z^{p-1}}{1+qZ}dZ - \int_0^1 \frac{Z^{p-1}}{1+sZ}dZ\right]}{\left[\frac{s-q}{s}\int_0^1 \frac{Z^{p-1}}{1+sZ}dZ + \int_0^1 \frac{Z^{p-1}}{1+qZ}dZ\right]^2}$$

$$\bar{R} = \text{Constant} \times \left[\frac{s-q}{s}\int_0^1 \frac{Z^{p-1}}{1+sZ}dZ + \int_0^1 \frac{Z^{p-1}}{1+qZ}dZ\right]$$

sidered. Thus, expressions for ΣN_n, ΣnN_n, and Σn^2N_n involve double integrals.

The number of adsorbed polymer molecules at steady state on those sites of adsorption energy Q_1 which are paired with sites Q_2 is:

$$C^2 \exp[-C(Q_1 + Q_2)]N_0 \sum_{n=2}^{\infty} \theta_{1n}(Q_1,Q_2)$$

where $C\exp(-CQ_1)$ and $C\exp(-CQ_2)$ are the fractions of total sites with adsorption energies Q_1 and Q_2 respectively; and θ_{1n} is the fraction of sites of adsorption energy Q_1, paired with sites Q_2, which are occupied by n-mer.

Similarly, the number of adsorbed polymer molecules on those sites Q_2 which are paired with sites Q_1 is:

$$C^2 \exp[-C(Q_1 + Q_2)]N_0 \sum_{n=2}^{\infty} \theta_{2n}(Q_1,Q_2)$$

Expressions for ΣN_n, ΣnN_n, and Σn^2N_n become:

$$\Sigma N_n = \int_0^{\infty}\int_0^{\infty} C^2 \exp[-C(Q_1 + Q_2)]N_0 [k_{d1}(Q_1) \sum_{n=2}^{\infty} \theta_{1n}(Q_1,Q_2) + k_{d2}(Q_2) \sum_{n=2}^{\infty} \theta_{2n}(Q_1,Q_2)]dQ_1dQ_2$$

$$\Sigma nN_n = \int_0^{\infty}\int_0^{\infty} C^2 \exp[-C(Q_1 + Q_2)]N_0 [k_{d1}(Q_1) \sum_{n=2}^{\infty} n\theta_{1n}(Q_1,Q_2) + k_{d2} \sum_{n=2}^{\infty} n\theta_{2n}(Q_1,Q_2)]dQ_1dQ_2$$

$$\Sigma n^2N_n = \int_0^{\infty}\int_0^{\infty} C^2 \exp[-C(Q_1 + Q_2)]N_0 [k_{d1}(Q_1) \sum_{n=2}^{\infty} n^2\theta_{1n}(Q_1,Q_2) + k_{d2} \sum_{n=2}^{\infty} n^2\theta_{2n}(Q_1,Q_2)]dQ_1dQ_2$$

As in the Rideal case,

$$\begin{aligned} k_{d1} &= B \exp(-Q_1/RT), \\ k_{d2} &= B \exp(-Q_2/RT) \end{aligned} \qquad (19)$$

The summations under the integrals are put in explicit form by considering the fraction of time that each of the sites is covered by n-mer. Let t_{1n} and t_{2n} be the fractions of time that site of energy Q_1 and site of energy Q_2 are covered by n-mer, respectively. Surface material balances for each polymer species are set up and summed exactly as before. The following expressions are obtained:

$$\sum_{n=2}^{\infty} \theta_{1n} = t_{11}k_{r2}t_{21}/k_{d1}$$

$$\sum_{n=2}^{\infty} \theta_{2n} = t_{21}k_{r1}t_{11}/k_{d2}$$

$$\sum_{n=2}^{\infty} n\theta_{1n} = k_{r2}t_{21}t_{11}(k_{r2}t_{21} + 2k_{d1})/k_{d1}^2$$

$$\sum_{n=2}^{\infty} n\theta_{2n} = k_{r1}t_{11}t_{21}(k_{r1}t_{11} + 2k_{d2})k_{d2}^2$$

$$\sum_{n=2}^{\infty} n^2\theta_{1n} = t_{11}t_{21}k_{r2}(2k_{r2}^2t_{21}^2 + 5k_{r2}k_{d1}t_{21} + 4k_{d1}^2)/k_{d1}^3$$

$$\sum_{n=2}^{\infty} n^2\theta_{2n} = t_{11}t_{21}k_{r1}(2k_{r1}^2t_{11}^2 + 5k_{r1}k_{d2}t_{11} + 4k_{d2}^2)/k_{d2}^3$$

where k_{r1} is the rate at which monomer leaves site Q_1 to react on site Q_2 and k_{r2} is the rate from Q_2 to Q_1. The rate-limiting step in surface reaction is considered to be the removal of monomer from the site upon which it is adsorbed and not the reaction on the site to which it goes. In other words, the activation energy for surface reaction is assumed to be the energy required to remove an adsorbed molecule laterally from its position. In general, the activation energy will be (7) Q/m where m is a number $\geqslant 1$. For a surface with a small number of sites m must approach unity. The reaction velocity constants are taken to be:

$$\begin{aligned} k_{r1} &= D \exp(-Q_1/RT), \\ k_{r2} &= D \exp(-Q_2/RT), \\ D &= \text{constant} \end{aligned} \qquad (20)$$

These simplifications do not affect the general conclusions which will be drawn.

Evaluations of t_{11} and t_{21} are done by making a surface material balance for monomer containing the following steps:

i. Rate of adsorption of monomer from the gas phase on site Q_1.
ii. Rate of transfer of monomer adsorbed on site Q_1 to vacant site Q_2.
iii. Rate of transfer of monomer adsorbed on site Q_2 to vacant site Q_1.
iv. Rate of reaction of monomer from site Q_1 with monomer or polymer on site Q_2.
v. Rate of reaction of monomer from site Q_2 with monomer on site Q_1.
vi. Rate of desorption of monomer from site Q_1.

A similar balance is made for site Q_2.

After making substitutions from Eq. (19) for k_{d1} and k_{d2}, from Eq. (20) for k_{r1} and k_{r2}, and then the following substitutions, $Z_1 = \exp(-Q_1/RT)$, $Z_2 = \exp(-Q_2/RT)$, in the monomer balance equations, there is obtained:

$$Z_2^2 t_{21}^2 t_{11} + (aZ_2 + 2hZ_2Z_1)t_{21}t_{11} + (ahZ_1 + hZ_1^2 + h^2Z_1^2)t_{11} - hZ_2Z_1t_{21} - ahZ_1 = 0 \quad (21)$$

$$Z_1^2 t_{11}^2 t_{21} + (aZ_1 + 2hZ_1Z_2)t_{11}t_{21} + (ahZ_2 + hZ_2^2 + h^2Z_2^2)t_{21} - hZ_1Z_2t_{11} - ahZ_2 = 0 \quad (22)$$

where $a = k_aP/B$ and $h = B/D$. Since the activation energy of adsorption has been assumed to be zero, k_a is assumed constant for all sites.

The final expressions for ΣN_n, ΣnN_n, and Σn^2N_n are:

$$\Sigma N_n = \text{constant} \times \int_0^1\int_0^1 t_{11}t_{21}(Z_1^pZ_2^{p-1} + Z_1^{p-1}Z_2^p)dZ_1dZ_2 \quad (23)$$

$$\Sigma nN_n = \text{constant} \times \int_0^1\int_0^1 t_{11}t_{21}Z_1^{p-1}Z_2^{p-1} \{[Z_2(Z_2t_{21} + 2hZ_1)/hZ_1] + [Z_1(Z_1t_{11} + 2hZ_2)/hZ_2]\}dZ_1dZ_2 = \bar{R} \quad (24)$$

$$\Sigma n^2N_n = \text{constant} \times \int_0^1\int_0^1 t_{11}t_{21}Z_1^{p-1}Z_2^{p-1} \{[Z_2(2Z_2^2t_{21}^2 + 5hZ_2Z_1t_{21} + 4h^2Z_1^2)/h^2Z_1^2] + [Z_1(2Z_1^2t_{11} + 5hZ_1Z_2t_{11} + 4h^2Z_2^2)/h^2Z_2^2]\}dZ_1dZ_2 \quad (25)$$

where $p = RTC$ and the constant $= R^2T^2C^2N_0D/2$.

From these expressions, $\bar{N}/M_1$, $\bar{W}/M_1$, $\bar{W}/\bar{N}$, and $\bar{R}$ may be determined as before.

These equations [(23), (24), (25)] have been solved by use of a high-speed digital computer for a range of values of a and h by splitting Z_1 and Z_2 into subdivisions and introducing the corresponding values of t_{11} and t_{21} from the monomer balance Eqs. (21) and (22).

V. Results and Discussion

A. Energetically Homogeneous Surfaces

By inspection of Eqs. (4) and (5), which give number and weight average molecular weight for the Rideal mechanism, it is seen that the lowest values of $\bar{N}/M_1$ and $\bar{W}/M_1$ (at $r = k_rP/k_d = 0$) are both 2, and the values increase without limit as pressure, P, or k_r/k_d increase. The same applies to the Langmuir-Hinshelwood mechanism, where r is replaced by R_L as in Eqs. (10 and 11).

It is also easy to show that there is a unique value of weight average molecular weight for each number average molecular weight for both the Rideal and Langmuir-Hinshelwood mechanisms. When these mechanisms apply, determination of either number average or weight average molecular weight automatically fixes the other.

Equations (6) and (11) for the weight average-number average ratios in the Rideal and Langmuir-Hinshelwood mechanisms are of particular interest. This ratio determines the broadness of the molecular weight distribution. It is not difficult to show from these equations that $\bar{W}/\bar{N}$ has no maximum or minimum in the physically allowable range of positive values of r and R_L. In this range, $\bar{W}/\bar{N}$ is a monotonic increasing function of r and R_L. At $r = R_L = 0$, $\bar{W}/\bar{N} = 1$. In the limit as r, $R_L \to \infty$, it may be shown by application of De l'Hopital's rule that $\bar{W}/\bar{N}$ approaches 2. Thus the allowable values for $\bar{W}/N$ over the entire range of positive values of r and R_L lie in the range, $1 \leqslant \bar{W}/\bar{N} < 2$. For systems which follow the Rideal or Langmuir-Hinshelwood mechanism with homogeneous sites, it does not appear possible to obtain polymers of broad molecular weight distribution.

In Fig. 1, Eq. (14) is plotted with $\bar{N}/M_1$ and $c = k_aP/k_d$ as variables for a range of values of the parameter $b = K_r/k_d$ (Langmuir-Hinshelwood mechanism). It will be observed that for each value of the parameter b, that is, for a specific catalyst surface, number average molecular weight (and, therefore, weight average molecular weight) approaches a maximum value asymptotically as the value of c increases. The maximum value increases with increasing value of b. For a particular catalyst surface, an increase in the value of c represents an increase in pressure. No such leveling off in molecular weight is observed for the Rideal mechanism. In that case, molecular weight increases without limit for a given catalyst as pressure increases, as may be seen from Eqs. (4) and (5).

Equation (7) for the rate of polymerization in a Rideal mechanism shows that the rate increases indefinitely with pressure. From Eqs. (12) and (13) it can be shown that the rate of polymerization in a Langmuir mechanism levels out with increasing pressure in a manner similar to the molecular weights.

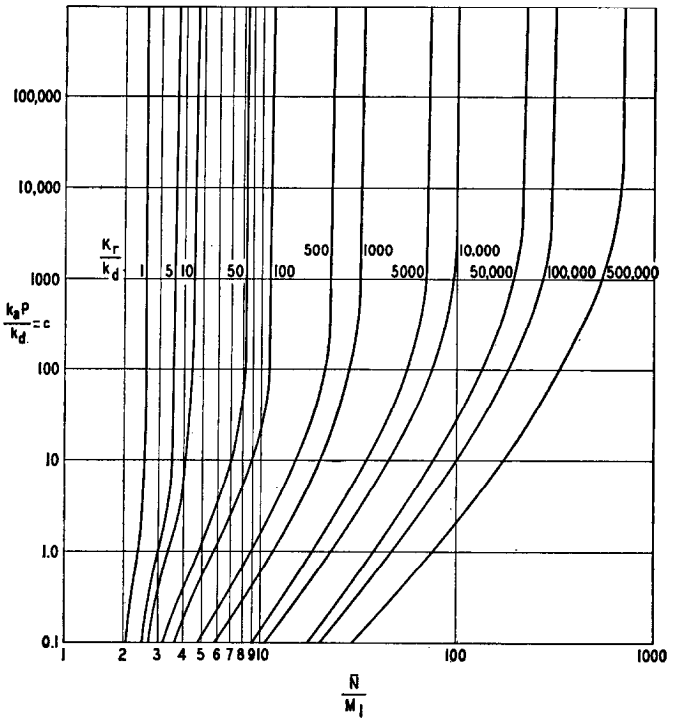

FIG. 1. $(1/M_1) \times$ number average molecular weight vs $k_aP/k_d = c$ with k_r/k_d as parameter; k_r = reaction velocity constant; k_a = adsorption velocity constant; k_d = desorption velocity constant; $\bar{N}$ = no. avg. mol. wt.; M_1 = mol. wt. of monomer. Langmuir-Hinshelwood mechanism, all sites of equal energy.

B. Energetically Heterogeneous Surfaces

In Figs. 2 and 3, typical curves of the Rideal mechanism are shown for the variation of weight average-number average ratio ($\bar{W}/\bar{N}$) with number average molecular weight ($\bar{N}/M_1$) at various values of the parameter k_a/k_r. For a given catalyst at constant temperature, $p = CRT$ represents the nature of the exponential distribution of sites. The greater the value of p, the more rapidly the number of sites falls off with increasing Q, (Ce^{-cq}). In Fig. 2, for $p = 2$, it will be observed that $\bar{W}/\bar{N}$ reaches a maximum which becomes higher and more pronounced the lower the value of the parameter k_a/k_r. A maximum of $\bar{W}/\bar{N} = 6$ is reached at the lowest value (0.0001) of

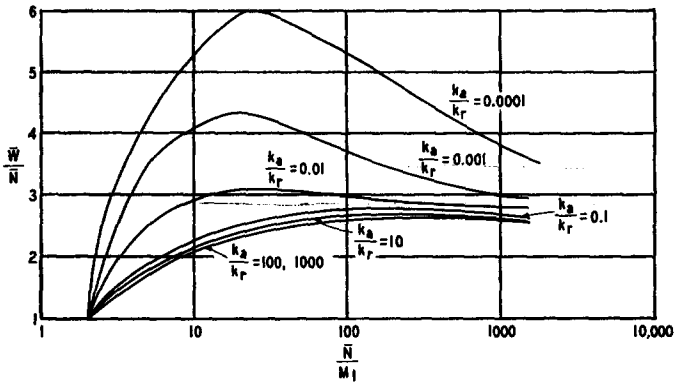

FIG. 2. Weight average–number average ratio vs $(1/M_1) \times$ number average molecular weight with k_a/k_r as parameter; $\bar{W}$ = wt. avg. mol. wt.; $\bar{N}$ = no. avg. mol. wt.; M_1 = mol. wt. of monomer; k_a = adsorption velocity constant; k_r = reaction velocity constant. Rideal mechanism, exponential distribution. $P = RTC = 2$.

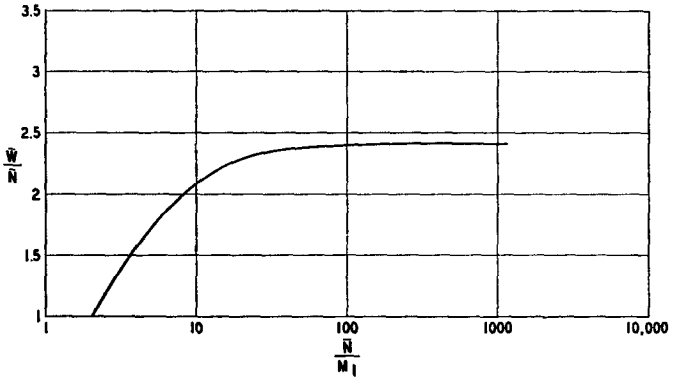

FIG. 3. Weight average–number average ratio vs $(1/M_1) \times$ number average molecular weight; $\bar{W}$ = wt. avg. mol. wt.; $\bar{N}$ = no. avg. mol. wt.; M_1 = mol. wt. of monomer; k_a = adsorption velocity constant; k_r = reaction velocity constant. Rideal mechanism, exponential distribution. $P = RTC = 3$; $k_a/k_r = 0.0001$ to 1000.

k_a/k_r plotted. In Fig. 3, for $p = 3$, the maximum $\bar{W}/\bar{N}$, approximately 2.4, is shallow. Contrary to $p = 2$, the sensitivity to the parameter k_a/k_r is very small so that there is essentially a unique value of $\bar{W}/\bar{N}$ for each number average molecular weight over a wide range. At all values of p, $\bar{W}/\bar{N}$ drops to 1 at $\bar{N}/M_1 = 2$ for all values of k_a/k_r. At $p = 4$ and higher, for the range of values of the parameter k_a/k_r plotted, $\bar{W}/\bar{N}$ remains at approximately 1 for all values of $\bar{W}/\bar{N}$. As the value of p for a given temperature increases, the number of high energy sites drops sharply. For values of $k_a/k_r < 0.0001$ and $p < 2$, it is possible to attain even higher values of $\bar{W}/\bar{N}$ than those shown. For values of $p \leqslant 1$, it is necessary to use a finite upper bound for Q in order to obtain finite values of $\bar{W}$ and $\bar{W}/\bar{N}$.

As in the Rideal case for homogeneous sites, molecular weights, and rates of polymerization increase without limit for a given catalyst as pressure is increased.

In Figs. 4 and 5, the number average and weight average molecular weights are plotted for the Langmuir-Hinshelwood mechanism as a function of $a = k_aP/D$ with $h = B/D$ as parameter. Figure 4 corresponds to $p = 1$ and Fig. 5 to $p = 4$. These are typical curves; intermediate values of p give intermediate sets of curves.

In general, these curves follow the pat-

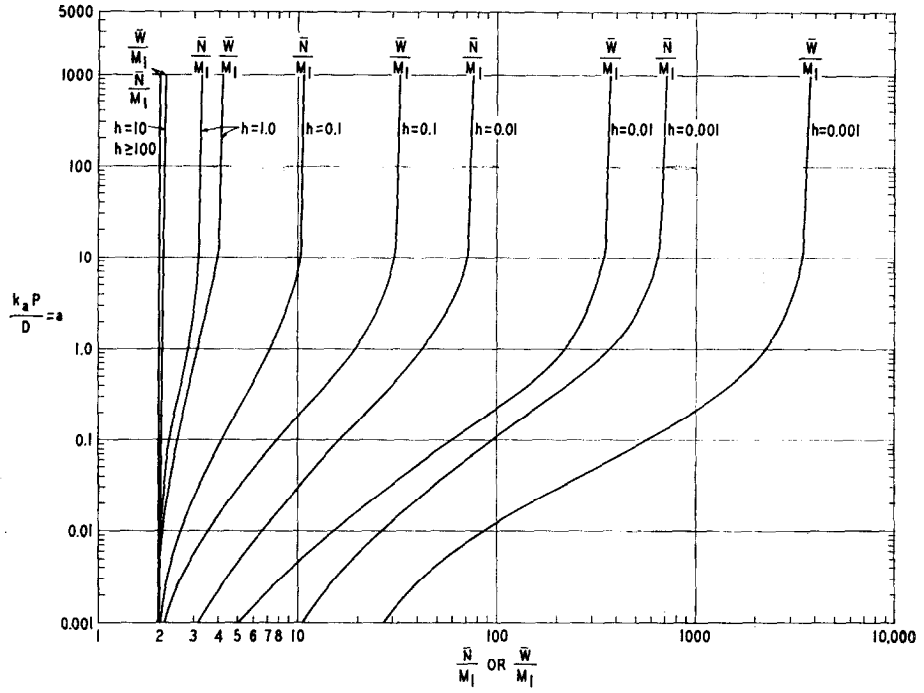

FIG. 4. Number average N/M_1 and weight average W/M_1 molecular weight vs k_aP/D with $B/D = h$ as parameter; $\bar{N}$ = no. avg. mol. wt.; $\bar{W}$ = wt. avg. mol. wt.; M_1 = mol. wt. of monomer; k_a = Adsorption velocity constant; P = pressure. Langmuir-Hinshelwood mechanism, exponential distribution. $p = 1.0$.

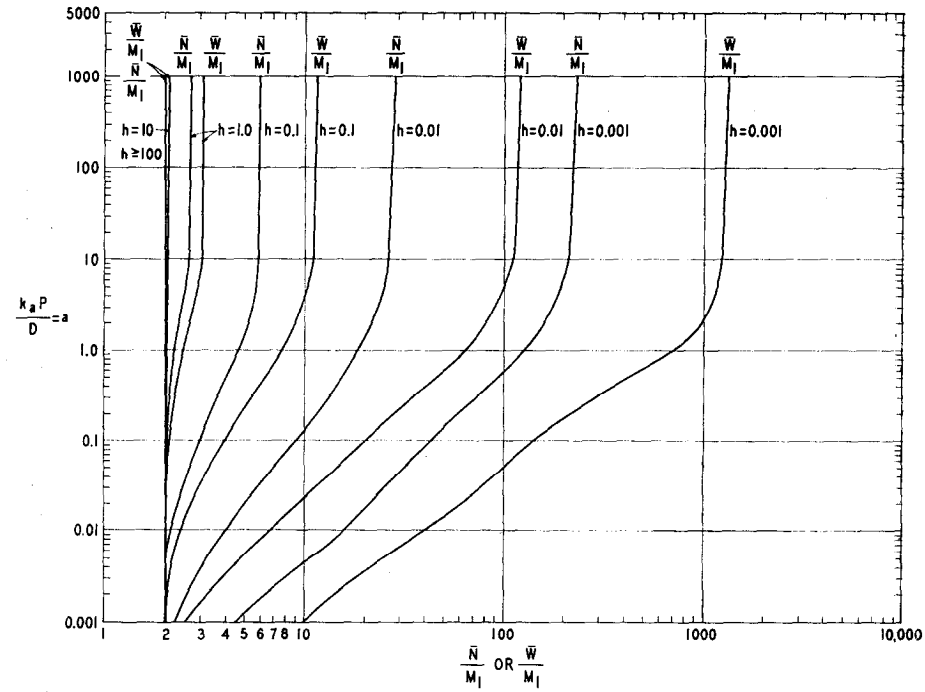

FIG. 5. Number average N/M_1 and weight average $\bar{W}/M_1$ molecular weight vs k_aP/D with $B/D = h$ as parameter; $\bar{N}$ = no. avg. mol. wt.; $\bar{W}$ = wt. avg. mol. wt.; M_1 = mol. wt. of monomer; k_a = adsorption velocity constant; P = pressure. Langmuir-Hinsehelwood mechanism, exponential distribution. $p = 4.0$.

tern of those obtained in reactions of the Langmuir-Hinshelwood type with homogeneous sites. It will be observed that for a specific catalyst molecular weights level out with increasing pressure to values dependent on the value of $h = B/D$. The smaller the value of h, the higher is the maximum molecular weight attainable. Increasing values of p at constant temperature correspond to increasingly weaker average energy of adsorption sites. Therefore, maximum attainable values of molecular weights for each value of h decrease as p increases. Maximum attainable molecular weights for given p and h occur at surface saturation. Rates of polymerization follow the same pattern.

In Figs. 6 and 7, number average molecular weight is plotted against $\bar{W}/\bar{N}$ for various values of the parameter h. Figure 6 represents the case for $p = 1$, and Fig. 7 the case

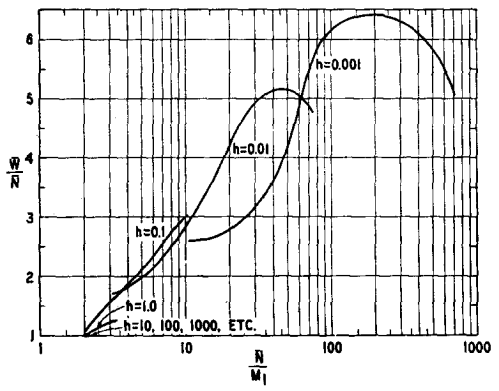

FIG. 6. Weight average–number average ratio vs. $(1/M_1) \times$ number average molecular weight, *RTC* $= p = 1.0$, h as parameter; $\bar{W}$ = wt. avg. mol. wt.; $\bar{N}$ = no. avg. mol. wt. Langmuir-Hinshelwood mechanism, exponential distribution.

for $p = 4$. For each figure, the curves end abruptly at their right-hand ends, corresponding to the point of maximum number average molecular weight for specified h.

At a value of $h = 0.001$, the maximum $\bar{W}/\bar{N}$ is approximately 6, which represents a rather broad molecular weight distribution. At values of $h < 0.001$ and $p < 1$, even higher values of $\bar{W}/\bar{N}$ may be obtained. Spot values as high as 12 have been estimated at $h = 0.0001$. It is difficult and time consuming on the computer to achieve numerical accuracy for values of $p < 1$ and $h < 0.001$.

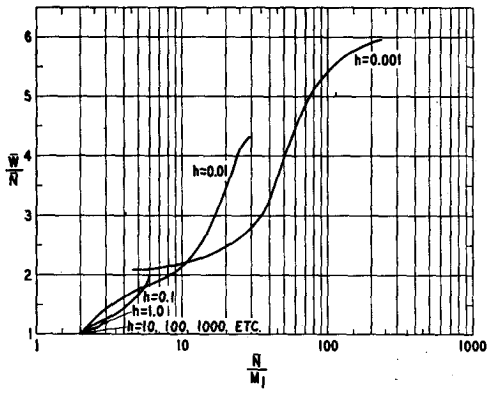

FIG. 7. Weight average–number average ratio vs $(1/M_1) \times$ number average molecular weight; *RTC* $= p = 4.0$; h as parameter; $\bar{W}$ = wt. avg. mol. wt.; $\bar{N}$ = no. avg. mol. wt. Langmuir-Hinshelwood mechanism, exponential distribution.

The models for solid surfaces have no exact counterparts in solution polymerizations. It is difficult to devise mechanisms in solution polymerizations with $\bar{W}/\bar{N}$ much in excess of 2.

Other peculiarities of solid surfaces may be mentioned briefly. For example, if the density of sites is not random over the catalyst surface then many specific effects dependent on the density distribution can be obtained. Assume the surface made up of patches of sites with the density of sites constant within each patch, but differing from that in other patches. Assume further a constant energy of adsorption. In the Langmuir-Hinshelwood mechanism it is not difficult to show from the equations of this paper that $\bar{W}/\bar{N}$ for each patch will be between 1 and 2. But weight average and number average molecular weights would change in going from patch to patch. The total polymer from all patches, since it is made up of polymers of different molecular weight ranges, may have $\bar{W}/\bar{N}$ greater than 2. However, $\bar{W}/\bar{N}$ is much more sensitive to a distribution of energy of sites than to a variation in site density over the surface. The Rideal mechanism would not be affected by this change in site density in the absence

of van der Waal's forces between adsorbed molecules.

One could also visualize a situation where the site density is uniform, and the surface energetically heterogeneous but with sites segregated into noninteracting patches, all sites within a patch having the same energy. In this case, $\bar{W}/\bar{N}$ would always be between 1 and 2 regardless of the values of the velocity constants for both mechanisms. Some randomness of the energy distribution over the surface appears essential to obtain larger values of $\bar{W}/\bar{N}$.

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