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LETTER TO THE EDITORS

Formation of High Polymers on Solid Surfaces
Some Remarks Concerning the Theory of Clark and Bailey

In a recent paper (*1*) published in this journal, Clark and Bailey have proposed a theory for the mechanisms of olefin polymerization on solid surfaces based on a usual scheme of contact catalysis: adsorption, reaction, desorption.

The solid catalyst has N_0 sites per gram of which the fraction $\theta_1, \theta_2, \ldots, \theta_n$ are covered respectively by the monomer, dimer, and polymer with a polymerization degree of n.

The adsorption (rate constant k_a) concerns gaseous monomer which is at a pressure P, maintained constant throughout the process. The reaction is the propagation of the polymerization process; it proceeds on the surface between monomer and the adsorbed polymeric species; its rate constant k_r is independent of n. Depending on whether the mechanism of Rideal or of Langmuir-Hinshelwood is operating the reaction involves gaseous or adsorbed monomer. The desorption is a spontaneous phenomenon which involves the monomer and the polymeric species; it leaves the sites free for further cycles of the process, and its rate constant k_d is assumed to be independent of n. Finally, in the steady state conditions, the fractions $\theta_1, \theta_2, \ldots, \theta_n$ do not vary with time.

Starting from these hypotheses, Clark and Bailey have derived equations for the polymerization rate $\bar{R}$, for the number $\bar{N}$, and the weight $\bar{W}$ average polymerization degrees, and for the polydispersity ratio $\bar{W}/\bar{N}$. Assuming at first that all sites possess the same activity, they obtain the following expressions:

(a) For the Rideal mechanism:

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

where

$$r = k_rP/k_d$$

and

$$\bar{R} = N_0k_ak_rP^2(k_rP + 2k_d)/(k_rP + k_d)(k_aP + k_d)$$

(b) For the Langmuir-Hinshelwood mechanism

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

where

$$R_L = K_r\theta_1/k_d \quad \text{and} \quad K_r = N_0k_r$$

and

$$\bar{R} = N_0K_r\theta_1^2(K_r\theta_1 + 2k_d)/k_d$$

Here, θ_1 is given by the equation

$$\frac{K_r^2\theta_1^3}{k_d^2} + \frac{k_aK_rP\theta_1^2}{k_d^2} + \frac{2K_r\theta_1^2}{k_d} + \frac{k_aP\theta_1}{k_d} + \frac{\theta_1 - k_aP}{k_d} = 0$$

These expressions show that when the pressure is increased, the rate and the average polymerization degrees increase without limit for the Rideal mechanism, but approach asymptotic values for the Langmuir-Hinshelwood mechanism. In the two cases, the polydispersity ratio approaches 2.

If it is assumed that the sites are energetically heterogeneous, the conclusions are not changed, except for the polydispersity ratio which may have much larger values.

However, the analogy between a polymerization process and the reactions usually studied in contact catalysis is perhaps not justified. The processes usually considered in contact catalysis are simple reactions which lead to stable products after a limited number of steps. Desorption occurs only of stable reactants and of products, and not of activated species (in a transition state). On the other hand, polymerization processes are chain reactions involving many steps: an initiation reaction which gives an activated species with a polymerization degree of one; a sequence of propagation reactions between monomer and activated polymeric species, which give again new activated polymeric species; and finally, a termination reaction which transforms an activated species into a stable polymer molecule. This termination reaction may be a true termination process, with destruction of the active center, or a transfer reaction, which is the sum of a termination reaction and of an initiation reaction, without destruction of the active center.

In the present case, monomer adsorption on a site can be validly compared with the initiation. The propagation rate constant k_r can be also considered to be independent of n, and the steady state conditions may be assumed to hold. This last assumption, however, implies particular forms for the termination reaction. The number of active sites has to remain constant, and therefore if a true termination occurs, with destruction of active centers, it follows that an equal number of active sites are formed; if not, the termination proceeds exclusively by transfer. We have to accept this last hypothesis, because a true termination occurs only in radical polymerizations, and in other cases, it excludes the possibility of a steady state. But the transfer may be spontaneous, or may involve further the participation of the monomer. With ethylene, the corresponding stages can be represented schematically as follows:

(a) Spontaneous transfer

$$\text{Cat} \ldots CH_2\text{—}CH_2\text{—}(CH_2)_m\text{—}CH_3 \rightarrow \text{Cat} \ldots H + CH_2 = CH\text{—}(CH_2)_m\text{—}CH_3$$

then

$$\text{Cat} \ldots H + CH_2 = CH_2 \rightarrow \text{Cat} \ldots CH_2\text{—}CH_3$$

and

$$\text{Cat} \ldots CH_2\text{—}CH_3 + CH_2 = CH_2 \rightarrow \text{Cat} \ldots CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_3 \text{ etc.} \ldots$$

(b) Transfer with monomer

$$\text{Cat} \ldots CH_2\text{—}CH_2\text{—}(CH_2)_m\text{—}CH_3 + CH_2 = CH_2 \rightarrow \text{Cat} \ldots CH_2\text{—}CH_3 + CH_2 = CH\text{—}(CH_2)_m\text{—}CH_3$$

The two mechanisms explain satisfactorily the structure of the polyethylene which has one vinyl and one methyl end group per molecule. In the olefin polymerization by Ziegler-Natta solid catalysts, Natta and Pasquon (*2*) have clearly demonstrated the simultaneous occurrence of these two kinds of transfer.

The desorption of polymer can occur only after these termination stages. It seems valid to assume that only one rate constant describes the two processes of termination and desorption. But it is necessary to differentiate between the two transfer reactions. Since, they do not involve the monomer in the desorption, Clark and Bailey make the implicit assumption that the termination occurs exclusively by spontaneous transfer. To take into account the two possibilities, we have to substitute $k_d + k_tP$ for k_d in the case of a Rideal mechanism and $k_d + k_tN_0\theta_1$ (or $k_d + K_t\theta_1$) to k_d in the case of a Langmuir-Hinshelwood mechanism; here k_d is the rate constant for desorption–termination by spontaneous transfer, and k_t is the rate constant for desorption–termination by transfer on monomer.

The assumption according to which the rate constant k_d does not depend on n may be criticized, because it is possible that the termination probability increases with the length of the polymeric chain which is adsorbed only at one extremity, and the rest of which is subjected to action of the solvent. However, as we do not know the relation between k_d and n, and also for simplicity's sake, we will make this assumption.

In the simple case where all the sites possess the same activity, it is easy to show that for the two transfer mechanisms, the expressions of Clark and Bailey for the average degree of polymerization $\bar{N}$ and $\bar{W}$ as a function of r (Rideal) and R_L (Langmuir) are not modified. But now, we have:

(a) For a Rideal mechanism

$$r = k_rP/(k_d + k_tP) \quad \text{instead of} \quad r = k_rP/k_d$$

(b) For a Langmuir-Hinshelwood mechanism

$$R_L = K_r\theta_1/(k_d + K_t\theta_1) \quad \text{instead of} \quad R_L = K_r\theta_1/k_d$$

In the two cases, the result is that the molecular weights approach asymptotic values when the pressure P is increased. It is thus incorrect to conclude that, if molecular weight has a tendency to level off, the process can be explained by a Langmuir-Hinshelwood mechanism, as postulated by Clark and Bailey (*3*) in their experimental work on ethylene polymerization catalyzed by a chromium oxide-silica-alumina system. Actually, molecular weight determinations do not make it possible to make a choice between the two mechanisms.

In regard to the polymerization rate, the theoretical results of Clark and Bailey remain valid: As the pressure is increased, the rate approaches a finite limit for a Langmuir mechanism, and increases indefinitely, according to a first order reaction, for a Rideal mechanism. In our opinion, however, their experimental conclusions are not convincing; their curve drawn through the experimental points does not pass through the origin, and the limiting value for high pressures is not clearly shown. We propose on the contrary, that, with a good approximation, a straight line can be drawn through the origin and the experimental points in accordance with a Rideal mechanism. This is shown in Fig. 1 which is a copy of Fig. 4A in the paper by Clark and Bailey (*3*).

Furthermore, in a kinetic study of propylene polymerization on the same catalysts, we have clearly shown (*4*) that the reaction was first order with respect to monomer concentration.

It thus seems more correct to conclude that, in the case of an olefin polymerization catalyzed by a chromium oxide-silica-alumina system, the mechanism occurring is that proposed by Rideal.

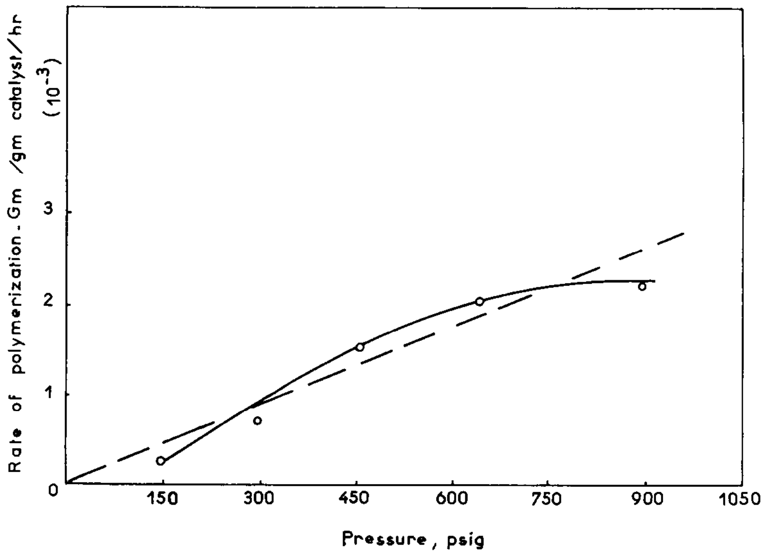

FIG. 1. Rate of polymerization versus pressure. Experimental temperature 150°C, ethylene —Cr—Si —Al system; ○, experimental results; ——— Clark and Bailey curve (Langmuir mechanism); ---- the author's interpretation (Rideal mechanism).

Summary

A review of the papers published in this journal by Clark and Bailey, on the formation of high polymers of olefins on solid surfaces has been presented. Taking into account the two possible termination processes, a spontaneous transfer and a transfer on monomer, it is shown that the choice between a Rideal or a Langmuir-Hinshelwood mechanism can only be made by polymerization rate determinations. In the two cases, molecular weights approach a limit when pressure is increased. Unlike, Clark and Bailey, the author thinks that the experimental results concerning olefin polymerization catalyzed by a chromium oxide-silica-alumina system indicate the occurrence of a Rideal mechanism.

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