

LETTERS TO THE EDITORS

Formation of High Polymers on Solid Surfaces: An Analysis of the Results of Clark and Bailey

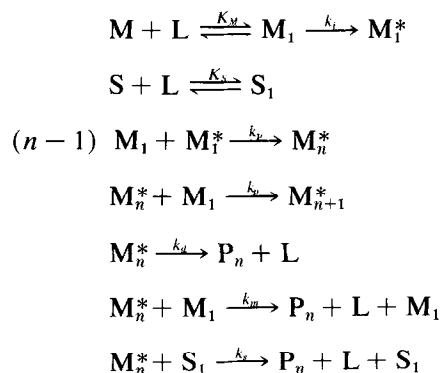
In course of our recent investigation on the kinetics of the polymerization of *N*-vinylcarbazole on solid oxides (V_2O_5 , MnO_2 , Cr_2O_3 , etc.), we had the occasion to make a critical analysis of the general applicability of Clark and Bailey's (1) theory on the formation of high polymer over solid surfaces. In deriving the rate expression, they assumed a steady state with respect to the concentrations of surface species including growing polymer molecule of every possible chain length. Also, the density of adsorption sites remained constant on the catalyst surface during polymerization and the rate constants for all the steps remained constant, being independent of the extent of adsorption and the length of the polymer chain.

Guyot (2), in a later communication, has raised some objections to these assumptions. First, the analogy between a polymerization process and a heterogeneous catalytic process is perhaps not justified. Second, the assumption that k_d , the desorption rate constant, is independent of n , the chain length, is subject to criticism since a longer chain will be more easily desorbed by the action of adsorbed monomer and solvent. Third, the most serious drawback perhaps lies in the assumption that desorption is the only process by which termination may occur. Termination by monomer as well as by solvent is, probably, of greater importance in a polymerization reaction. Accordingly, necessary corrections should have been introduced in the rate expression.

Guyot has also pointed out that the conclusion drawn by Clark and Bailey (3)

from their experimental results is not correct and has claimed that the results could be better explained in terms of Rideal mechanism rather than Langmuir-Hinshelwood mechanism.

We agree with Guyot about the general drawbacks of the Clark and Bailey's treatment and his views on the importance of different termination steps in describing the overall rate of polymerization. In fact, in a recent publication (4) Clark has reviewed the present status of kinetic studies of the polymerization of ethylene and has referred to the work of Ivanov *et al.* (5) to show that in certain cases the contribution of termination by monomer does exclusively predominate over that of spontaneous termination. Although, Ivanov *et al.* recommend a Rideal mechanism for the polymerization and their results are possibly in considerable error, the importance of transfer by monomer must not be underestimated. However, we ignore the first two objections as raised by Guyot and suggest the following reaction scheme for polymer formation on solid surfaces via Langmuir-Hinshelwood mechanism.



The scheme is very similar to that of Clark with certain modifications introduced. First, it distinguishes between simple unimolecularly adsorbed monomer molecule M_1 and the monomeric ionic species M_1^* which is just active to undergo polymerization. Second, it takes into account all the possible surface termination processes viz. the spontaneous termination, termination by adsorbed monomer and by adsorbed solvent molecule.

Proceeding in the line of Clark and Bailey, the following expression for the rate of polymer formation can be derived:

$$\begin{aligned}
 R_L &= \delta \left(\sum_{n=2}^{\infty} n [P_n] \right) / \delta t \\
 &= k_d \cdot \sum_{n=2}^{\infty} n [M_n^*] + k_s \cdot \sum_{n=2}^{\infty} n [M_n^*] [S_1] \\
 &\quad + k_m \cdot \sum_{n=2}^{\infty} n [M_n^*] [M_1] \\
 &= [M]^2 \frac{a \cdot [M] + b}{c \cdot [M]^3 + d \cdot [M]^2 + f[M] + g}
 \end{aligned}$$

where $a, b, c, d, f,$ and g are constants and are composite functions of rate constants and equilibrium constants for different steps in the above scheme. In deriving the expression, an assumption has been made that the total concentration of the prop-

agating species $\sum_{n=1}^{\infty} [M_n^*]$ is negligibly small compared to either $[M_1]$ or $[S_1]$. The above assumption appears to be justified since, in a sequence of steps proceeding through active centres, the concentrations of the active intermediates are very small compared to those of the stable species and the steady-state concentration of them could be maintained throughout the course of polymerization.

The general feature of the rate expression is that at very low values of monomer concentration $R \propto [M]^2$ and at very high values, R is a constant. Also, a sigmoid curve would be obtained when the rate is plotted against the monomer concentration. The experimental results reported by Clark and Bailey are in excellent agreement with the above contention. For the sake of comparison we have reproduced, in Fig. 1, the results of Clark and Bailey together with its interpretations by Guyot and by us. We strongly feel that the Langmuir-Hinshelwood mechanism, rather than Rideal mechanism as suggested by Guyot, is obeyed in the polymerization of ethylene over chromia-alumina-silica catalyst.

Furthermore, we have observed (6) in

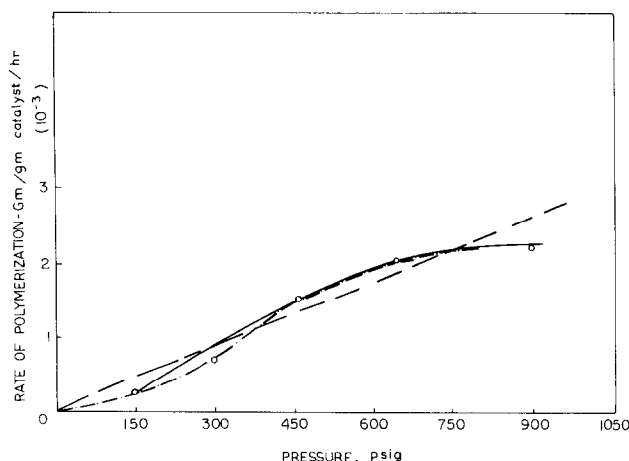


FIG. 1. Rate of polymerization versus pressure. Experimental temperature 150°C, ethylene-Cr-Si-Al system; O, experimental result; —, Clark and Bailey curve (Langmuir-Hinshelwood mechanism); ---, Guyot's interpretation (Rideal mechanism); - · - · - author's interpretation (L-H mechanism with termination by adsorbed monomer and solvent molecules).

the polymerization of *N*-vinylcarbazole on vanadium pentoxide that the rate data could be satisfactorily interpreted in terms of Langmuir-Hinshelwood mechanism.

Regarding the degree of polymerization, however, the situation remains unaltered and for both the mechanisms \bar{N} levels off as the monomer concentration is increased. Thus no inference could be drawn about the mechanism of polymerization from the study of the variation of \bar{N} with monomer concentration.

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