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Formation of High Polymers on Solid Surfaces II. Polymerization of Ethylene on Chromium Oxide-Silica-Alumina Catalysts

ALFRED CLARK AND GRANT C. BAILEY

From the Phillips Petroleum Company, Research Division, Bartlesville, Oklahoma

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The four models of the preceding paper (*1*) (Part I) are compared with the experimental results of polymerizing ethylene over chromium oxide-silica-alumina catalyst. Experimental curves are shown for number average molecular weights, weight average molecular weights, their ratios, and rates of polymerization as functions of pressure. The effects of temperature variations on these quantities are discussed qualitatively. The conclusion is reached that the Langmuir-Hinshelwood mechanism on an energetically heterogeneous surface duplicates the general character of the experimental curves most closely.

I. INTRODUCTION

In the preceding paper (*1*) (Part I) four models were set up for adsorption and polymerization on solid surfaces. In two of the models it was assumed that all adsorption sites have the same adsorption energy. The first of these (Rideal mechanism) assumed 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) assumed that polymerization occurs by reaction of an adsorbed monomer molecule with an adjacently adsorbed monomer molecule or growing polymer chain. The other two models were counterparts of these with a variation of adsorption energies among the sites.

It was shown that for the Rideal mechanism the number and weight average molecular weights, and rates of reaction increase without limit as pressure is increased. This is true whether the adsorption sites all have the same energy or not. In contrast, for the Langmuir-Hinshelwood mechanism the molecular weights and reaction rates approach a maximum value asymptotically as pressure is increased for both cases of site-energy distribution. It was further shown that the ratio of weight-average to number-average molecular weights lies between 1 and 2 for all values of velocity constants and pressure for both mechanisms if all the adsorption energies are equal. With a distribution of adsorption energies this molecular weight ratio can have values far in excess of 2 for both mechanisms.

The object of this paper is to compare these theoretical conclusions with data obtained for the polymerization of ethylene in the presence of chromium oxide-silica-alumina catalyst, to see if the experimental results offer definitive support for one of the mechanisms.

II. EXPERIMENTAL

The experiments reported here are part of the large amount of research done in developing Phillips process for making Marlex (trademark for Phillips family of olefin polymers) polyethylene. They were not conducted with the objective of testing this theoretical study. Some averaging and cross plotting has been done to obtain the points shown on the curves, but all data were obtained on the same group of samples. Selection of experiments included was done entirely on the basis of accuracy and reproducibility of the experiments.

A. Catalyst

The catalyst support used for these experiments was a silica-alumina having the following properties:

Wt. % Al_2O_3	13
Surface area	529 m^2/g
Pore volume	0.88 cc/g
Avg. pore diameter	67 Å

To prepare the catalyst a sample of the silica-alumina was calcined at 540°C to determine the moisture loss. The amount of water required to wet the original support was also determined. From this data a weighed amount of silica-alumina was wetted with the proper amount of water in which enough CrO_3 had been dissolved to produce an activated catalyst containing 2.5% chromium. After impregnation the catalyst was dried in an evaporating dish on a hot plate, stirring continuously until a temperature of 150°C was reached. The catalyst was activated by fluidizing in dry air at 540°C for 5 hr.

B. Reagents

The ethylene was Phillips polymerization grade. Moisture was removed immediately before use by passing it over activated alumina. Phillips polymerization grade cyclohexane was used as the solvent. It was boiled to remove air and stored under prepurified nitrogen pressure. Water and other impurities were removed immediately before use by passing it through activated alumina while being charged to the reactor.

C. Polymerization Equipment and Procedure

All tests were made in a 1.3-liter, jacketed, stirred reactor equipped with a two-bladed stirrer operated at 360 rpm. The reactor was made of carbon steel and the inside surfaces were chromium plated and polished.

The reactor was purged with purified nitrogen, and purging was continued while it was heated to within 3°C of reaction temperature and the catalyst was charged. Solvent was then admitted and flashed briefly to displace the nitrogen. The reactor outlet was closed, and when the temperature was within 1°C of the operating temperature ethylene was admitted. The rate of flow was adjusted so that the pressure increased about 150 psig per minute. When the desired operating pressure was reached the reactor was considered to be on stream, and the pressure was held by allowing ethylene to flow on demand from a pressure regulator.

At the end of 1-hr feed flow was stopped and the reactor immediately depressurized by loosening the flange. Within a few minutes after being removed from the reactor the polymer was double chopped and vacuum dried for 15 min to remove most of the remaining cyclohexane. It was then sprayed with antioxidant solution while being tumbled in a thin layer. The polymer was finally dried 30 min in a vacuum oven at 110°C.

Rate of polymerization was reported as grams of polymer produced per gram of catalyst for the 1-hr test. Vinyl unsaturation was determined by infrared analysis and used to calculate the number average molecular weight. Weight average molecular weight was calculated from the melt index of the polymer.

III. Discussion and Results

A. Effect of Pressure on Molecular Weights and Rates of Polymerization

Experimental curves for number-average and weight-average molecular weights as functions of pressure are shown in Figs. 1A and 2A, respectively. All experiments were carried out at a reaction temperature of 130°C. Both curves rise and then level out with increasing pressure. In Fig. 3A, weight average-number average molecular weight ratio is plotted against pressure. The ratios lie between 9 and 12, indicating a broad molecular weight distribution. The curve drops with increasing pressure and ultimately levels out. In Fig. 4A, the rate of polymerization is seen to rise and then level out with increasing pressure.

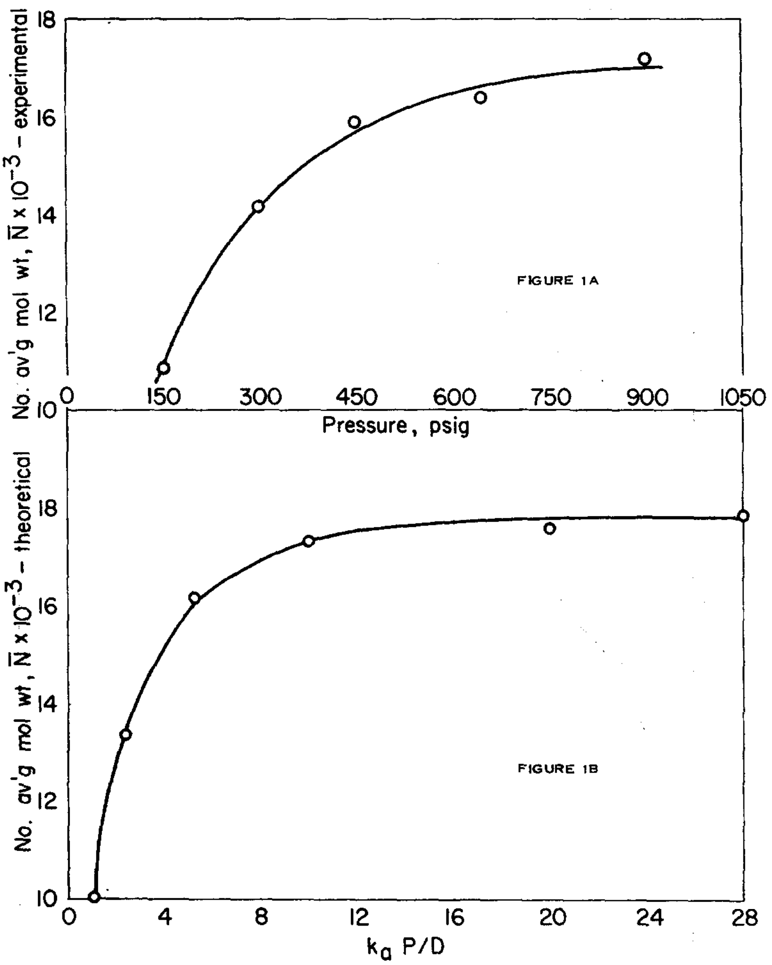

FIG. 1A. Number average molecular weight versus pressure. Experimental reaction temperature, 130°C; ethylene-Cr—Si—Al system.

FIG. 1B. Number average molecular weight versus constant × P at constant temperature, theoretical.

In Part I, it was shown that in the Rideal mechanism molecular weights and rates of polymerization increase without limit as the pressure increases for both energetically homogeneous and heterogeneous surfaces. Also, it was shown that weight average-number average ratios always lie between 1 and 2 for energetically homogeneous surfaces regardless of the mechanism—Rideal or Langmuir-Hinshelwood. The Langmuir-Hinshelwood mechanism with a distribution of adsorption-site energies appears to duplicate the general character of the experimental curves most closely. In Figs. 1B, 2B, 3B, and 4B the theoretical curves for this model are shown for comparison with the experimental curves. Figures 1B and 2B for number and weight average molecular weights are replots of Fig. 4 of Part I with $p = 1.0$ and parameter $h = 0.001$. This set of conditions was selected because it closely duplicates the number average molecular weight range of the experimental curves. However, the important point is the general similarity of the shapes of the experimental and theoretical curves, and the similarity holds regardless of the set of conditions

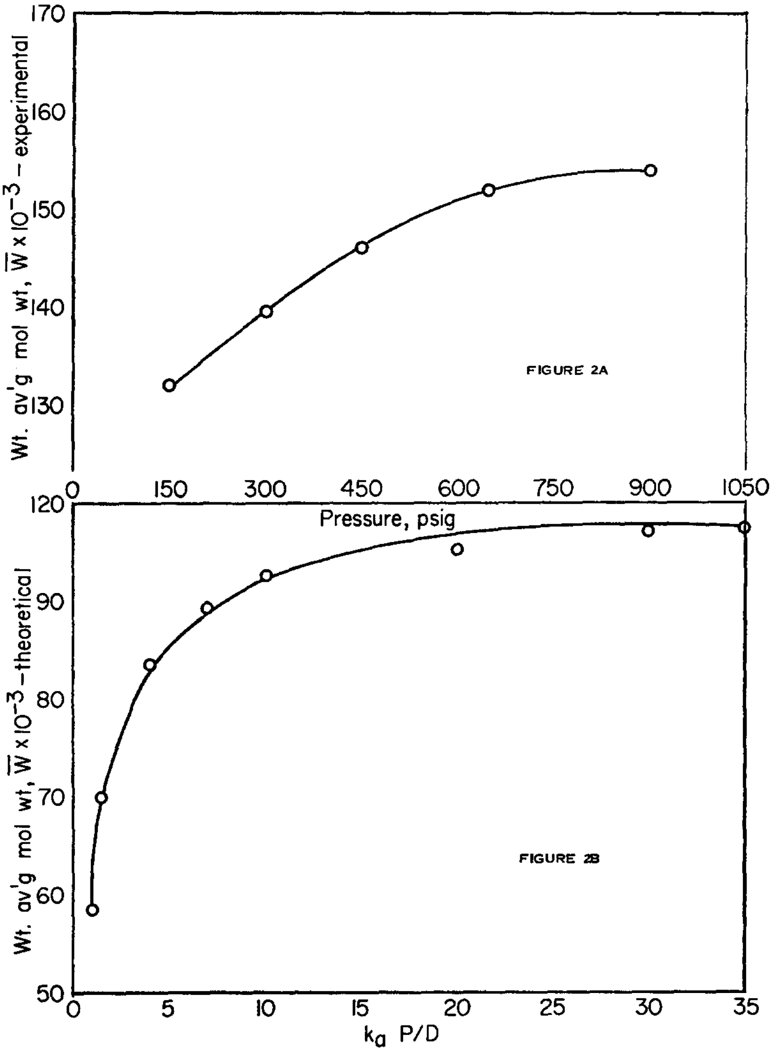

FIG. 2A. Weight average molecular weight versus pressure. Experimental reaction temperature, 130°C; ethylene-Cr—Si—Al system.

FIG. 2B. Weight average molecular weight versus constant × P at constant temperature, theoretical.

selected. Figure 3B for weight average-number average ratio is a crossplot from Fig. 4 and Fig. 6 of Part I. The values of the ratios $\bar{W}/\bar{N}$ are somewhat below those of the experimental curve, but the curves are similar in shape. Theoretical curves with higher values of $\bar{W}/\bar{N}$, showing the same trends, can be obtained. But, as explained in Part I, it is time consuming on the computer to obtain numerical accuracy in this region. It was not possible experimentally to reach the maximum in the ratio, $\bar{W}/\bar{N}$, at lower pressure, shown by the theoretical curve, because the rate of reaction was then too low to obtain a representative sample of polymer. There is no question, however, that ultimately the rising branch of the experimental curve must drop with decreasing pressure.

The curve for rate of polymerization in Fig. 4B is a plot of k_aP/D versus rate $\bar{R}$, at $p = 1.0$ and parameter $h = 0.001$. From

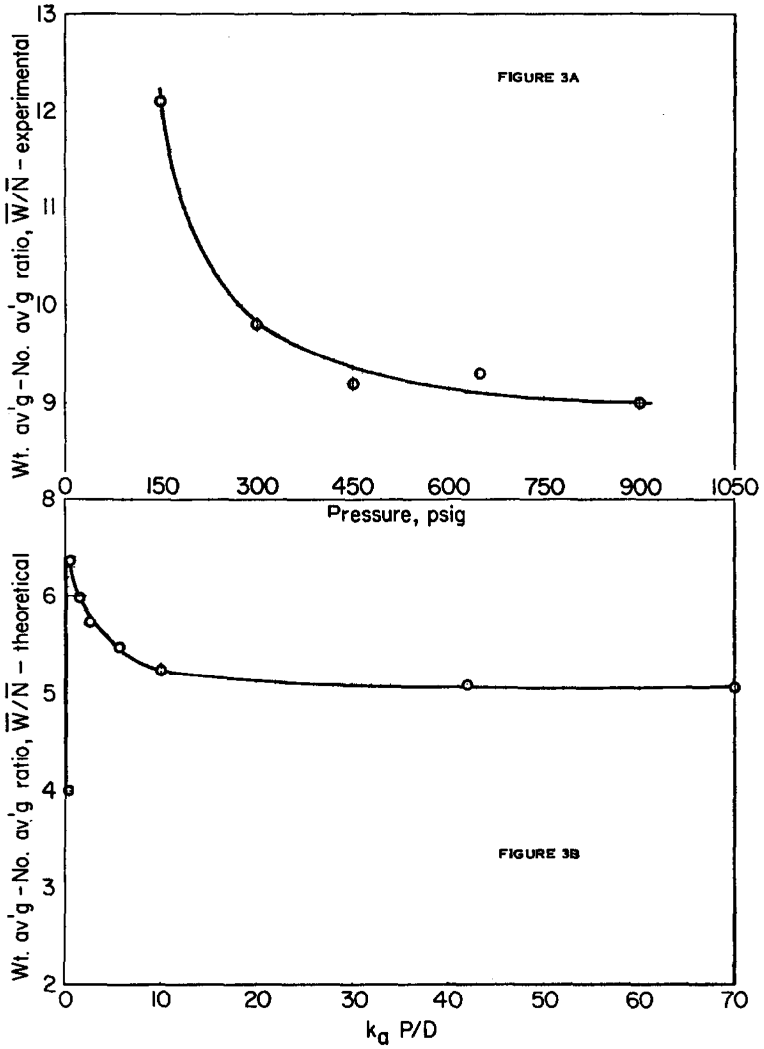

Fig. 3A. Weight average–number average ratio versus pressure. Experimental reaction temperature, 130°C; ethylene—Cr—Si—Al system.

Fig. 3B. Weight average–number average ratio versus constant × P at constant temperature, theoretical.

Eq. 24, Part I, it will be observed that a temperature dependent constant has been dropped. This constant cancels out in the molecular weight expressions.

Theoretical curves for the two molecular weights and the rate of polymerization rise more steeply than the experimental curves. This is the detailed effect of the site-energy distribution function that was selected. Without a more detailed knowledge of the actual adsorption energy distribution function, it is not possible to proceed further in this direction.

B. Effect of Temperature on Molecular Weights and Rates of Polymerization

Studies of temperature effects are not nearly so informative. Such studies are limited experimentally to a range of approximately 60°C. In this range, number average, weight average molecular weights, and their ratios decline linearly with in-

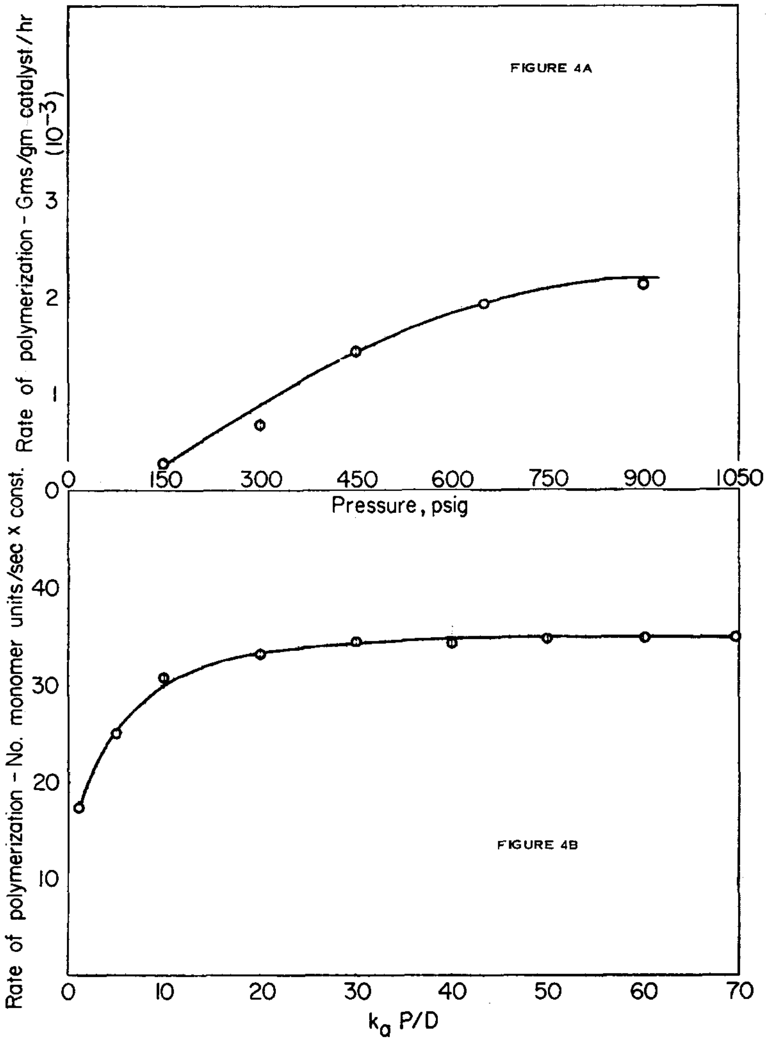

FIG. 4A. Rate of polymerization versus pressure. Experimental reaction temperature, 150°C; ethylene—Cr—Si—Al system.

FIG. 4B. Rate of polymerization versus constant × P at constant temperature, theoretical.

creasing temperature. By putting rate constants into their Arrhenius form in the theoretical expressions, it can be shown without much difficulty that the four theoretical models also exhibit a linear decline in these quantities with increasing temperature. Thus, no information is gained with respect to mechanism.

The experimental curve for rate of polymerization as a function of temperature shows a maximum at approximately 130°C. The Rideal mechanism shows a linear increase of reaction rate with increasing temperature. With the Langmuir-Hinshelwood mechanism, there may or may not be a maximum in the rate–temperature curve depending on the value of the parameter $h = b/d$. For small values of h ($<1/2$ for energetically homogeneous surfaces) there is a maximum. Since the parameter h represents the ratio of the desorption velocity constant to the surface reaction velocity constant, small values should favor the formation of high molecular weight polymers. Thus one would expect a maximum in the present case. A knowledge of the absolute values of the rate constants for surface reaction and desorption is necessary to make further conclusions based on temperature studies.

ACKNOWLEDGMENT

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REFERENCE

1. CLARK, ALFRED, AND BAILEY, GRANT C., *J. Catalysis* **2**, 230 (1963).