

A Study of the Surface-Catalyzed Polymerization of Ethylene on Chromic Oxide-Silica-Alumina Catalysts

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Synopsis

This investigation was an exploratory study of the phenomena associated with the polymerization of ethylene on a chromic oxide-silica-alumina catalyst. The polymerization was carried out in a batch reactor fed on demand at 500 psi gage and at 135°C. The catalyst was 3% chromic oxide on an 87% silica-13% alumina support, activated at 450°C for 5.25 hr in dry air. The catalyst particles were found to reduce in size during the polymerization. The particles decreased in size from 18/20 mesh to an average diameter of 9.6 μ . This reduction in particle size was found to cease at a yield of 40.0 g per gram of catalyst. By determining the monomer reaction rate versus time, the catalyst activity was found to change greatly during the polymerization. The activity increased to a maximum, then decreased. The period of increasing catalyst activity corresponded to the period of catalyst particle size reduction. The period of decreasing activity was considered to be due to the build-up of a polymer film diffusion layer and true catalyst deactivation. The molecular weight distributions for a series of samples from each polymerization test were determined on a gel permeation chromatograph. These distributions for each test were characterized by an increase in the high molecular weight tail as the yield increased, while the peak position and low molecular weight end remained essentially constant.

INTRODUCTION

Since the discovery of the chromic oxide-silica-alumina polymerization catalyst^{1,2} several studies have been presented in the literature.³⁻⁶ These studies have been aimed at obtaining a better understanding of this polymerization catalyst. While such supported catalysts have been found to be the key to linearity, not all the characteristics of these polymerizations are known. A better knowledge and understanding of the general features of these reactions are necessary in order to build a comprehensive model of the mechanism.

The work described here was primarily an effort to determine how the molecular weight distribution of the polyethylene produced changed as the yield increased, but additional information was gathered regarding the rate and mechanism of the polymerization.

EXPERIMENTAL

The catalyst used was a 89 wt-% silica-13 wt-% alumina support impregnated to give 3 wt-% chromic oxide. The catalyst particles were 18/20 mesh on a U. S. standard sieve basis.

The catalyst was activated in a stream of dry air at 450°C for 5.25 hr and then purged for 0.25 hr in dry nitrogen.

The active catalyst was placed in the reactor containing the cyclohexane solvent. This slurry of 0.3 to 0.6 g of catalyst and 0.5 liters of solvent was brought to the reaction temperature of 135 \pm 3°C. The reactor was a Parr Series 4500 pressure reaction apparatus having a total capacity of 1 liter and the stirrer was operated at 630 rpm.

Upon reaching the reaction temperature, ethylene was charged to the reactor until a pressure of 500 psi gage was reached. The reaction was allowed to proceed at constant pressure with the monomer fed on demand. Samples of the polymer in the reactor were obtained at various reaction times. The reaction was terminated by adding water, a catalyst poison, to the reactor.

The reaction rate was determined by stopping the ethylene flow and noting the time required for the reactor pressure to decrease 20 psi. The reaction rate was determined at various times during the polymerization in this way.

The molecular weight distributions of the polyethylene samples were determined on a Waters' Model 200R gel permeation chromatograph.⁷ This unit, set up with 10^7 , 10^6 , 10^3 , and 10^2 angstrom columns, was calibrated with a set of polystyrene standards and a set of polyglycol standards. The unit was operated at 135°C and with a flow of 1.88 cc/min. The polyethylene samples were $1/8$ wt-% polymer in 1,2,4-trichlorobenzene. Antioxidant 330, produced by the Ethyl Corporation, was added to the solutions (0.5 wt-% based on the amount of polymer). The cyclohexane was of 98 wt-% purity and the ethylene was of 99.8 mole-% purity. Both were produced by the Phillips Petroleum Corporation. The polymer standards were purchased from Waters' Associates. The chromic acid was Fisher certified reagent grade and the support was silica-alumina (catalyst grade 979) from W. R. Grace and Company.

RESULTS AND DISCUSSIONS

Catalyst Particle Size Reduction

After each polymerization a reduction in catalyst particle size was noted. This size reduction appeared to be related to the yield. Therefore the average catalyst particle size was determined after polymerizations to various yields. The results of these measurements are presented in Figure 1.

The size of the catalyst particles was found to decrease from an average initial diameter of 920 μ to an average diameter of 9.6 μ as the yield in-

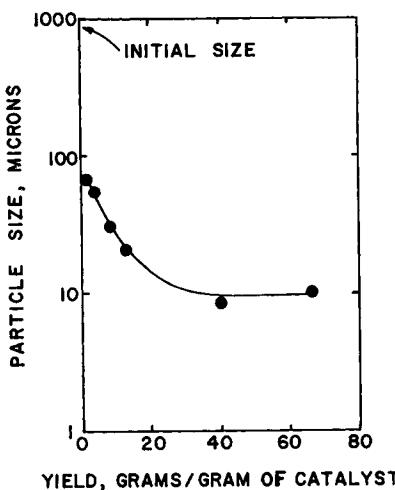


Fig. 1. Catalyst particle size versus yield.

creased from 0 to 66 g of polymer per gram of catalyst. This data indicates that the size reduction ceases at a yield of approximately 40 g of polymer per gram of catalyst.

This phenomenon was pictured as a physical destruction of the catalyst pore structure by the polymer being produced. Presumably, as polymer was produced within the catalyst's pores, it first filled the available pore space but then continued to grow with monomer being fed to the active sites. Therefore the polymer had either to diffuse out or make more room. Apparently, it could not diffuse out as fast as it was being produced, and this resulted in the breakdown of the catalyst, this occurring until most of the active area of the catalyst within the pores was exposed directly to the ethylene-laden solvent.

Catalyst Activity

The reaction rate for all polymerizations increased sharply to maximum, then decreased, and finally appeared to approach a constant value. These rate curves were extrapolated to zero time, assuming the rate was zero at zero time. Typical data is presented in Figure 2.

From the calculations for yield versus reaction time and an examination of the reaction rate versus time curves, the maximum in the reaction rate was found to occur at a yield of about 40.0 g of polymer per gram of catalyst. This is noted as point S on Figure 2. Therefore the period of increasing rate was viewed as due to the continuous reduction in particle size, with the result that there was an increase in active surface area accessible to the monomer for polymerization.

The decreasing reaction rate after the maximum was seen as the result of two phenomena. First, the activity of the catalyst was probably decreasing; the active sites were dying. Second, the physical structure of

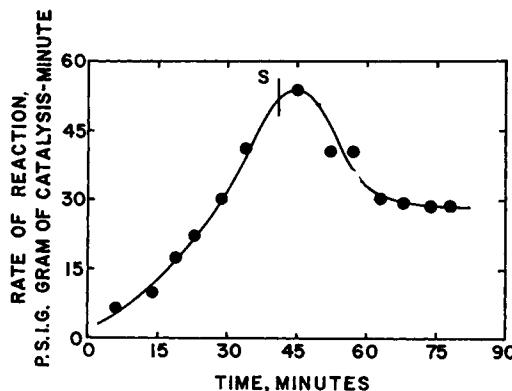


Fig. 2. Reaction rate versus time for test A.

the catalyst had become stable at this point, allowing polymer to build up around the particles in a layer. This layer would be a diffusion boundary for the monomer, this boundary growing until a balance was established between the polymer leaving at the outer perimeter and the polymer produced at the inner perimeter. This increasing resistance to monomer migration to the surface would result in a decreasing rate which would level out as the limits of the boundary were established. In essence, the decreasing rate after the maximum was considered to be due to an increasing film resistance and decreasing activity.

Molecular Weight Distributions

The molecular weight distributions for polyethylene samples were obtained as change in refractive index versus cumulative volumetric flow through the chromatograph. Using a calibration curve, the distribution was converted to change in refractive index versus molecular size. To convert from molecular size to molecular weight, the molecular size was multiplied by the *Q* factor. The *Q* factor was considered a constant charac-

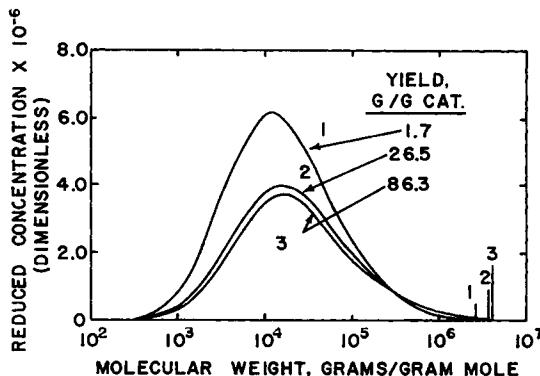


Fig. 3. Normalized molecular weight distributions for test A.

teristic of a given polymer. In actuality, this is the average molecular weight per unit angstrom size and should be some function of molecular size. This procedure put the abscissa of the distributions on a conventional basis.

In handling the solutions at 135°C, some of the solvent vaporized, causing slight changes in the solution concentrations. This was detected in the resulting distributions. Therefore the resulting curves were normalized. Ideally, this normalization procedure converted the ordinates to weight per cent, and for the concentrations used here, the change in refractive index has been shown to be directly proportional to the concentration.⁸ However this change in refractive index has also been found to be some function of the molecular weight.⁴ Therefore the ordinates of the distributions reported here were labeled as the reduced concentration.

A computer was used to perform the integrations necessary for the normalization and for the calculation of the molecular weight averages by the trapezoid rule method.

One other problem may have occurred using the gel permeation chromatograph to obtain molecular weight distributions. If the molecular weight distribution is narrow, the distribution must be corrected for resolution effects. However if the polydispersity factor (the weight-average to number-average ratio) is greater than five, the resolution effects have been shown to be negligible.⁹ Since the distributions presented in Figures 3, 4, and 5 have polydispersity factors of greater than five, this correction was not necessary.

The molecular weight distributions exhibited some interesting characteristics. The distributions were essentially constant except for the continuous appearance of high molecular weight species as the yield increased. There was neither a detectable shift in the low molecular weight species being produced as the yield increased, nor was there a significant change in the position of the peak in the distribution. In general, these same characteristics were exhibited for the distributions of each test. Figures 3, 4, and 5 show the molecular weight distributions for tests A, B, and C, respectively. The molecular weight distributions for three representative samples, each taken at a different level of conversion, are shown for each test. Figure 6 shows the maximum molecular weight as a function of yield for test A. A similar correlation holds for the other tests.

The absence of a detectable change in the character of the distributions at the low molecular weight end indicated that there was a minimum of readsorption of polymer on the catalyst from the bulk solution. Initially, this was postulated as a possible occurrence during the polymerization.

The relatively stable peak position in conjunction with the increasing tail of the distributions was pictured as due to the diffusion layer postulated previously. After the layer was built up around the particles, the growing species were pictured as held there, even after desorbing from the surface. Due to their bulk, diffusion away from the surface would be greatly hindered. Therefore the olefin endgroup was viewed as still being in the

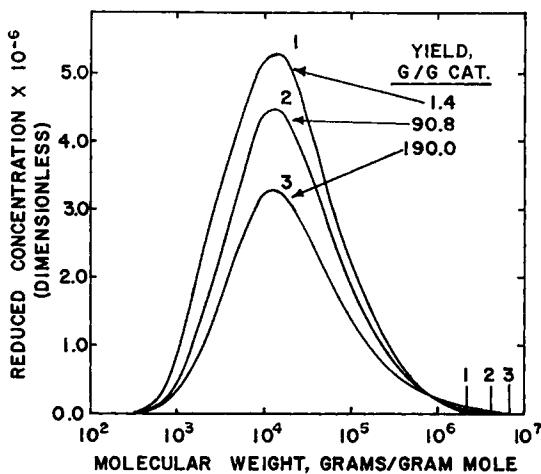


Fig. 4. Normalized molecular weight distributions for test B.

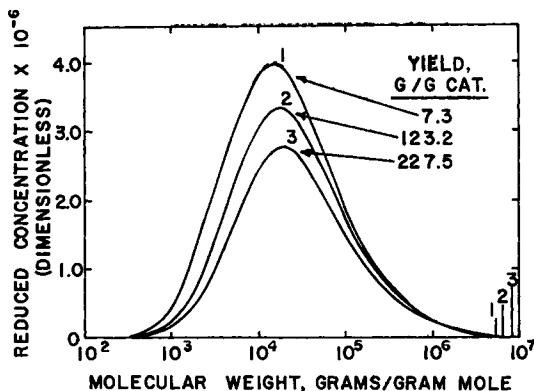


Fig. 5. Normalized molecular weight distributions for test C.

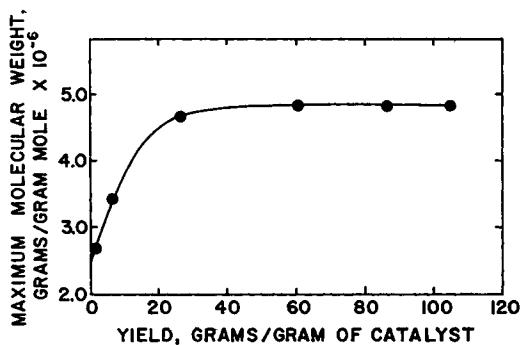


Fig. 6. Maximum molecular weight produced versus yield for test A.

proximity of the surface, allowing it upon occasion to readsorb and resume growing.

An alternate explanation was the possibility of termination by combination. As the polymer layer built up around the particles, the rate of polymerization was pictured as decreasing until it matched the rate at which monomer diffused to the surface. At this point the surface would be practically void of adsorbed monomer. If the adsorbed polymer molecules were mobile, the possibility of combining existed. Also, a polymer molecule held in the diffusion layer was viewed as possibly readsorbing to an active site in the same manner as a monomer molecule and thereby combining with a growing chain such that termination occurred. Either or both of these proposals can be considered as explanations for the lack of shift in the medium molecular weight peak and the appearance of higher molecular weight species as the yield increased.

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