The Role of Diffusion in the Ziegler Polymerization of Ethylene

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Synopsis

A theoretical and experimental study has been made of the polymerization of ethylene in a slurry reactor using a highly active Ziegler catalyst in the presence of hydrogen. A model of the polymerization system has been set up in which polymerization is assumed to proceed with encapsulation of catalyst subparticles. Allowance is made for an experimentally observed first-order decay in intrinsic catalyst activity. The theoretical prediction of the model for the monomer absorption rate behavior and the molecular weight characteristics of the polymers formed are in agreement with experimental findings. Experimental evidence is presented that in the earliest moments of a polymerization significant amounts of polymer are formed with molecular weights 100 times those in the balance of the polymerization. It is concluded that in this system the polymerization is diffusion controlled throughout the major part of the catalyst lifetime. This diffusion phenomenon, together with the gradual loss of active sites, is of vital importance in determining the molecular weight and molecular weight distribution of the polyethylene product.

INTRODUCTION

Over the past few years in publications concerning the heterogeneous polymerization of olefins, there have been frequent suggestions that monomer diffusion through polymer to the active site should be considered when attempting an explanation of the polymerization rate and molecular weight distribution behaviour. Begley[1] has reviewed the experimental work up to 1966 and studied the polymerization behavior of three catalysts with proplylene. Begley's conclusions are that monomer diffusion is unimportant and that a second-order site decay explains the polymerization rate fall. Unfortunately, no information about molecular weight behavior is given. On the other hand, Guttman and Guillet,[2] who also studied propylene polymerization, state that for an occluded site, monomer diffusion through polymer can be the rate determining step.

It would appear that each polymerization catalyst should be regarded as unique and that a rational explanation of the catalyst behavior in any monomer environment should be sought by considering both diffusion and

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Fig. 1. Typical structure of polyethylene ($\times 1200$) made with the catalyst.   Yield $= 1.98$ kg/g TiCl₃.

site decay phenomena.   A start in this direction has been made by Schmeal and Street[3] and Singh and Merrill,[4] who have considered various physical models of the polymerization in which there is no site decay but in which diffusional effects are taken into account.

We have used these concepts to investigate the polymerization of ethylene in the presence of hydrogen in slurry reactors using a highly active catalyst.   The physical model chosen to represent the catalyst was one where polymer is assumed to grow around the catalyst subparticles. Each subparticle is assumed to grow polymer independently of its neighbors even though together they may form part of a larger agglomerate.   Graff et al.[5] describe in qualitative terms polymerization proceeding in this manner.   This growth mechanism readily lends itself to an explanation of the phenomenon of replication described by Mackie et al.[6]   Still further evidence in support of this physical model comes from stereoscan photographs of polyethylene made with this catalyst in the presence of ethylene and hydrogen.   Figure 1 shows the knobbly structure suggestive of discrete growth around each subparticle.

THEORY

In setting up a mathematical model for the polymerization, it is assumed that each catalyst subparticle can be thought of as a solid sphere with

active sites on its surface. The mathematical treatment for each catalyst subparticle is therefore equivalent to the treatment given by Schmeal and Street[3] for their solid-core model. As our experiments were done in a semibatch reactor where the slurry phase has a unique residence time and the ethylene and hydrogen are bubbled through the stirred slurry before leaving the reactor, a gas/liquid mass transfer step was also included in the mathematical model. For simplicity, the gas phase in the reactor was assumed to be of constant composition. This condition is approached at high gas-flow rates or low polymerization rates.

The termination rate at each active site for the growing polymer chains has been assumed to be constant throughout the polymerization. If hydrogen is regarded as the predominant terminating agent, this implies constant hydrogen concentration at the catalyst site (or surface). We are thus assuming that the rate of consumption of hydrogen is kinetically controlled. Kinetic control is very much more likely for hydrogen than for monomer because the rate of hydrogen consumption is very small compared to the polymerization rate. To the extent that the kinetic control assumption is valid, the hydrogen concentration at the catalyst surface will be essentially the same as the equilibrium concentration at the polymer/solution boundary.

We also recognise the important effect of a subparticle size distribution upon the polymer molecular weight distribution for cases of diffusion control. This follows from the different dependencies of the polymerization and termination rates upon the linear subparticle size.[3] This is because of the different rate-controlling steps for the respective rates. However, a complete treatment in a semibatch reactor which allows for this distribution effect would be complex and has not been undertaken. Instead an average subparticle size has been assumed which allows the essential predictions of the model to be made but not the exact numerical ones which would result if subparticle size distribution had been included.

A nonsteady-state mass balance for the monomer in solution gives

$$k_L a V_L (C_0 - C_R) = V_L \frac{dC_R}{dt} + N_P 4\pi S^2 k_S(t) C_S. \qquad (1)$$

Equation (1) states that monomer transferred from the gas phase equals the accumulation of monomer in solution plus that which polymerizes; $k_S(t)$ is a rate constant based on unit surface area of catalyst which has embodied in it both the number of active sites and their inherent activity; N_P is the number of catalyst subparticles of radius S present in the liquid/slurry phase of volume V_L; C_S, C_R, and C_0 are, respectively, monomer concentrations at the catalyst surface, in the bulk solution, and in equilibrium with the gas-phase monomer concentration; and $k_L a$ is the volumetric mass transfer coefficient which is taken to be constant and thus independent of increasing slurry concentration. This is reasonable for the present study due to the low slurry concentrations encountered experimentally ($<1\%$ w/w).

Assuming that all the monomer converted forms a deposit of polymer distributed uniformly over the catalyst surface, we can write a further mass balance:

$$\frac{N_P \rho 4\pi R^2 dR}{dt} = N_P 4\pi S^2 k_S(t) C_S \tag{2}$$

where ρ is the density of the polymer barrier of radius R.

A further relationship can be derived if it is assumed that the monomer concentration at the outer shell of polymer is the same as in the bulk solution and that a pseudosteady-state rate of monomer transfer exists through the polymer surrounding the catalyst subparticle. The latter assumption allows the monomer transfer rate through the polymer to be set equal to the polymerization rate. From such a balance we can write

$$\frac{C_S}{C_R} = \frac{1}{1 + [k_S(t)S/D](1 - S/R)} \tag{3}$$

where D is the effective diffusivity of monomer through the polymer barrier surrounding the catalyst.

The dimensionless group $D/[k_S(t)S]$ is a Thiele modulus and is all important in determining the behavior of the polymerizing system. A large value of the modulus indicates that the intrinsic kinetics are rate controlling, while a small value indicates that monomer diffusion through the polymer is rate controlling. (In saying earlier that hydrogen consumption rate is kinetically controlled, we are in effect saying that its Thiele modulus is very large.) A polymerizing system with a decaying catalyst therefore becomes increasingly kinetically controlled.

However, when monomer is transferred into the liquid phase from a gaseous phase, as in the present work, the physical rate of gas/liquid mass transfer must also be considered in assessing the control of the overall polymerization rate. The previous discussion of the Thiele modulus relates only to the balance of control between the intrinsic kinetics and monomer diffusion through polymer stages. In the present work, evaluation of the Thiele modulus alone is insufficient in determining the controlling stage of the polymerization rate.

Further simplification of eqs. (1)–(3) can be done by expression in terms of the catalyst mass m and density ρ_C and by writing $C = C_R/C_0$, $Y = R/S$, $A(t) = D/[k_S(t)S]$. This gives two simultaneous first-order differential equations

$$\frac{dC}{dt} = k_L a(1 - C) - \frac{3mDC}{S^2 \rho_C V_L [A(t) + (1 - Y^{-1})]} \tag{4}$$

and

$$\frac{dY}{dt} = \frac{DC_0 C}{S^2 \rho Y^2 [A(t) + (1 - Y^{-1})]}. \tag{5}$$

Monomer absorption intensity is given by

$$R_M = k_L a C_0 (1 - C),\qquad(6)$$

polymerization intensity by

$$R_P = \frac{3mDC_0C}{S^2 \rho_C V_L [A(t) + (1 - Y^{-1})]}.\qquad(7)$$

For a reactor which is initially saturated with reactants before the catalyst is added, eqs. (4) and (5) are solved with the initial condition that at $t = 0$, $Y = 1$ and $C = 1$. If catalyst is already present when reactants are introduced, the initial condition is that at $t = 0$, $Y = 1$ and $C = 0$.

In evaluating the molecular weight characteristics of the polymer being formed, we assume that the decay in hydrogen consumption rate showed by us experimentally is caused by a loss of active sites rather than by a gradual decrease in intrinsic activity of the sites. Even though the total rate of consumption of hydrogen falls throughout the polymerization, its concentration at the catalyst surface remains constant, as discussed earlier, and is not a function of yield. Reaction of hydrogen is assumed to be the predominant terminating mechanism.

Thus we can state that the average instantaneous degree of polymerization, $\bar{P}$, at any time during the polymerization is

$$\bar{P} = \frac{R_P(C,t,Y)}{R_T(t)}\qquad(8)$$

where $R_T(t)$ is the termination rate intensity. From eq. (8), the cumulative number- and weight-average degree of polymerization can be shown to be

$$\bar{P}_N = \frac{\int_0^t R_P(C,t,Y)dt}{\int_0^t R_T(t)dt}\qquad(9)$$

and

$$\bar{P}_W = \frac{\int_0^t \dfrac{R_P{}^2(C,t,Y)}{R_T(t)} dt}{\int_0^t R_P(C,t,Y)dt}.\qquad(10)$$

EXPERIMENTAL

Trioctyl aluminum was obtained from Schering A.G. and used as obtained. Isooctane (2,2,4-trimethylpentane) was obtained from Esso Chemical Company Limited and was distilled from high-surface sodium and sparged with dry nitrogen before use. All the gases used were passed over manganous oxide and Linde 4A molecular sieves; moisture and oxygen

levels were maintained well below 5 ppm.   The ^{14}C ethylene and ^{3}H hydrogen were obtained from the Radiochemical Centre, Amersham.   The titanium trichloride-type catalysts were made by reduction of reagent-grade titanium tetrachloride (ex BDH Ltd) with an alkylmagnesium compound.[7,8]   The development of these catalysts will be described in a forthcoming publication.[9]

Polymerizations were carried out at atmospheric pressure and at 80°C as well-stirred slurry in isooctane.   The gas mixture (measured by rotameters) was bubbled through the reactor until the solvent was saturated; the trioctylaluminum cocatalyst was then added, followed by the catalyst. The rate of ethylene absorption was monitored by measuring the rate of gas exit with an automated wet test meter.[10]   The polymerizations were terminated by addition of butan-2-ol.   This was followed by the addition of aqueous HCl and extraction with water to remove catalyst residues from the polymer.   Isooctane was removed by steam distillation; the polymer was then dried at 100°C in air.

Radioactive polymers were prepared under experimental conditions identical to those described above.   The polymerization reactor was designed in such a way that a quantity of ^{14}C ethylene or ^{3}H hydrogen could be metered into the ethylene/hydrogen stream when desired during a polymerization.

The radioactive polymers were counted by the coincidence scintillation technique on 1% w/v gels prepared as follows: 70 mg of tritiated polymer was added to 6.5 ml of xylene and 0.5 ml of scintillator (Isotope Development Limited NE 213 fluid).   The resulting mixture was heated at 120°C for 10 min, then allowed to cool over 20–30 min to form a gel.   Samples of the ^{14}C-labeled polymers, 10 mg, were fractionated into seven zones by gel permation chromatography in trichlorobenzene at 135°C.   Inactive polymer, 70 mg, was added to each zone and the trichlorobenzene was then evacuated at 100°C in vacuo with a nitrogen bleed.   The residues were formed into gels as described above.

Intrinsic viscosity measurements were made in decalin at 120°C. Molecular weight distributions of polymers not fractionated by gel permeation chromatography were calculated from rheological data.[11]

RESULTS AND DISCUSSION

A series of polymerizations with tritiated hydrogen were carried out to different times, and the tritium content of the final polymers was determined.   The rate of hydrogen uptake and thus the termination rate was then evaluated.   The observed decay in this rate is interpreted as being caused by a fall in the number of active sites.

With alternative assumptions of first and second-order decay in the number of active sites, integrated forms of the hydrogen consumption rate expression were fitted to the experimental data.   This is shown in Figure 2. A first-order plot forms the most satisfactory fit.   (It could be that had
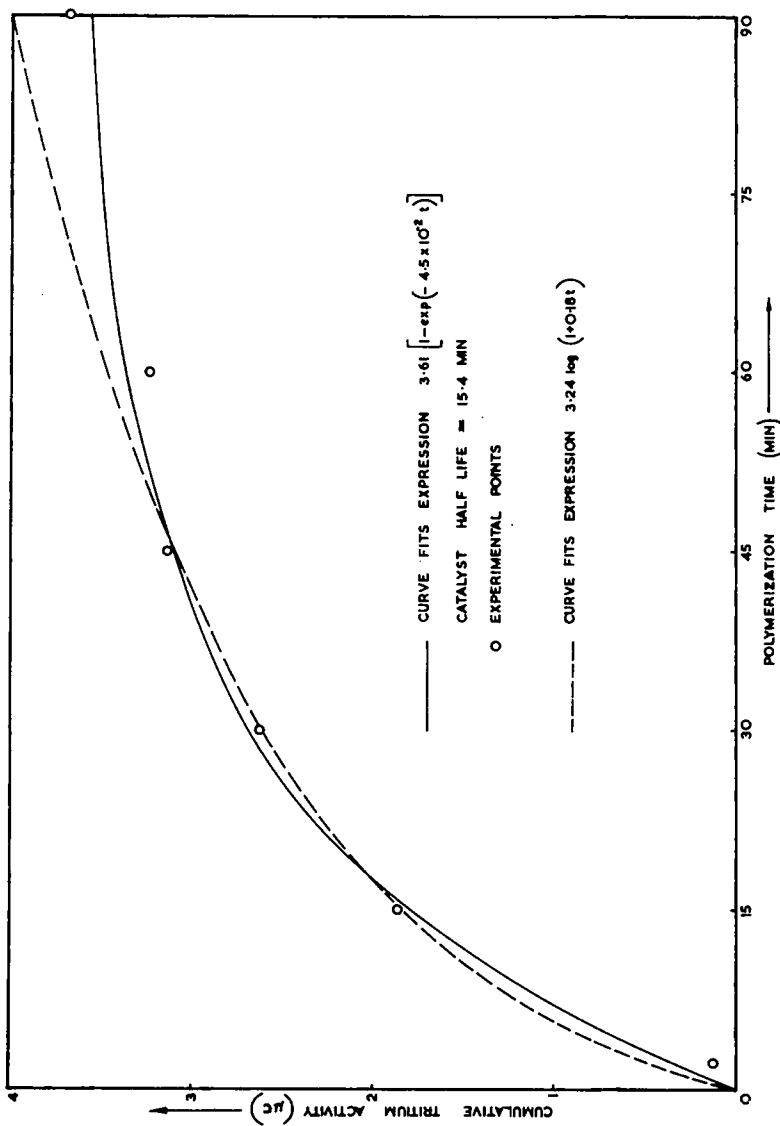
Fig. 2. Cumulative tritium activity of polymer vs. polymerization time.

the experiments been conducted for a time longer than 90 min a different conclusion might have been reached.) Accepting the first-order decay in the number of sites, it is concluded that the half-life of the catalyst is 15.4 min, and thus the decay constant is 7.5×10^{-4} sec^{-1}. We use the mathematical form of a first-order decay in evaluating the polymerization model. (In principle, any mode of site decay could be used.) Thus, the expression for the termination rate is taken as

$$R_T(t) = R_{T_0} \exp(-kt) \tag{11}$$

and the Thiele modulus, as

$$A(t) = A_0 \exp(kt). \tag{12}$$

(Thiele modulus is inversely proportional to the polymerization rate constant $k_S(t)$, which has embodied in it the number of active sites.)

Equations (4) and (5) have been solved using a fourth-order Runge–Kutta technique with the initial condition that at $t = 0$, $Y = 1$ and $C = 1$. The values of the constants in the equations (shown in Fig. 3) are arbitrary yet realistic and, if $k = 0$, would represent a case of diffusion control in the absence of any site decay. We use this set of data to illustrate the predictions of the model.

Experimentally it is common to monitor only the monomer absorption rate as a function of polymerization time. The prediction of the model for this readily observable quantity is shown in Figure 3. This curve falls into three distinct parts. Initially, the monomer absorption rate rises rapidly to a peak before falling off. The falloff is quite rapid at first but slows down, giving a slowly falling rate which lasts for an appreciable time. Eventually, the slow falloff in the rate curve is seen to be obeying a different mechanism.

The explanation of this result is that the initial peak arises from the nature of the transient characteristics of the reactor after start-up. When starting up from a saturated solution, the monomer absorption rate at $t = 0$ is zero, even though the initial polymerization rate is very high. In the limit at $t = 0$, the polymerization rate is 100% kinetically controlled; but once polymerization has begun, control begins to move away, diffusion and gas/liquid transfer effects becoming important. Polymerization with a highly active catalyst (such as our data represents) suffering no serious gas/liquid mass transfer restriction very soon becomes diffusion controlled. The subsequent rapid falloff away from the peak is caused by the increasing polymer yield and the transients in the reactor which are still present at this stage. Even though there is site decay occurring, the polymerization rate is still diffusion controlled. The polymerization rate is held to a slow decay by the increasing monomer concentration at the catalyst surface which offsets somewhat the loss of active sites. Gradually, the loss of sites becomes the dominant factor and the monomer absorption rate begins to fall more rapidly. During this process, control of the polymerization rate shifts from a bias toward diffusion control to one of kinetic control. In
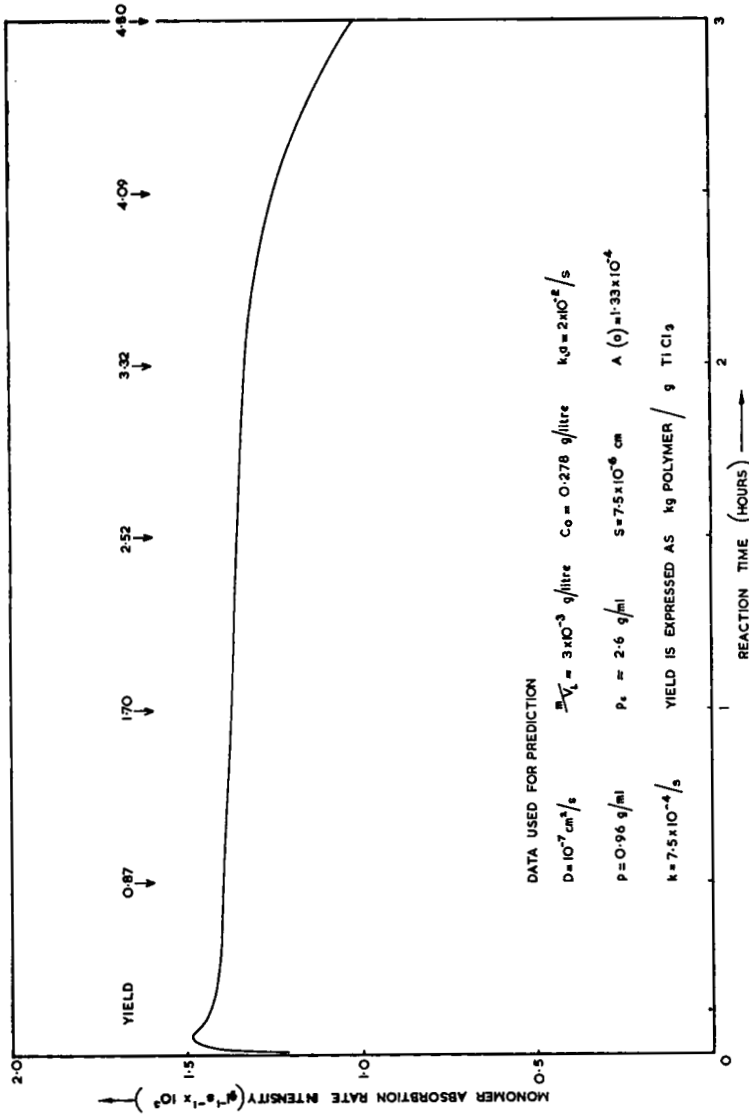
Fig. 3. Typical predicted monomer absorption rate intensity profile with first-order site loss.

Figure 3, diffusion control of the polymerization rate is still dominant, even after 3 hr.

Figure 4 shows a typical experimental monomer absorption rate curve. It has all the above mentioned characteristics and thus lends support to the theory.

It should be noted that the monomer absorption rate can only be regarded as the polymerization rate once start-up-related transient effects (rapid changes from the start-up conditions while concentration gradients are being established) are negligible. In the system studied, such transients typically remain significant for the first 5 to 10 min after the start of the polymerization. For a highly active catalyst, the polymerization rate is predicted to fall rapidly (by several orders of magnitude) during the very early part of the transient period. This precipitous rate decline could not be observed experimentally from the usual measurements of absorption rate. Bulk solution monomer concentration, on the other hand, falls only fractionally to a minimum, coincident with the maximum in the monomer absorption rate curve. After this point, the bulk solution monomer concentration rises gradually and in sympathy with the monomer absorption rate curve until it regains its initial level, once the catalyst has completely died. Mathematically this takes an infinite time to achieve.

The very large fall in the initial polymerization rate has implications for the molecular weight of the polymer then being formed. Predictions for the average instantaneous degree of polymerization as defined by eq. (8) indicate a proportionately large fall followed by a gradual rise. At infinite time, when the catalyst is completely dead, the instantaneous degree of polymerization is the same as that at the start of the polymerization. Thus we have a picture of an initially very high instantaneous molecular weight which rapidly falls, then slowly rises, all coupled with a decreasing polymerization rate. Cumulative molecular weight shows less severe changes and asymptotes to a value at infinite reaction time which is less than that at zero reaction time. For the case of no loss of active sites in stantaneous molecular weight will be directly proportional to polymerization rate, accordingly a drop in molecular weight asymptoting to some constant value is predicted. Figure 5 illustrates these trends in both cases. (It should be realized that in the very earliest stages of the polymerization, the molecular weight of the polymer cannot be accurately derived from eq. (8). Even though the mathematically defined degree of polymerization is falling rapidly from a finite initial value, the molecular weight must be rising.)

Radiolabeling experiments using ^{14}C ethylene during selected time intervals have shown that higher molecular weight polymer is made during the initial stages of the polymerization as predicted by the model. Figure 6 shows the molecular weight distribution curves obtained from GPC analysis and the activity distribution obtained from counts on the polymer fractions. The former curves represent the MWD of the entire polymer, while the activity distributions represent the MWD of the polymer formed
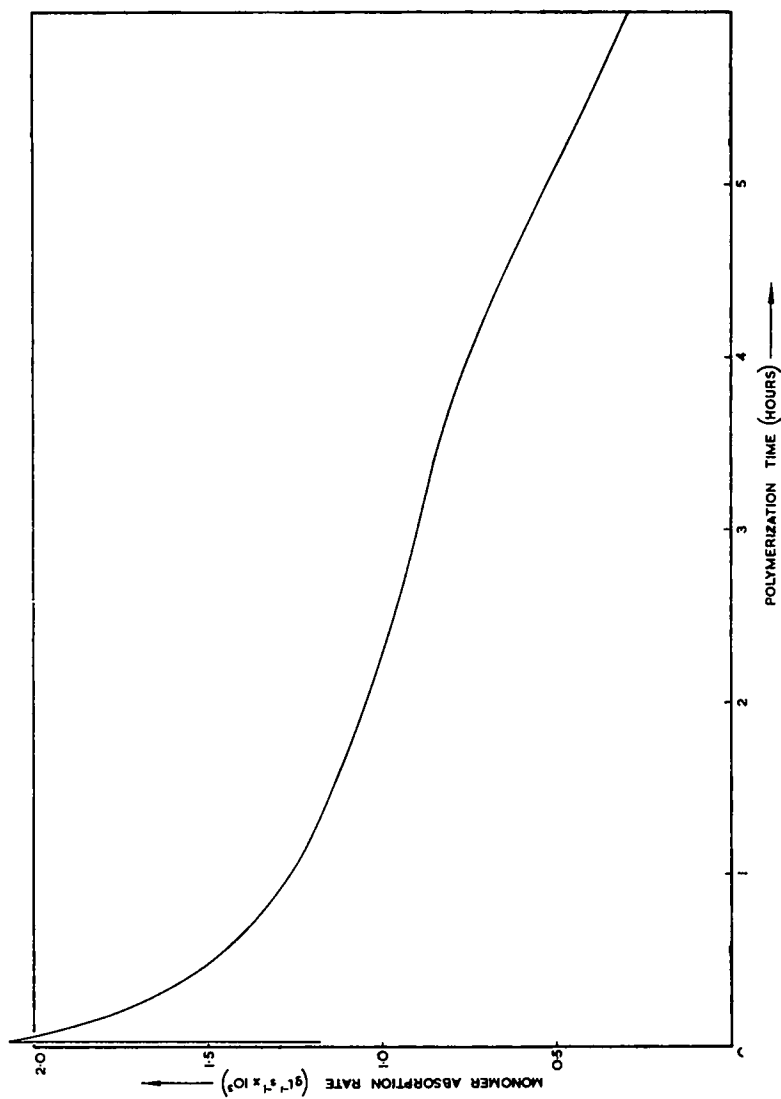
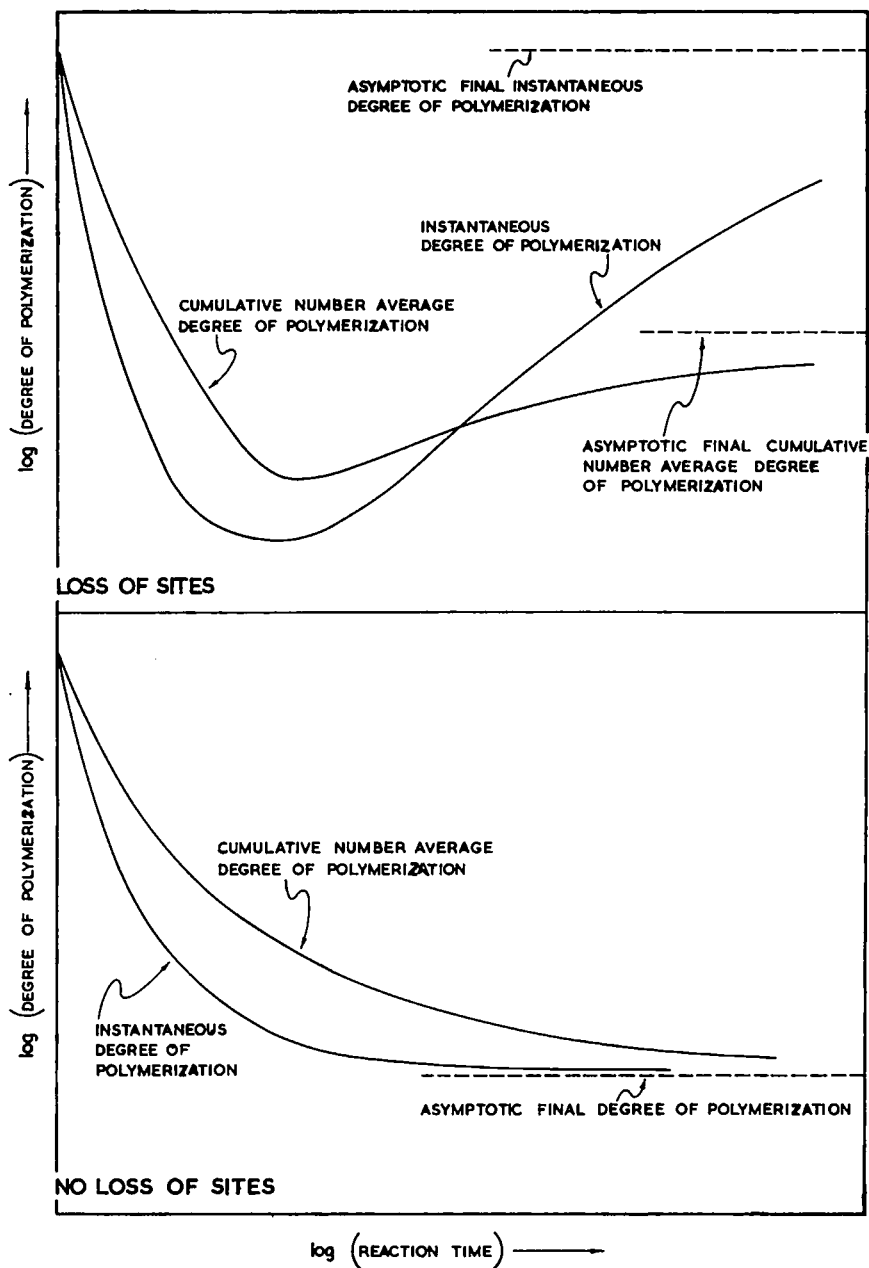Fig. 4. Experimental monomer absorption rate intensity profile.

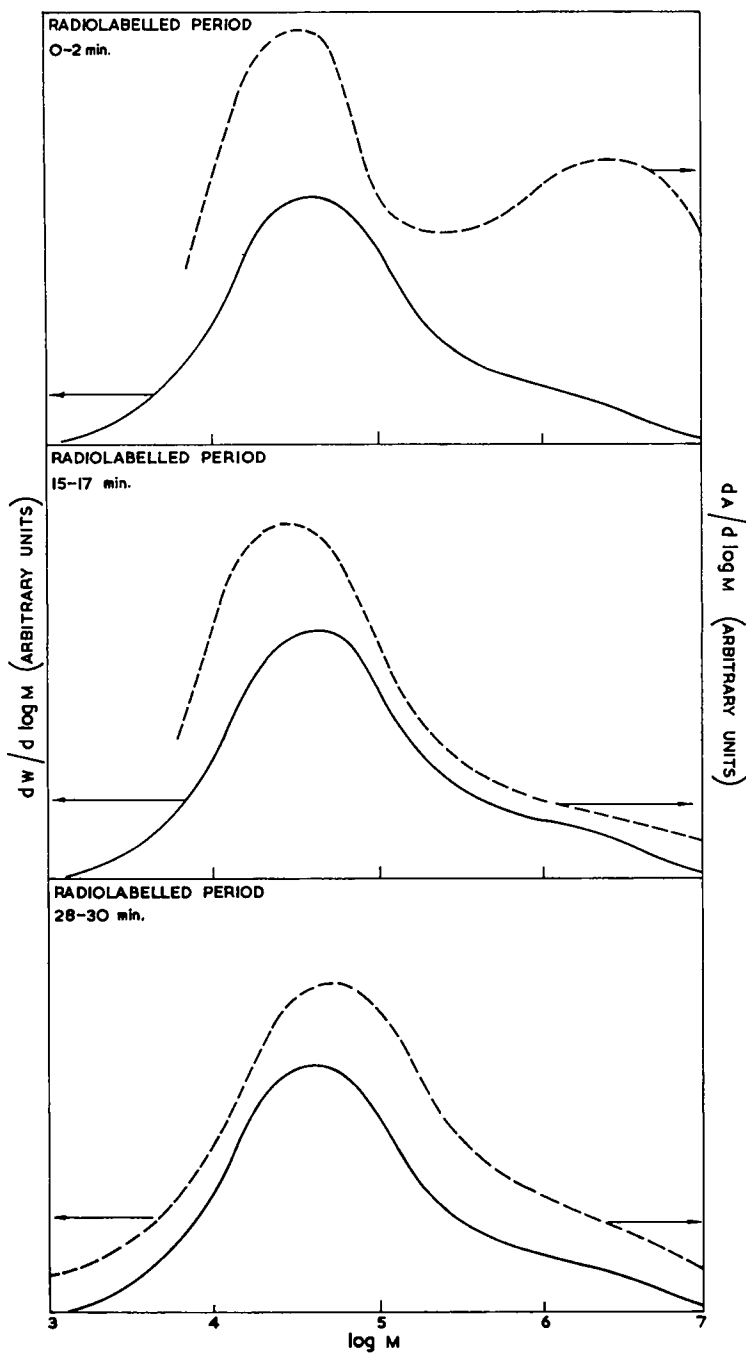Fig. 5. Predicted degree of polymerization profiles with and without loss of active sites (schematic).

Fig. 6. Distribution functions with respect to molecular weight (—) and to radioactivity (——) for radiolabeled polyethylenes.

during and, because of residence time distribution effects for the monomer, after the introduction of the labeled ethylene. The two curves are seen to become more synonymous the later in the polymerization the radiolabeled ethylene fraction is introduced. The bimodel distribution for the first 2-min period is especially significant. Our interpretation is that the higher molecular weight portion, peaking at about 100 times the value for the bulk polymer, is formed in the earliest moments of this initial period when the active sites are relatively unhindered by polymer, so that their intrinsically very high propagation rate can be fully realized.

The trend evident in Figure 6 of a slight increase in the molecular weight of the polymer made in the last 2-min period over the middle period is supported by two independent experimental sources. The first, an indirect one, involves the calculation of number-average cumulative molecular weight using the results of the tritiated hydrogen experiments. These results indicate a fall followed by a rise with increasing polymerization time. Significantly, these calculated number-average cumulative molecular weights, which assume one molecule of hydrogen introduced into the polymer for each termination event, agree well with those determined by gel permeation chromatography. This is indirect confirmation of the assumption that termination by hydrogen is the predominant termination mechanism under the conditions of the experiment. Table I shows typical values. The second source is the plotting of intrinsic viscosity of polymer made to various reaction times (or yields) against the reaction time (or polymer yield). These show a decline followed by a very gradual rise. Figure 7 illustrates the trend.

TABLE I
Number-Average Cumulative Molecular Weights for Tritiated Polymers

Polymerization time, (min)	$M_n \times 10^{-4}$ (calculated)	$M_n \times 10^{-4}$ (GPC)
2	3.77	3.80
15	2.29	
30	2.96	2.60
45	3.31	
60	3.90	
90	4.40	

Experimental evidence from various sources thus suggests a molecular weight trend which is in very good agreement with our theoretical predictions.

For a nondecaying catalyst under diffusion control, the polymerization model predicts that the polydispersity factor (defined in this work as $\bar{P}_W/\bar{P}_N$) should at first increase rapidly to a maximum and then decline with increasing polymer yield to an asymptotic constant value. If the polymerization is essentially kinetically controlled, we obtain the result that the polydispersity factor is constant and independent of the polymer yield.
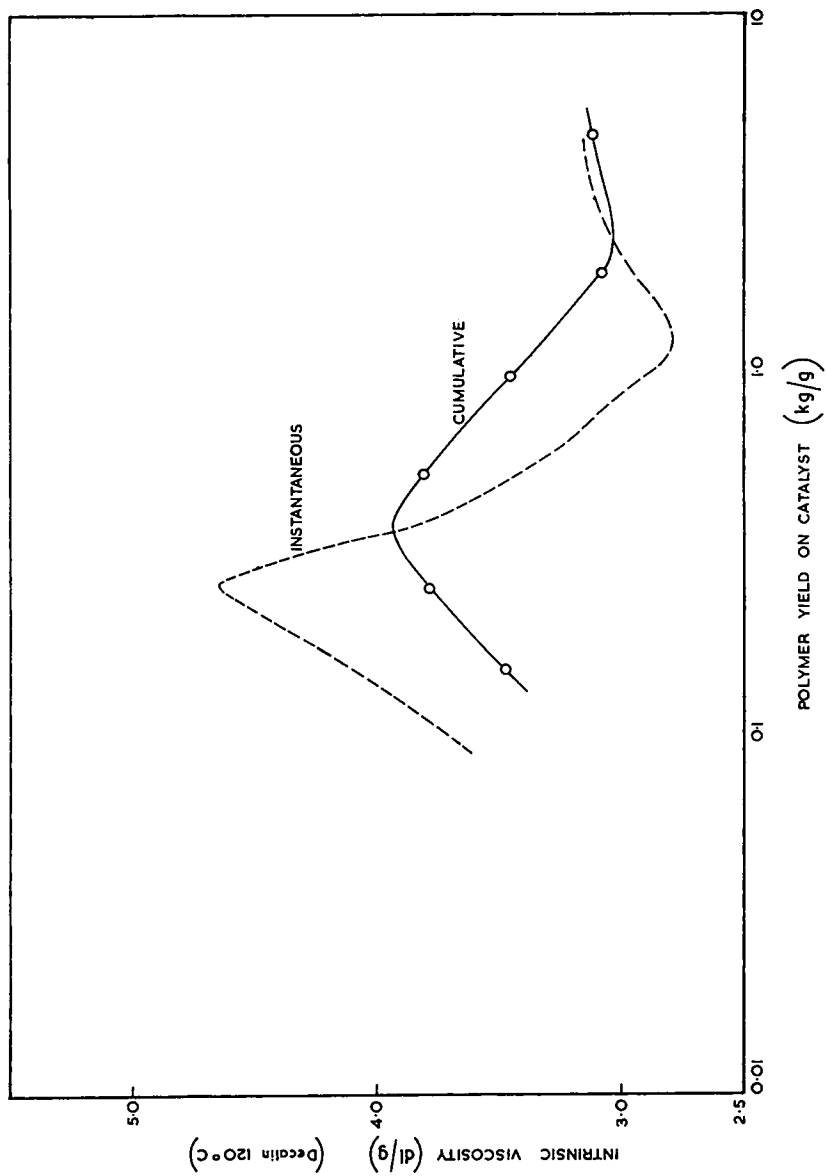
Fig. 7. Variation in molecular weight with yield on catalyst. Polymerization carried out with 40% H_2 in the gas feedstream.
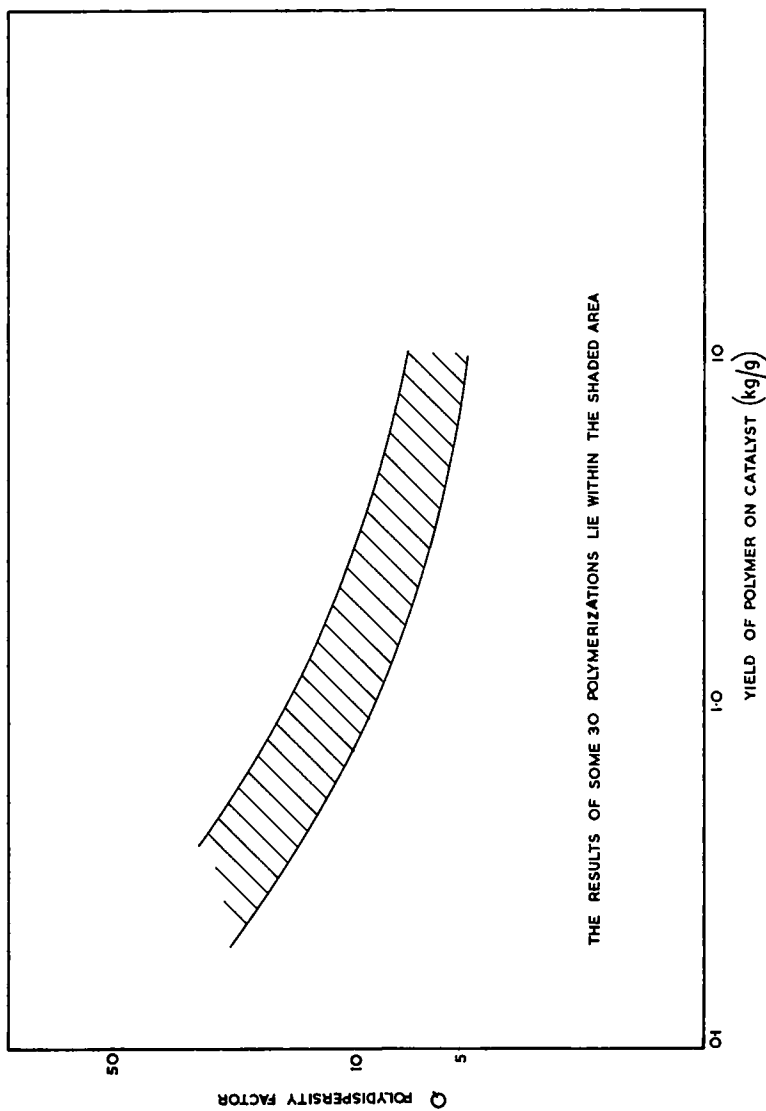
Fig. 8. Effect of yield on catalyst on overall molecular weight distribution.

Even with a decay in the number of active sites, with kinetic control we expect to see a polydispersity factor which is constant and independent of yield.

Our evaluation of the polydispersity behavior with reaction time for the case of diffusion importance and loss of sites has not proved satisfactory owing to numerical calculation difficulties. The problem is not insuperable, but lack of time and other priorities have not allowed its exact enumeration. Tentatively, we suggest that the polydispersity factor rapidly increases to a maximum, then slowly falls to a shallow minimum before an even slower rise to an asymptotic final value. The final asymptotic value is little different in magnitude from the minimum.

The results of many experiments using different batches of catalysts have shown a narrowing of the molecular weight distribution with increasing polymer yield. Typical maximum yields of 10 kg of polymer per g of $TiCl_3$ at atmospheric pressure have been reached. The overall picture is shown in Figure 8, where it is seen that the Q value (ratio of weight- to number-average molecular weight) is apparently asymptoting to a value of around 4. We suggest that this experimental trend is strong evidence in support of the proposed model.

CONCLUSIONS

Experimental analysis has shown that site decay is a feature of the catalyst used. Incorporation of this into a simplified polymerization model which takes into account the overall nature of the reactor has led to predictions for the monomer absorption rate/time curves which contain all the elements of those seen experimentally.

With this mechanism as a model, the molecular weight characteristics have been explored as a function of reaction time and compared with the predictions made from the model. Thus, for the polymerization of ethylene in the presence of hydrogen with the catalyst described in the paper, we conclude that (1) subparticle encapsulation is conceptually correct for the mode of polymer growth; (2) initially during its lifetime in the reactor, the catalyst is diffusion controlled yet decaying in the number of active sites rather than in intrinsic activity; (3) this latter combination of effects gives rise to the molecular weight characteristics of the polymer formed; in particular, high molecular weight polymer is made in the initial stages of the polymerization; the cumulative molecular weight later falls before rising slowly to an asymptotic value; (4) molecular weight distribution is predicted to be rather wide during the early stages but narrows with increasing yield or reaction time.

Nomenclature

$A(t)$ Thiele modulus
C dimensionless bulk solution monomer concentration
C_0 monomer concentration in equilibrium with the gas phase (ML^{-3})

C_R bulk solution monomer concentration (ML^{-3})

C_S monomer concentration at the catalyst surface (ML^{-3})

D effective diffusivity of monomer through polymer surrounding a catalyst subparticle (L^2T^{-1})

k first-order site decay constant (T^{-1})

$k_L a$ volumetric gas/liquid mass transfer coefficient (T^{-1})

$k_S(t)$ surface rate constant for the overall polymerization rate (LT^{-1})

m mass of catalyst in the reactor (M)

N_P total number of subparticles in the reactor

$\bar{P}$ instantaneous degree of polymerization

$\bar{P}_N$ cumulative number-average degree of polymerization

$\bar{P}_W$ cumulative weight-average degree of polymerization

ρ bulk density of polymer surrounding a subparticle (ML^{-3})

ρ_c density of a catalyst subparticle (ML^{-3})

R radius of the outer shell of polymer surrounding a catalyst subparticle (L)

R_M monomer absorption rate intensity $(ML^{-3}T^{-1})$

R_P polymerization rate intensity $(ML^{-3}T^{-1})$

R_T termination rate intensity $(ML^{-3}T^{-1})$

S radius of a catalyst subparticle (L)

t reaction time (T)

V_L volume of the reactor liquid phase (L^3)

Y linear subparticle encapsulation ratio $(= R/S)$

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