

# Modeling of Transfer Phenomena on Heterogeneous Ziegler Catalysts: Differences Between Theory and Experiment in Olefin Polymerization (An Introduction)

T. F. MCKENNA,\* J. DUPUY, and R. SPITZ

C.N.R.S.-L.C.P.P., B.P. 24, 69390 Vernaison, France

## SYNOPSIS

This article begins by briefly reviewing the more important contributions to the area of modeling heat and mass transfer, and particle growth during the polymerization of olefins on Ziegler-Natta catalysts. It is shown that these models are capable of identifying the critical areas involved in heat and mass transfer, and of modeling polymerizations where the observed activity is less than approximately 5,000 g of polymer per gram of catalyst per hour (g/g/h). However, it is not possible to use these models "as-is" to model more modern catalysts whose activity levels can surpass the 50,000 g/g/h mark because they predict prohibitively large concentration gradients inside the growing particles during slurry polymerizations, and temperature gradients outside the particles during polymerization in the gas phase. An analysis of the mass and heat transfer Peclet numbers ( $Pe$ ) reveals that certain simplifying assumptions may not always be valid.  $Pe$  values in the transition range suggest that convection inside the particles during polymerization in the liquid phase may help to explain why observed mass transfer rates are higher than the predicted rates. In an opposite vein, a  $Pe$  analysis shows that conductive heat transfer may play an important role at length scales characteristic of those in the early stages of polymerization. A new mechanism for heat transfer at reduced length scales is proposed. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Due to its great commercial importance, the "low pressure/low temperature" polymerization of olefins on heterogeneous catalysis has attracted a great deal of attention over the last 15 years. Considerable effort has been made in modeling the polymerization kinetics, the morphology of the catalyst and polymer particles, and the transfer of matter and energy in and out of the growing polymer-catalyst complex. In the present work we will examine the state of the art in modeling the transport phenomena, and briefly look at aspects of particle morphology.

Successful attempts at modeling transport phenomena in Ziegler-type catalysts have been presented by Chiovetta et al.,<sup>1-6</sup> and by the research

group of Ray at the University of Wisconsin.<sup>7-15</sup> These models, based on physical observations of catalyst and polymer particles, were used to evaluate transport resistances and the development of temperature and concentration profiles in the growing particles.

The model originally developed by Laurence and Chiovetta,<sup>2</sup> and later extended by Ferrero and Chiovetta,<sup>3-6</sup> dealt with modeling catalyst particle fragmentation, and the relationship between fragmentation and the development of concentration and temperature profiles in the growing polymer particle during the initial stages of polymerization. The model first used by Floyd et al.,<sup>8</sup> later refined by Hutchinson et al.,<sup>15</sup> was used to examine both intra- and extraparticle gradients and resistances, and their potential influence on the properties of the polymer being produced. The results of these studies revealed the areas where heat and mass transfer resistances are, and are not important.

\* To whom correspondence should be addressed.

Roughly speaking, resistances were found to be greatest for heat transfer at the exterior of the polymer particles in gas phase polymerizations, and at the interior of the particles for mass transfer in liquid/slurry phase polymerizations. It was also found that diffusion resistance could generally not explain the wide molecular weight distributions often observed in these systems.

These models are physically well founded and answered a great number of questions about the evolution of heat and mass transfer, as well as the importance of aspects of particle morphology (elementary crystal size, complexity of models, etc.) during particle growth. However, at the time the original models were developed, average catalytic activities considered were rather low (on the order of 1000–5000 g of polymer per gram of catalyst per hour, e.g. Choi and Ray<sup>16</sup>). Since then much progress has been made in the area of catalysis for the polymerization of olefins, and average activities of over 25,000 g of polymer per gram of catalyst per hour are commonly observed in our laboratories and others (e.g., Nooijen<sup>17</sup>), as well as in industrial practice for both the gas and slurry phase polymerization of ethylene and propylene.

It is the purpose of the current study to discuss areas where currently accepted models of mass and energy transfer during the polymerization of olefins on Ziegler-type catalysts do not function well. We will begin by looking at the catalyst/polymer particle morphology and continue with problems encountered in the modeling of transport phenomena using this description of particle geometry.

## PARTICLE MORPHOLOGY AND CURRENT MODELS

It is important to have an acceptable model of the morphology of catalyst/polymer particle complex if we are to attempt to describe how matter and energy are transferred in and around these “microreactors.” And, in a somewhat circular vein, it is necessary to be able to describe heat and mass transfer in order to predict how polymer particles grow, and how their morphology evolves with time. The steps in the evolution of Ziegler-type catalysts have been widely examined by a great number of researchers, and Xie et al.<sup>18</sup> summarized the conclusions on the evolution of the morphology of a catalyst particle as the polymerization progresses as follows. We begin with a catalyst particle on the order of 10s of microns in diameter that is composed of primary crystals on the order of 10–200 Å wide, held together by van der

Waal’s forces. The particle contains active sites distributed throughout its porous matrix that are located on the primary crystals. At the onset of polymerization, the monomer(s) diffuses through the pores of the catalyst particle toward the active sites where the reaction takes place. Polymer forms on the surfaces of the primary crystals, and begins to fill the interstices between them. At this point the catalyst particle becomes a growing polymer particle. As polymer is formed, one of two things can happen. If the hydraulic forces created by the production of polymer around the primary crystals are not sufficient to cause these crystals to break apart from one another, Webb et al.<sup>19,20</sup> have shown that the polymerization rate is drastically reduced, and can even stop due to diffusion limitations. However, in most cases the hydraulic forces created inside the growing polymer particle are sufficiently large that the primary crystals break apart, but the polymer particle is held together in its original shape by the polymer chains. In this manner, the primary crystals, and thus the active sites, are more or less evenly dispersed in the polymer particle. Ferrero et al.<sup>21</sup> showed that total catalyst breakup occurs at extremely low production rates. It can thus be assumed that catalyst fragmentation into polymer particles, made up of an agglomeration of micrograins, is rapid. Due to the breakup of the primary crystals the polymer particle continues to grow isotropically until the end of the reaction when they will have attained diameters on the order of 200–500 μm, or even more.

To develop a model for this type of process the following questions need to be addressed.

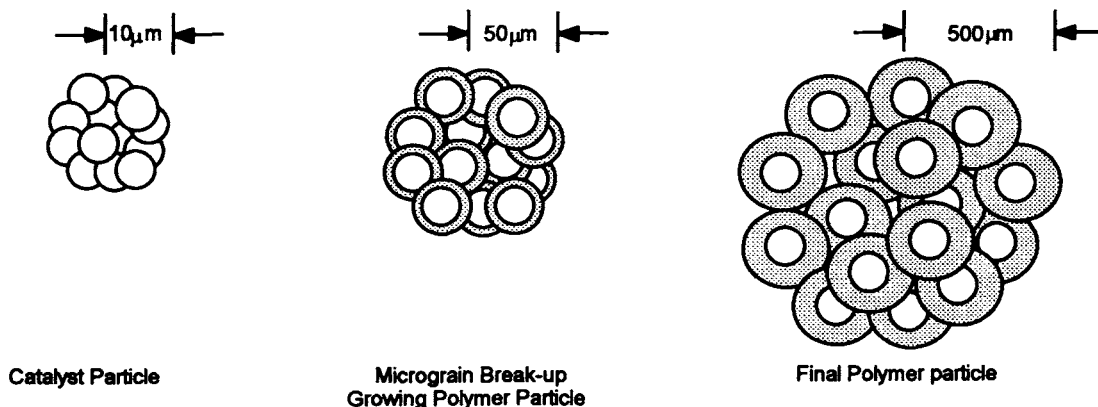
What simplifications and assumptions are justifiable in predictive models in light of the observed results? For example, what is the minimum length scale that needs to be included in the model, what is the relationship between minimum length scale and activity, when can convective effects be neglected? The importance of primary crystal size on mass transfer efficiency has been examined, but potential resistances at the beginning of the reaction have been neglected in certain models. Convection may play an important role in mass transfer in slurry systems.

What are reasonable values for model parameters and correlations? Literature values are coherent as far as diffusivity in the growing polymer particles is concerned, but the diffusivity of monomers in the semicrystalline polymer layer takes on a wide range of values. Assumptions on the validity of correlations used to estimate external heat transfer coefficients need to be verified.

How is the evolution of the geometry and morphology of the catalyst particle best modeled? How do we best describe the transition between virgin catalyst and growing polymer particles? Laurence and Chiovetta<sup>2</sup> and Ferrero and Chiovetta<sup>3-6</sup> modeled this transition assuming different values for monomer diffusivity, porosity, and tortuosity in polymerized and unpolymerized parts of the catalyst particle. Hutchinson et al.<sup>15</sup> looked at the evolution of void volume in the macroparticle and allowed the diffusion coefficient to change according to the well-known law  $D = D_{\text{bulk}}(\epsilon/\tau)$ .

What happens during the initial instants polymerization? This needs to be looked at from kinetic (activation/reactivation of sites, mass transfer of the cocatalyst) and physical (fragmentation/initial resistances) points of view.

The multigrain model (MGM), presented by Taylor et al.<sup>22</sup> and shown in Figure 1, has been used in similar forms by the different authors shown in Table I to describe catalyst particle morphology. This model generally includes two levels of morphology: the macroparticle, or growing polymer particle, and the microparticle, the primary crystallites and the polymer layer that covers them. Simplifications include the assumption that all of the original primary crystals in the catalyst are spheres of the same size, and that the catalyst particle is originally spherical as well. In its original form, the MGM equations looked at mass and energy transfer on two different levels: first through the polymer layer around the microparticles, and then in and around the macroparticle, where the macroparticle was treated as a pseudohomogeneous medium. The MGM equations used to describe the transfer processes occurring in the model for a growing polymer particle (macroparticle) are written in the following form:



**Figure 1** Schema of the multigrain model (MGM) of catalyst particle morphology. The length scales shown are very approximate and will vary from catalyst to catalyst.

Mass transfer:

$$\frac{\partial C_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_i \frac{\partial C_i}{\partial r} \right) - R_{p_i} \quad (1)$$

with the initial and boundary conditions:

$$C_i = C_i^0 \quad \text{at} \quad t = 0 \quad (1a)$$

$$\frac{\partial C_i}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad \text{or} \quad (1b)$$

$$\left. \begin{array}{l} C_i = C_i^{\text{bulk}} \\ \text{or} \\ \frac{\partial C_i}{\partial r} = 4\pi(R_1)^2 k_g (C_i(R_1) - C_i^{\text{bulk}}) \end{array} \right\} \text{at } r = R_1. \quad (1c)$$

Energy transfer:

$$\frac{\partial T}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 k_f \frac{\partial T}{\partial r} \right) - \sum - \Delta H_{p_i} R_{p_i} \quad (2)$$

with the boundary conditions:

$$\frac{\partial T}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad (2a)$$

and

$$\frac{\partial T}{\partial r} = 4\pi R_1^2 \frac{h}{\rho c_p} (T(R_1) - T^{\text{bulk}}) \quad (2b)$$

and the initial condition:

$$T = T_0 \quad \text{at} \quad t = 0 \quad (2c)$$

Table I Recent Modeling Approaches to the Treatment of Macroparticle/Microparticle Problem

Author	Microparticle	Macroparticle
Chiovetta <sup>1</sup>	Numerical solution to transient equations of mass and energy balances	Model macroparticle as agglomeration of concentric layers of microparticles; mathematical relationships to estimate number of microparticles (total/per layer)
Laurence and Chiovetta <sup>2</sup>		Look at transients of fragmentation process layer-by-layer from exterior to center of macroparticle; layer considered fragmented when polymer accumulation reaches critical value; assume diffusivities in macroparticle 100 times less in unfragmented core; also assume unfragmented core has lower porosity (0.3 vs. 0.42 for fragmented layers)
Ferrero and Chiovetta <sup>3-6</sup>		Find that development of temperature and concentration profile depends on fragmentation speed (depends on diffusivities/critical amount polymer); rapid fragmentation leads to high temperature excursions in macroparticle; fragmentation time varies from 5 to 500 s Maximum activity on order of 3-4000 g/g/h; activities on order of 20,000 g/g/h in liquid phase studies, and approximately 6000 in gas phase (propylene only); do not consider catalyst decay Fragmentation faster in gas phase because lower mass transfer resistance QSSA, analytical solution to mass and energy balance equations; implicitly assume complete catalyst fragmentation at beginning of reaction
Floyd et al. <sup>8,9</sup>	Quasi-steady-state approximation (QSSA), analytical solution of concentration drop	Model conceived for gas/slurry polymerization of both ethylene and propylene High activity considered to be on order of 4,000 g/g/h Consider "activation" period, or fragmentation time; this period modeled by assuming catalyst activity increases exponentially from zero to maximum in time specified as break-up time; gradients, especially temperature, depend strongly on break-up time as with Laurence and Chiovetta
Floyd et al. <sup>10</sup>	As above	Use Ranz-Marshall correlations for film-side transfer coefficients As with Floyd et al. <sup>10</sup> except consider catalysts with time-dependent deactivation and activity peaks near 15-20,000 g/g/h; average activities remain 4-5,000 g/g/h Numerical solutions to mass and energy balance, and MWD moment equations, with and without QSSA
Hutchinson et al. <sup>15</sup>	As above	Diffusion resistance cannot account for wide MWDs observed in reality; must be due to multiplicity of active sites Modify MGM approach to include copolymerizations; macroparticle equations solved on grid of isochoric shells (only one level of morphology considered important); this allows us to account for variable void volume and thus variable macroparticle diffusivity, uneven growth from shell to shell (i.e. concentration profiles) lead to different void fractions as function of particle radius; show that prepolymerization can be used to control development of void fraction Assume isothermal macroparticle Account for uneven distribution of active sites (weight fraction of transition meta <sup>1</sup> in macroparticle) by imposing empirical polynomial weight fraction profile Predict significant mass transfer resistance in macroparticle for slurry polymerization Model with observed peak activities of 6,500 g/g/h (gas phase) and 8,700 g/g/h (slurry) in copolymerization; (ethylene + butene), < 2,700 g/g/h for propylene slurry homopolymerization Used three or four of organization (microparticles of MGM composed of agglomerates of smaller particles, etc.) Included convection in model equations
McKenna and Schweich <sup>23</sup>	QSSA for mass transfer, isothermal microparticles	Model macroparticle as collection isochoric shells, include only one level of morphological organization Diffusivities of monomer in macroparticle must equal bulk diffusivity to explain observed rate behavior
Spitz et al. <sup>24,25</sup>	Assume no gradients	

**Table II Conclusions on Significance of Heat and Mass Transfer Resistances According to Results of Modeling Studies in Table I**

Phase	Resistance to	External Film	Macroparticle	Microparticle
Liquid	Mass transfer	Negligible	Can be important especially at beginning of reaction or for high activities	Can be important at beginning of reaction, especially for catalysts containing large primary particles
Gas	Heat transfer	Negligible	Negligible	Negligible
	Mass transfer	Negligible	Generally negligible except for large, active particles at beginning of reaction Modeling more than two levels of morphology does not change predictions of heat and mass transfer	Can be important at beginning of reaction, especially for catalysts containing large primary particles
	Heat transfer	Can be important especially for large, active particles at beginning of reaction	Generally negligible except for large, active particles at beginning of reaction	Negligible

where  $C_i$  is the concentration of species  $i$ ,  $r$  the radial direction of the macroparticle,  $R_1$  the external radius of the growing particle,  $D_i$  the effective diffusivity of species  $i$  in the macroparticle,  $R_{pi}$  the rate of reaction of species  $i$  per unit volume of macroparticle,  $k_g$  the film-side mass transfer coefficient,  $T$  the temperature in the particle,  $h$  the film-side heat transfer coefficient,  $\rho$  the density of the polymer particle, and  $c_p$  the heat capacity of the particle. The choice between boundary conditions in eq. (1c) depends on the importance of the resistance to mass transfer between the bulk environment in the reactor and the exterior of the growing particle. The microparticle equations are simply the well-known diffusion equations with a reactive boundary condition at the microparticle surface:

$$\frac{\partial C_{2i}}{\partial t} = \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \left( r_2^2 D_{pi} \frac{\partial C_{2i}}{\partial r_2} \right) \quad (3)$$

$$\frac{\partial C_{2i}}{\partial r_2} = \frac{(k_{pi} C^*) C_{2i}}{D_{pi}} \quad \text{at } r_2 = R_0 \quad (3a)$$

$$C_{2i} = C_i^{\text{eq}} \quad \text{at } r_2 = R_2 = \phi_2 R_0 \quad (3b)$$

where  $D_{pi}$  is the diffusivity of monomer  $i$  in the polymer layer around the microparticles, the subscript 2 refers to the microparticle, and we have assumed the reaction rate can be expressed as  $(k_{pi} C^*) C_{2i}$  with  $C^*$  being the active site concentration on the microparticle surface,  $R_0$  is the radius of the unpolymerized microparticle where the reaction takes place,  $R_2$  is the radius of the microparticle plus polymer layer, and it is assumed that the concentration

in the polymer at the exterior of the microparticle is equal to that in the gas phase. The energy balance equations for the microparticle are completely analogous.

Based on electron micrographs of certain supported Ziegler catalysts, and on the results of porosity studies such as those presented by Ferraro et al.,<sup>21</sup> McKenna and Schweich<sup>23</sup> added up to two additional levels of morphological organization to the original MGM. Simulations with three levels of organization, where the primary particles were on the order of 20–50 Å diameter, showed that such additional levels of morphological organization did not reveal any noticeable transfer resistances at this level, even at very high activity levels. It can be concluded from their simulations that including more than two levels of morphological organization in a physical model of this type of catalyst is unnecessary.

Hutchinson et al.,<sup>15</sup> and more recently Spitz et al.,<sup>24,25</sup> added certain simplifications to the model, treating it as a pseudohomogeneous medium where eqs. (1) and (2) could be solved on a numerical grid composed of concentric isochoric shells. Hutchinson et al.<sup>15</sup> do not specify the minimum length scale used in the solution of their model equations, but Spitz et al.<sup>25</sup> claim that using numerical grids finer than 1- $\mu\text{m}$  wide does not change the values of the model solution, and that modeling the heat and mass transfer phenomena at the scale of the microparticle is not necessary.

The conclusions drawn from the simulations presented in Table I are shown in Table II. Most studies

point to the conclusion that resistance to mass and energy transport is essentially negligible at the level of the microparticles, and it is commonly assumed that modeling the polymer particle as a pseudohomogeneous medium is acceptable.

## MASS TRANSFER CONSIDERATIONS

The conclusions presented in Table II show that the most important mass transfer resistance encountered during olefin polymerization occurs at the level of the macroparticle in liquid/slurry polymerizations. This is especially evident in the work of Hutchinson et al.<sup>15</sup> where simulation results predict that the concentration of propylene at the center of the macroparticle can be less than 30% of its value in the bulk phase during slurry polymerization in heptane. The corresponding rate curves for this last study showed peak activities on the order of 2,600 g/g/h.

Spitz et al.<sup>25</sup> used their model along with the parameters used by both Floyd et al.<sup>8</sup> and Hutchinson et al.,<sup>15</sup> and were able to reproduce the same concentration profiles shown in the latter two works. However, upon increasing the average intrinsic activity of the catalysts to the order of 15,000–20,000 g/g/h (slurry polymerization of ethylene), they were unable to simulate observed experiments using

the diffusion coefficients shown in Table III. It was found that the simulations showed that the concentration gradient in the macroparticle was simply too high to permit the predicted activity levels to reach the intrinsic level. To achieve polymerization rates on the order of those mentioned, it was necessary to increase the monomer diffusivity in the pores of the catalyst to values on the order of  $10^{-4}$  cm<sup>2</sup>/s, the same order of magnitude as the diffusivity in the bulk phase. Although it may be reasonable to use such values of the diffusivity because certain workers such as Ferrero et al.<sup>26</sup> have shown that macropores on the order of 10–20  $\mu$ m diameter do exist in polymer particles, other physical explanations should also be considered.

The diffusivities used by Floyd et al.<sup>8</sup> agree well with those reported by Herrmann and Böhm.<sup>27</sup>

Note that the polymer phase (microparticle) diffusivities presented in Table III are those in semicrystalline polymers. While it is proposed that the polymer formed at the active sites is probably completely amorphous, it is not unreasonable to suppose that the majority of the polymer in the layer around the micrograins is semicrystalline at the temperatures commonly used in catalyzed polymerizations. Furthermore, mass transfer resistances using these conservative values of the diffusivity in semicrystalline polymers are not found to be very important, and using even higher values for completely amor-

**Table III Monomer Diffusivities Used in Gas and Liquid Phase Transport Models**

Milieu, Diffusivity (cm <sup>2</sup> /s)	Floyd et al. <sup>7-9</sup>	Chiovetta et al. <sup>1-6</sup>
<b>Bulk</b>		
Gas phase	4*10 <sup>-3</sup> (propylene) 6*10 <sup>-3</sup> (ethylene)	3*10 <sup>-3</sup> a,b
Liquid phase	8*10 <sup>-5</sup> (propylene) 1*10 <sup>-4</sup> (ethylene)	10 <sup>-6</sup> –10 <sup>-5</sup> a,c
<b>Macroparticle</b>		
Gas phase	10 <sup>-4</sup> –10 <sup>-3</sup> d	6.25*10 <sup>-5</sup> –2.4*10 <sup>-4</sup> a,b 6.25*10 <sup>-7</sup> b,e
Liquid phase	10 <sup>-6</sup> –10 <sup>-5</sup> d	3.23*10 <sup>-6</sup> –1.92*10 <sup>-5</sup> a,c
<b>Microparticle</b>		
Gas phase	10 <sup>-8</sup> –10 <sup>-6</sup> d	10 <sup>-11</sup> –2.*10 <sup>-9</sup> a,b 2.4*10 <sup>-11</sup> a,e
Liquid phase	10 <sup>-8</sup> –10 <sup>-6</sup> d	2.4*10 <sup>-11</sup> –2.4*10 <sup>-12</sup> a,c

<sup>a</sup> For propylene only.

<sup>b</sup> Chiovetta.<sup>1</sup>

<sup>c</sup> Ferrero and Chiovetta.<sup>5,6</sup>

<sup>d</sup> For both ethylene and propylene without distinction.

<sup>e</sup> Ferrero and Chiovetta.<sup>3</sup>

phous polymer would by no means change the conclusions of any of the modeling studies reported here.

With one exception, the models presented in Table I do not consider any convective contribution to heat and mass transfer. Equations (1) and (2), which are used in virtually all of the models presented there, are simplified forms of the continuity equations for mass and energy transport that take the general form

$$\frac{\partial C_i}{\partial t} = \nabla \cdot N_i - R_{p_i} \quad (4)$$

where  $N_i = D_i \nabla C_i - C_i u$  and

$$\frac{\partial T}{\partial t} = \nabla \cdot (k_e \nabla T) - \rho c_p u \nabla T + \sum \Delta H_{p_i} R_{p_i} \quad (5)$$

where  $u$  is a superficial convective velocity in the pseudohomogeneous macroparticle and  $N_i$  the molar flux of species  $i$  with respect to stationary coordinates.

In writing eqs. (1) and (2), it was (implicitly in some cases) assumed that convective effects were entirely negligible, and that the fluxes in the mass and energy balance equations were purely diffusional. This assumption is most likely valid in normal situations for gas phase polymerization where Floyd et al.<sup>8,9</sup> have shown that concentration gradients are negligible, but may be less widely applicable in the case of slurry phase polymerizations. If we write eq. (4) in dimensionless form for spherical coordinates

$$\frac{\partial x_i}{\partial y} = \frac{1}{y^2} \frac{\partial}{\partial y} \left\{ y^2 \frac{\partial x_i}{\partial y} - \text{Pe}(y^2 x_i) \right\} - \phi^2 x_i \quad (6)$$

where  $x_i$  is a dimensionless concentration (e.g. with respect to the bulk phase),  $y = r/R_1$ , Pe the Peclet number =  $R_1 u/D_i$ , and  $\phi^2$  is the Thiele modulus =  $k_p R_1^2/D$ . Note that in writing the Thiele modulus it has been assumed that the pseudohomogeneous reaction rate can be written as first order with respect to the monomer concentration (e.g.  $R_{p_i} = k_p C_i$ ). Note that even though the reaction takes place at the surface of the microparticles, the concentration at the active sites is proportional to the concentration of monomer in the pores of the macroparticles via boundary condition (3b), so we can define a pseudorate constant  $k_{p_i}$  that is characteristic of the overall rate of reaction.

It can be inferred from eq. (6) that any convective effects will be negligible if the Peclet number is much

less than unity. To evaluate (order of magnitude) Pe it is necessary to have an estimate for  $u$  in the growing polymer particle. In order to know the velocity profile, and thus the Pe at all positions in the particle, it would be necessary to solve the mass and energy balance equations. However, we can estimate the importance of the Pe, and therefore of convection in the solution of the balance equations, by using the convective velocity at the surface of the particle as an order of magnitude estimate of the velocity in the outer layers of the particle. This can be done by dividing the flow rate of fluid (gas or liquid) "drawn" toward a single particle due to the reaction by the surface area of the particle. In a slurry polymerization the monomer flow rate  $Q_m$  (volume/time) toward a given polymer particle is proportional to the observed rate of reaction

$$Q_m = \frac{R_{OB_i} \hat{m}_c}{\rho_m} \quad (7)$$

where the mass of catalyst per macroparticle of radius  $R_0$  is

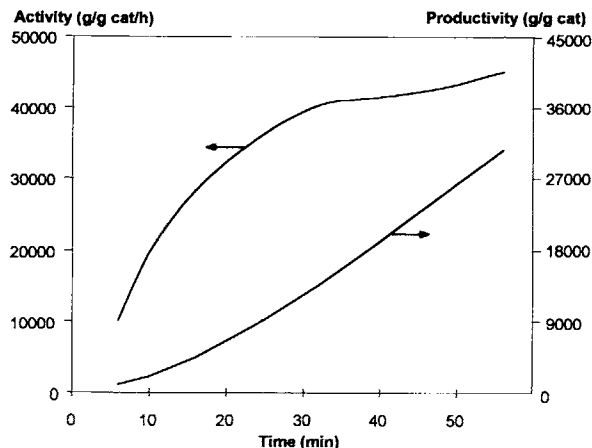
$$\hat{m}_c = \frac{4}{3} \pi R_0^3 (1 - \epsilon_0) \rho_c \quad (8)$$

and the surface area of the same particle is

$$\hat{S}_p = 4 \pi R_1^2 \quad (9)$$

The velocity of the monomer at the surface of the particle is then obtained by dividing the flow rate in eq. (7) by the surface area in eq. (9). An experimental slurry phase polymerization of ethylene is shown in Figure 2. For this system, the monomer density can be estimated at  $\rho_m = 0.38 \text{ g/cm}^3$ , the porosity of the catalyst particle at 0.4, the density of the catalyst (real)  $\rho_c = 2.8 \text{ g/cm}^3$ . It can be assumed that the diffusivity of ethylene in the pores near the surface of the polymer particle is on the order of  $5 \cdot 10^{-6} \text{ cm}^2/\text{s}$ , a value in the range suggested in Table III for bulk phase liquid slurry diffusivities. After approximately 10 min, the activity has already increased to approximately 20,000 g/g/h, with a productivity in the area of 2,000 g/g. Using these values, and the parameter values given immediately above, the Peclet number can be estimated at approximately Pe = 0.3 for catalyst particles that were initially 20  $\mu\text{m}$  in radius. While this figure is less than 1, it can certainly not be considered to show that convection is significantly less than diffusion in this case.

For a given batch of catalyst, particle sizes will cover a certain range. The Peclet number is thus

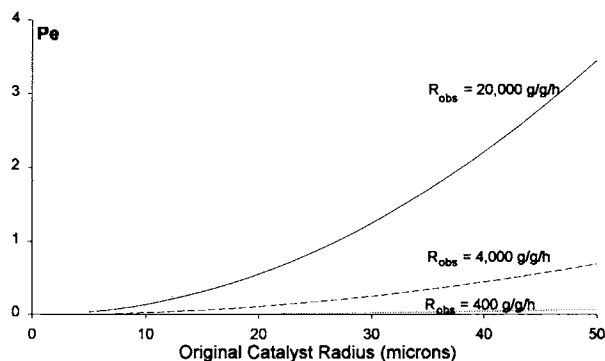


**Figure 2** Slurry phase polymerization of ethylene (10 bars ethylene, 80°C). Observed activity and productivity are indicated in grams of polymer per gram of catalyst (per hour). At approximately 10 min, the activity has attained almost 20,000 g/g/h for a productivity of approximately 2000 g/g, the latter value corresponding to a growth factor of just over 12.

calculated in Figure 3 for the slurry polymerization of ethylene as a function of the size of the original catalyst particle. Note that for the purposes of this example,  $Pe$  was calculated assuming that the polymer particle had grown to 12 times the size of the original catalyst particle. For comparison's sake we have also included low activity catalysts (with the same value of growth factor). It can clearly be seen that  $Pe$  is significantly less than unity for the very low activity system (400–4,000 g/g/h), but that for reasonable particle sizes and levels of activity,  $Pe$  is near or greater than one. However, it can clearly be seen for cases where the activity is on the order of experimentally realizable orders of magnitude, the  $Pe$  approaches or exceeds unity for reasonable particle sizes.

If convection were to play a role in monomer transport, this may well explain why Spitz et al.<sup>25</sup> needed to use diffusivities approaching those in the bulk phase, because convection was not included in that model. That the other authors in the upper half of Table I did not notice any problems with the diffusivity when modeling slurry polymerizations is not surprising because they were concerned with much lower levels of activity.

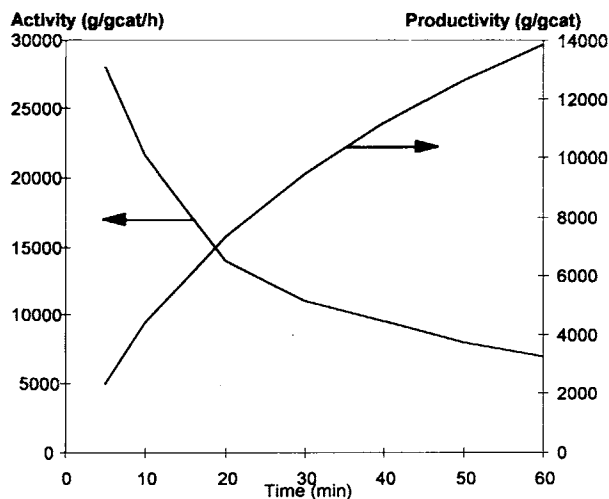
The situation is somewhat different for gas phase polymerizations. The results of similar calculations are shown in Figures 4 and 5 for the gas phase polymerization of ethylene in stirred bed reactors. Due to the increased diffusivity of the monomer in this case (taken to be the average value given by Floyd



**Figure 3** Peclet number at polymer particle surface as a function of unpolymerized catalyst particle radius (microns) for different observed activities in slurry phase polymerization of ethylene shown in Figure 2. Diffusivity =  $5 \cdot 10^{-6}$  cm<sup>2</sup>/s and particle growth factor equal to 12 (see range of values in Table III).

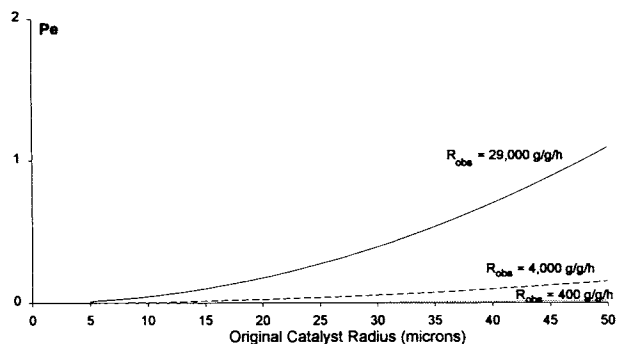
et al.<sup>8</sup>), the contribution of convection to the mass transfer process only becomes potentially important at activities higher than those considered in most of the modeling studies shown in Table I. For activities on the order of 29,000 g/g/h, the  $Pe$  is on the order of unity at the particle surface for reasonable catalyst particle sizes.

Note that the preceding analysis provides us with an upper limit on the value of the  $Pe$  because the convective velocity will drop toward the center of



**Figure 4** Gas phase polymerization of ethylene (10 bars ethylene, 85°C). Observed activity and productivity are indicated in grams of polymer per gram of catalyst (per hour). At approximately 10 min, the activity has attained almost 29,000 g/g/h for a productivity of approximately 2000 g/g, the latter value corresponding to a growth factor of just over 12. The reaction was carried out in a stirred bed reactor.





**Figure 5** Peclet number at polymer particle surface as a function of unpolymerized catalyst particle radius (microns) for different observed activities in gas phase polymerization of ethylene. Convective effects are significantly reduced with respect to slurry phase reactions. Diffusivity =  $5 \cdot 10^{-4}$  cm<sup>2</sup>/s and particle growth factor equal to 12. Monomer pressure 10 atm, and gas assumed to be ideal.

the macroparticle, and will also decrease as a function of time because the radius of the polymer particle increases rapidly at this stage of the reaction. However, to correctly model the high activity portion (i.e., the portion of the reaction where the activity is highest and the particle size at a minimum) of the growth of a polymer particle, it may be necessary to account for the "facilitation" of monomer diffusion due to convection. A complete model of particle growth and transport phenomena should include convection. Furthermore, it should be noted that while this discussion has centered only on homopolymerization reactions, copolymerization adds a second degree of complexity, especially when we are concerned with ethylene copolymers. McKenna and Schweich<sup>23</sup> have shown that convective currents in the growing polymer particles can lead to the build-up of the less reactive butene during the gas phase production of LLDPE. The accumulation and eventual condensation of heavier comonomers like butene and 1-hexene can lead to comonomer-rich particle cores, with different rates of reaction throughout the growing particles. As demonstrated by Hutchinson et al.,<sup>15</sup> this distribution of reaction rates can effect the morphological development of the polymer particles.

It should also be noted that the diffusivity values selected by Chiovetta and coworkers<sup>1-6</sup> (Table III) are significantly lower than those used in the other studies. This obviously has an impact on the importance of diffusion resistances in both particle break-up and the development of temperature peaks and concentration drops. The lower values may have been chosen in order to avoid the prediction of sig-

nificant particle overheating in the gas phase. This point will be discussed.

## HEAT TRANSFER CONSIDERATIONS

Again, referring to Table II, it can be seen that the most important heat transfer resistance is encountered at the level of the energy exchange between the growing polymer particle and the bulk phase in the reactor for gas phase polymerizations. However, it should not be forgotten that the activity levels considered in most of the studies presented in Table I, upon which the conclusions in Table II are based, used activities well under 10,000 g/g/h. If we refer to the work of Floyd et al.,<sup>8</sup> they state that for gas phase olefin polymerizations (reaction temperature = 70°C, bulk phase concentration = 1 mol/L): "for the most active catalysts in use today, catalyst particles below 20 microns would insure no intraparticle (macroparticle) temperature gradients (i.e. < 2 K)." Judging from the graphical solutions they present to the energy balance equations, one can estimate the value of "most active" at approximately 18,000–20,000 g/g/h. However, we have stated before that polymerizations much more active than this are commonly performed at the current time, and with particle diameters greater than 20 μm. Furthermore, McKenna and Schweich<sup>23</sup> have shown that the temperature rise in macroparticles during the gas phase copolymerization of ethylene and butene can be on the order of 15 K for observed catalyst activities of 30,000 g/g/h. Similarly, Ferrero and Chiovetta<sup>6</sup> have predicted internal temperature gradients on the order of 25 K at the start of polymerization during the gas phase production of polypropylene. It would thus be unwise to dismiss the possibility of temperature gradients at the interior of growing catalyst particles.

Coming back to the problem of heat transfer between the bulk phase in the reactor and the particle surface, it can be seen from boundary condition (2b) that this is controlled by the film-side convective heat transfer coefficient "*h*." Typically, values of *h* are estimated from Nusselt number correlations of the form

$$\text{Nu} = \frac{hd_p}{k_f} = A + B(\text{Re}^a \text{Pr}^b) \quad (10)$$

where  $d_p$  is the particle diameter; Re and Pr are the well-known Reynolds and Prandtl numbers, respectively; and *A*, *B*, *a*, and *b* are all empirically determined constants. Floyd et al.<sup>9</sup> discuss several of the

commonly available correlations for use in low Reynolds number flows. Briefly, these correlations show that the heat transfer coefficient depends on the particle radius, fluid properties, and the relative particle/bulk phase velocities used in the Re calculation,  $u_{rel}$ .

As an order of magnitude estimate of the importance of this coefficient, we can look at a steady-state energy balance around the polymer particle:

$$4\pi R_1^2 \cdot h \cdot (T_{surface} - T_{bulk}) = \frac{4}{3}\pi(1 - \epsilon_0)R_0^3 \cdot \rho_c R_{ob}(-\Delta H_p). \quad (11)$$

By rearranging eq. (11), we can estimate the temperature gradient  $\Delta T$  for a given observed rate, catalyst particle, and degree of advancement, or, conversely, determine the minimum heat transfer coefficient required to limit the temperature gradient to a fixed amount.

Consider again the early stages of the gas phase polymerization shown in Figure 4, where the observed activity is on the order of 29,000 g/g/h for a particle growth factor of approximately 12 ( $R_1 = 300 \mu\text{m}$ ). Using the parameters shown in Table IV, and the Ranz–Marshall Correlation<sup>28</sup>

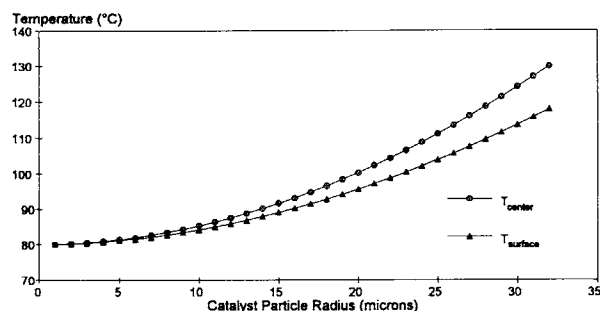
$$\text{Nu} = 2 + 0.6\text{Re}^{1/2}\text{Pr}^{1/3}$$

$$\text{with Re} = \frac{2R_1\rho_m u}{\mu_m}, \text{Pr} = \frac{\mu_m C_{p, \text{gas}}}{k_f} \quad (12)$$

we can calculate a heat transfer coefficient of  $h = 0.068 \text{ cal/cm}^2/\text{s/K}$  for a stirred bed reactor if we assume that the relative gas/particle velocity is on the order of 2 cm/s. These values lead to an estimate of a  $\Delta T = 30 \text{ K}$  temperature rise between the particle surface and the gas phase of the reactor. Let us consider further the temperature rise inside the polymer

**Table IV Parameters for Gas Phase Ethylene Example**

Property	Value (Units)	Source
$k_f$	$7.0 \cdot 10^{-5} \text{ cal}/(\text{cm s K})$	Floyd <sup>8</sup>
$\mu_{rel}$	2 cm/s	Floyd <sup>8</sup>
$\mu_m$	$1.2 \cdot 10^{-4} \text{ g}/(\text{cm s})$	Floyd <sup>8</sup>
$\rho_m$	$0.028 \text{ g}/\text{cm}^3$	Floyd <sup>8</sup>
$\epsilon$	0.4	Floyd <sup>8</sup>
$\Delta H_p$	25.7 kcal/mol	Floyd <sup>8</sup>
$C_{p, \text{gas}}$	0.423 cal/(g K)	Smith and van Ness <sup>32</sup>
$R_0$	15 $\mu\text{m}$	Estimate
$\rho_c$	2.8 g/cm <sup>3</sup>	Hutchinson et al. <sup>15</sup>



**Figure 6** Maximum temperature rise inside and outside a growing particle as a function of initial particle size. External gradients calculated using the Ranz–Marshall correlation.

particle. The model calculations of Spitz et al.,<sup>25</sup> shown in Figure 6 for intrinsic activities of only 12,000 g/g/h [using the Ranz–Marshall correlation and the solution to equation (2)], show that the maximum internal temperature rise for particles on the order of 30  $\mu\text{m}$  in diameter (catalyst particle) is over 10K. If we suppose that the internal temperature rise would be proportionally larger for the activities shown in Figure 4, i.e., nearly 30 K, then the combined temperature rise would surely lead to the meltdown of the particle core. If this is combined with the probability that the observed activity is even higher than shown on the graph in Figure 4 during the first minute or so of polymerization (it is very difficult to measure the first few moments of the reaction rate with sufficient precision, but all indications point to the possibility that it is higher than the activity reported at 5 min), then it can be supposed that the current models do not satisfactorily model the heat transfer that is actually taking place. It should also be noted that the Ranz–Marshall correlation used here and by the authors in Ray's group, provides the most favorable estimate of Nu of all of the correlations considered by Floyd et al.,<sup>9</sup> using the other correlations developed in the literature for fluid/particle beds (e.g. Nelson and Galloway<sup>29</sup>) would lead to even more disastrous predictions.

If we assume that the internal temperature rise in the particle is only slightly influenced by the transfer at the surface, then a Nu two to three times higher than that predicted with the Ranz–Marshall correlation would be needed to maintain an internal temperature under the melting point of 130°C for gas phase ethylene polymerization. Note that the melting temperature is 10–20° lower for ethylene- $\alpha$ -olefin copolymers, whereas the observed activities are the same order of magnitude, if not higher than those shown in Figure 4.

Because high activity, gas phase reactions are in practice possible under conditions where the models predict that they are not, it is necessary to look at where the models might break down. One of the weak points in the models is the use of empirical correlations for the heat transfer coefficient. It is most likely that these correlations were developed for particles of which the characteristic lengths were on the order of millimeters, or tenths of millimeters (e.g. Brian and Hales,<sup>30</sup>  $R_{\min} = 0.4$  mm), and not for the tens of microns that we encounter when polymerizing a Ziegler-type catalyst particle. Although the correlations tested by Floyd et al.<sup>9</sup> give similar results (order of magnitude) for particles greater than approximately 0.1 mm, we can ask ourselves about whether or not they can be readily applied in the early stages of polymerization on this type of catalyst particle.

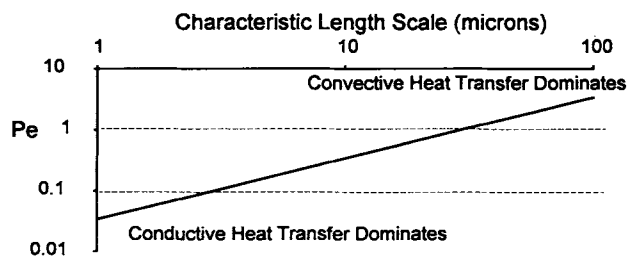
An order of magnitude analysis using the heat transfer Peclet number ( $Pe_H$ ):

$$Pe_H = \frac{L\rho u c_p}{k_f} = \frac{\text{convective heat transfer}}{\text{conductive heat transfer}} \quad (13)$$

where  $L$  is a characteristic dimension. If we use the values in Table IV, and a relative particle fluid velocity of 2 cm/s, it turns out that the  $Pe_H$  is on the order of 0.3 for characteristic lengths of 10  $\mu\text{m}$ . This means that conduction in the fluid around the particle is more important than convection at this length scale.

Extending this calculation to different lengths leads to the relationship illustrated in Figure 7. It is not until we get to length scales on the order of a 100  $\mu\text{m}$  that convective heat transfer takes the upper hand with respect to conduction. The situation is similar in fluidized beds where the relative velocities are on the order of tens of centimeters per second, except that convection becomes slightly more important more quickly. It should also be noted that the gas velocity right at the particle surface is lower than the relative particle-fluid velocity. Although convection rapidly becomes the most important means of evacuating the energy produced in a growing polymer particle, this rapid analysis suggests that conduction around the particle might play an important role in the very early stages.

Reflecting on the length scales involved, it can be seen that this conductive length scale is of the same size as the growing polymer particles at the beginning of the reaction, and in this event the method of heat transfer between the particle and its immediate surroundings is different from that



**Figure 7** Relationship between the Peclet number and the characteristic length scales for heat transfer in the gas phase polymerization of ethylene. Convection is not dominant until the length scale concerned is over 60–70  $\mu\text{m}$ .

encountered for larger particles. These smaller particles would very rapidly exchange their thermal energy with the molecules of gas in the surrounding fluid, thereby creating a sort of isothermal “boundary layer” around themselves. In practical terms this means that the surface/volume ratio of the growing particles at the onset of polymerization would be higher than the value of  $3/R_1$  that would be predicted from geometric arguments. If this hypothetical layer indeed existed, and if it were on the order of 10- $\mu\text{m}$  thick, then the effective heat transfer surface area of a particle with a radius of 20  $\mu\text{m}$  would be  $30^2/20^2 = 2.25$  times higher than if there were no layer at all. However, if this layer remained more or less the same size throughout the polymerization, once the particle grew to much over 100  $\mu\text{m}$  in diameter (a matter of a few minutes at most), the contribution of the “isothermal layer” to the relative heat transfer surface area would become negligible, and the classic chemical engineering correlations would be applicable. In conclusion, it would appear that heat transfer around particles on the order of  $< 100$   $\mu\text{m}$  in diameter, while occurring on a scale too large to be considered purely molecular, is best described by some intermediate regime, lying somewhere between measurable macroscale phenomena and molecular scale phenomena described by the kinetic theory of gases.

Although much work remains to be done to prove or disprove this concept of the effect of the proposed particle boundary layer on increasing the heat transfer surface area, it would certainly explain why highly active particles do not reach the melting point of the polymer when the simulations predict that they should. Additionally, the spectacular meltdowns seen from time to time in industrial applications can be more easily explained using this model of heat transfer. If we accept that

there is most likely an internal temperature rise of at the very least 5 or 10 K (see above) at moderate to high activities, then overheating in the external boundary layer would lead to melting of the polymer beginning in the center of the particle. Meltdown of the polymer at the particle core would almost immediately lead to a decrease in the observed reaction rate because the melted polymer would fill the pores and interstices of the particle, the hydraulic forces pushing the microparticles apart, and maintaining the void volume being severely reduced. It is even likely that this rate reduction could occur before meltdown because the softening point of the polymer would be reached and it would begin to fill the void spaces in the particle. This filling of the interstices would significantly increase the diffusion resistance in the particle (diffusion length scale increases, diffusivity decreases) and therefore lead to a decrease in the concentration of monomer at the active sites, and a decrease in the overall rate of polymerization. However, if the presence of an external boundary layer controls the heat transfer capacity of a given particle, then physical reduction of this boundary layer, for instance by prolonged contact with an inert surface (reactor wall) or another particle would remove a portion of the "enhancement" offered by the boundary, and the temperature in the region of the contact would increase. This would mean that the surface temperature of the particle could increase, perhaps even faster than the temperature in the center, and the particle would stick to the reactor wall, or to another particle. Once the fusion process has begun, the reduced heat transfer surface area and increased length scales for energy evacuation would lead to the formation of hot spots in the reactor.

It is also evident from eqs. (1)–(5) that the heat and mass transfer problems are coupled. Therefore increased mass transfer resistances would lead to lower observed reaction rates, and therefore lower heat generation rates. Ferrero and Chiovetta<sup>3–6</sup> use the correlation for heat transfer developed by Kunii and Levenspiel<sup>31</sup> which predicts  $Nu$  even lower than that predicted by the Ranz–Marshall correlation.<sup>28</sup> However, the diffusivities that they use in their simulations (see Table III) are much lower than those used in the other studies. Their simulations predict much greater diffusion resistances at shorter times than is the case with the simulations of Floyd et al.<sup>8,10</sup> It is therefore not surprising that they do not encounter serious overheating in the macroparticle at comparable intrinsic activity levels. This shows that the choice of diffusivities also has an impact

on the heat transfer behavior of the polymerizations, and that thought should be given to choosing the correct values.

## MORPHOLOGICAL, KINETIC, AND START-UP CONSIDERATIONS

The MGM in its basic form explains the development of particle morphology once the fragmentation process has begun. The growth of the polymer layers around the microparticles that are "free" to expand independently of their neighbors helps to explain the replication of particle shape and relative size distributions between the original catalyst charge and the final polymer product, as well as explaining the conservation of the void fraction found in the original catalyst particle.

Where it seems to have more difficulty in explaining the development of particle morphology is right at the beginning of the reaction. Chiovetta et al.<sup>1–6</sup> modeled this portion of the reaction using an idealized MGM-type model as outlined above. They considered that the effective macroparticle diffusivity was a factor of 100–200 higher in the fragmented portion of the catalyst than in the unfragmented core. Fragmentation was said to be complete when a prespecified polymer layer thickness was obtained. Although this model is qualitatively correct, there is no real way of evaluating this critical thickness for a given catalyst system, and it is sure to vary from catalyst type to catalyst type because different methods of preparation will impart different physical strength to the catalyst matrix. They did show, as did Floyd et al.<sup>9</sup> that the rapidity with which the fragmentation process occurs has a significant impact on the speed and size of the temperature gradient at the interior of the macroparticle. Ferrero et al.<sup>26</sup> have shown that fragmentation on magnesium-supported catalysts is complete at very low productivities (less than 60 g of polymer per gram of catalyst), but there does not appear to be any way of identifying just when this critical step is complete, nor how it proceeds.

Floyd et al.,<sup>11</sup> McKenna and Schweich,<sup>23</sup> and Spitz et al.<sup>25</sup> used a similar style of empirical formulation to fix the time at which the maximum intrinsic activity level of a catalyst is attained. This was, in part, to account for the fragmentation process, and assumed that the catalyst became "activated" once it was completely fragmented. Although the results of previous studies (e.g. Webb et al.<sup>19,20</sup>) have shown that lack of fragmentation can lead to severely reduced rates, or even reaction extinction,

there are other phenomena that are included in this empirical "activation" phase, notably the chemical activation of the active sites themselves caused by the temperature in the reactor, the presence of the monomer and comonomer, and the diffusion of the rather large molecules of cocatalyst through the particle toward the active sites.

Hutchinson et al.<sup>15</sup> attempted to demonstrate the significance of this last point by examining the impact of a nonuniform distribution of active sites inside a macroparticle by using an arbitrary empirical distribution function. It turns out that nonuniformities can have a significant effect, especially on the development of void volume, and therefore on the diffusivity of the monomer(s) in the growing particles. This effect was also demonstrated experimentally by Nooijen<sup>17</sup> who showed that the development of polymerization activity, and the morphology of the particles may depend on the method of preparation of the catalyst for reaction start-up (with and without prepolymerization/preheating, etc.). It is postulated in this work that the diffusion of co-catalyst molecules toward the active sites is a very important factor in how fast the reaction begins, and this in turn has a strong impact on the development of the void volume (bulk density) of the final particles. To the best of our knowledge, none of the currently available models of particle growth, and mass and energy transport take these phenomena into account in a less than completely empirical manner.

Given the extreme sensitivity of the morphology and material nature of Ziegler-type catalysts to preparation conditions (it is common to hear of wide variations in catalyst properties from batch to batch where the same preparation steps were used to make catalysts from the same batches of raw materials), it is not unreasonable to continue to use a sort of "informed guess" and empirical correlations to model the activation of the catalyst active sites. However, given the importance of the initial phase of the reaction, it is necessary to incorporate some physical effects (diffusivity of comonomers, temperature rise, diffusivity of cocatalysts, mass transfer resistances in unfragmented portions of the catalyst, etc.) into the modeling of reaction start-up.

## CONCLUSIONS

We have seen that the models originally developed to describe the phenomena underlying heat and mass transfer, and particle growth during the polymerization of olefins on Ziegler-type catalysts were able

to qualitatively predict the areas of critical interest to the different types of problems, i.e., macroparticle mass transfer during slurry polymerization, and external heat transfer during gas phase polymerization. However, these models predict that experimentally observable polymerizations are impossible. Solving the model equations using the original transport equations and parameter values leads to the conclusion that catalyst particles with activities on the order of 25,000 g/g/h would lead to polymer particles that melt in the gas phase, or lead to the creation of large concentration gradients that would prevent the polymerization from reaching their intrinsic rates in slurry phase reactions.

An analysis of the dimensionless transport rates using mass and heat transfer Peclet numbers has revealed that convection might play a more important role in macroparticle mass transfer during slurry polymerization than was originally suspected, especially during the early stages of the polymerization so critical to the development of particle morphology. Convective currents established inside the macroparticle during the first few moments of polymerization could facilitate the transport of monomer to the active sites in the catalyst.

In a similar vein, but in the opposite sense, an analysis of the heat transfer Peclet number suggests that conduction in the gas phase around the nascent polymer particles might contribute to the evacuation of the heat of polymerization. While the underlying mechanisms are still not clear, it is evident that heat transfer cannot be described using classical chemical engineering correlations such as the Ranz-Marshall correlation to estimate the particle Nusselt number.

In conclusion it would appear that the original MGM description of particle morphology is still useful in the modeling of highly active olefin polymerizations if certain modifications are made. First of all, an in-depth look must be taken at how heat transfer occurs around the growing particles. Classical chemical engineering correlations cannot adequately estimate the real value of the heat transfer coefficient, and a new method must be found. Also, it is necessary to include convection in the mass transport model equations in order to explain how monomer can reach the active sites during the slurry phase polymerization of olefins at activities over a given level (around 10,000–15,000 g/g/h for ethylene). This would be a good place to point out that diffusional barriers should more correctly be reported in terms of molar, rather than mass consumption rates. For example an activity level of 11,200 g/g/h of ethylene in a slurry phase corresponds to a molar polymerization rate of 400 mol/

g/h. Any diffusional barriers etc. (given that the diffusivity of propylene is similar to that of ethylene in the slurry phase process) would then be associated with a polymerization rate of 400 mol of propylene per gram per hour. In conventional units this corresponds to 16,800 g/g/h. Therefore it is preferable to compare the two systems on the basis of molar and not mass rates. If this is done, it would appear that there is no basis for distinguishing between the behavior of the two systems (other than the slightly different physical properties) in terms of modeling transport rates and particle growth.

## REFERENCES

1. M. G. Chiovetta, *Heat and Mass Transfer during the Polymerization of Alpha-Olefins from the Gas Phase*, Ph.D. Thesis, University of Massachusetts at Amherst, 1983.
2. R. L. Laurence and M. G. Chiovetta, in *Polymer Reaction Engineering: Influence of Reaction Engineering on Polymer Properties*, K. H. Reichert and W. Geisler, Eds., Hanser Publishers, Munich, 1983.
3. M. A. Ferrero and M. G. Chiovetta, *Polym. Eng. Sci.*, **27**(19), 1436 (1987).
4. M. A. Ferrero and M. G. Chiovetta, *Polym. Eng. Sci.*, **27**(19), 1447 (1987).
5. M. A. Ferrero and M. G. Chiovetta, *Polym. Eng. Sci.*, **31**(12), 886 (1991).
6. M. A. Ferrero and M. G. Chiovetta, *Polym. Eng. Sci.*, **31**(12), 904 (1991).
7. S. Floyd, *Heat and Mass Transfer Resistances in Polymerization of Olefins Over Solid Catalysts*, Ph.D. Thesis, University of Wisconsin at Madison, 1986.
8. S. Floyd, K. Y. Choi, T. W. Taylor, and W. H. Ray, *J. Appl. Polym. Sci.*, **32**, 2935 (1986).
9. S. Floyd, K. Y. Choi, T. W. Taylor, and W. H. Ray, *J. Appl. Polym. Sci.*, **31**, 2231 (1986).
10. S. Floyd, R. A. Hutchinson, and W. H. Ray, *J. Appl. Polym. Sci.*, **32**, 5451 (1986).
11. S. Floyd, T. Heiskanen, T. W. Taylor, G. E. Mann, and W. H. Ray, *J. Appl. Polym. Sci.*, **33**, 1021 (1987).
12. R. A. Hutchinson and W. H. Ray, *J. Appl. Polym. Sci.*, **34**, 657 (1987).
13. R. A. Hutchinson and W. H. Ray, *J. Appl. Polym. Sci.*, **41**, 51 (1990).
14. R. A. Hutchinson and W. H. Ray, *J. Appl. Polym. Sci.*, **43**, 1271 (1991).
15. R. A. Hutchinson, C. M. Chen, and W. H. Ray, *J. Appl. Polym. Sci.*, **44**, 1389 (1992).
16. K. Y. Choi and W. H. Ray, *Chem. Eng. Sci.*, **40**(12), 2261 (1985).
17. G. A. H. Nooijen, *Eur. Polym. J.*, **30**(1), 11 (1994).
18. T. Xie, K. B. McAuley, J. C. C. Hsu, and D. W. Bacon, *Ind. Eng. Chem. Res.*, **33**, 449 (1994).
19. S. W. Webb, W. C. Conner, and R. L., *Macromolecules*, **22**, 2885 (1989).
20. S. W. Webb, E. L. Weist, M. G. Chiovetta, R. L. Laurence, and W. C. Conner, *Can. J. Chem. Eng.*, **69**, 665 (1991).
21. M. A. Ferrero, E. Koffi, R. Sommer, and W. C. Conner, *J. Polym. Sci. A, Polym. Chem.*, **30**, 2131 (1992).
22. T. W. Taylor, K. Y. Choi, H. Yuan, and W. H. Ray, in *Transition Metal Catalyzed Polymerizations, MMI Symposium Series 11*, Harwood Academic Publishers, New York, 1981.
23. T. F. McKenna and D. Schweich, in *Fourth Annual Workshop on Polymer Reaction Engineering*, K. H. Reichert and H. O. Moritz, Eds., VCH, Berlin, 1992, pp. 169-178.
24. R. Spitz, J. Dupuy, and J. Terle, Paper presented at the Fourth Annual French Conference on Process Engineering, Grenoble, France, 1993.
25. R. Spitz, J. Dupuy, J. P. Broyer, and T. F. McKenna, Paper presented at the International Symposium on Synthetic, Structural and Industrial Aspects of Stereospecific Polymerization, Milan, Italy, 1994.
26. M. A. Ferrero, R. Sommer, P. Spanne, K. W. Jones, and W. C. Conner, *J. Polym. Sci. A, Polym. Chem.*, **31**, 2507 (1993).
27. H. F. Herrmann and L. L. Böhm, *Polym. Comm.*, **32**(2), 58 (1991).
28. W. E. Ranz and W. R. Marshall, *Chem. Eng. Prog.*, **48**, 141 (1952).
29. P. A. Nelson and T. R. Galloway, *Chem. Eng. Sci.*, **30**, 1 (1975).
30. P. L. T. Brian and H. B. Hales, *A.I.Ch.E. J.*, **15**(3), 419 (1968).
31. D. Kunii and O. Levenspiel, *Fluidization Engineering*, Wiley, New York, 1969.
32. J. M. Smith and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 4th ed., McGraw-Hill, Toronto, 1987.

Received September 30, 1994

Accepted February 8, 1995