

A Method for Determining Diffusion Resistance in Polymer Particles During Polymerization

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SYNOPSIS

Polyolefins are usually made in the form of particles, with the catalyst distributed inside these particles and monomers in gas or liquid form on the outside. Mass transfer restriction of monomers and other molecules into the polymer particles could be of significance. A method of studying this restriction is shown in this article. This method is based on a novel two-phase (pore phase and polymer phase) transport theory developed here, with a dimensionless number for the competitiveness of pore vs. polymer phase transport as the key parameter. Data of mass transfer from polymer particle drying experiments are, by means of this dimensionless transport parameter, generalized so that diffusion resistance during the preceding polymerization of these particles can be calculated. It is believed that this has not been attempted before. This method is used on an example of ethylene diffusion resistance when making polyethylene (PE). The calculated result is that diffusion resistance is significant for slurry polymerization in this case. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Diffusional mass transfer in as-polymerized polyolefin particles is an important process. The main part of industrial production of polyolefins is based on small solid catalyst fragments embedded in polymer particles.

Between the surface area of a catalyst fragment and its surroundings diffusional mass transfer takes place of

- Monomers to the fragment to be polymerized
- Liquid cocatalyst and other adjuvants to react with the fragment surface
- Catalyst poisons to the fragment surface, and, in some cases, removal of poisons formed at the fragment surface.

Mass transfer is also important for removal of volatiles or extractables and, in some cases, for the later distribution of additives in the polymer. The polymer particles are porous, and mass transfer takes place in the polymer phase and in the pore phase (liquid

or gas), both in series in these two phases as well as in parallel (Fig. 1).

The significance of monomer diffusion resistance has been evaluated earlier by polymerization experiments in view of its claimed effects on kinetics¹ and on polymer properties.² Results of calculations of monomer transport are also seen^{3,4}; however, these calculations are based on examples of effective diffusion coefficients and not on actual measured values.

THEORY

General Two-Phase Transport

Diffusion transport in porous systems consisting of two phases, out of which one phase is unable to transport any migrant at all, has been well studied. Theories have been developed predicting macroscopic transport properties from the pore structure and transport properties of the conducting phase. Tools for correlating macroscopic transport properties also exist.⁵ However, to the author's knowledge, no theory has been developed for systems in which both phases can conduct the migrant. So some theoretical development will be made in this section.

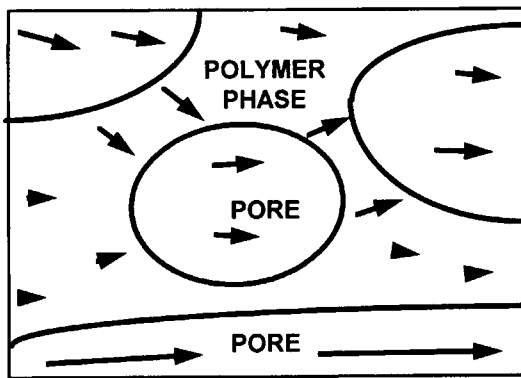


Figure 1 Principle of two-phase parallel and series transport.

(General diffusion transport theory can be found in Satterfield.⁵)

Consider a migrant in a structure consisting of a polymer phase and pore phase. The transport property of the (pure) polymer phase is given by the solids diffusion coefficient D_S . The transport property of the (pure) pore phase (gas or liquid), as long as convection is negligible (Fick's law applies), is determined by the ordinary diffusion coefficient D'_P . However, instead of D'_P , here it is more practical to use what will be called the pore diffusion coefficient D_P , defined by

$$D_P = D'_P S \quad (1)$$

where S is the ratio between the equilibrium concentration of monomer in pore phase and in polymer phase. If the pore phase is an ideal gas, then

$$S = \frac{M}{H_S RT} \quad (2)$$

If the pore phase is a liquid, then instead (see Nomenclature)

$$S = \frac{H_L}{H_S} \quad (3)$$

Since D_P and D_S now both are based on migrant gradients in the polymer phase, the ratio

$$\Theta_{PS} = \frac{D_P}{D_S} \quad (4)$$

is a number (dimensionless) that indicates the competitiveness of pore versus polymer phase transport for a given polymer/pore structure. Θ_{PS} will be called the transport parameter.

Drying Process

Consider a polymer particle with equilibrated migrant initially. Then, from time zero, the partial pressure of the migrant externally to the particle is reduced in one step to a new lower value. The migrant then starts diffusing out of the particle.

A relative migrant residue in the polymer particle is defined as

$$E = \frac{\text{Migrant residue} - \text{new migrant equilibrium residue}}{\text{Initial migrant residue} - \text{new migrant equilibrium residue}}$$

By dimensional analysis,⁶ the relative migrant residue is given by

$$E = f(D_S t, \Theta_{PS}) \quad (5)$$

or (6)

$$E = g(D_P t, \Theta_{PS})$$

By ordinary chemical engineering principles, Eqs. (5) and (6) are valid for all migrants, temperatures, and pressures as long as

1. Polymer particle morphology is constant.
2. Outside particle partial pressure of monomer is constant (or zero as a special case).
3. Partial pressure of migrant is much less than total pressure. (Else convection term in transport equation is no longer negligible and Fick's law no longer applies.⁶)
4. Amount of monomer in pores is negligible compared to amount of monomer in polymer phase.
5. Equilibrium migrant content of migrant in polymer is proportional to migrant partial pressure.

These conditions can be achieved (this is discussed further in the section titled "Discussion").

The relative migrant residue E of Eq. (5) can be approximated by the following series:

$$E = \sum_{i=1}^n E_i = \sum_{i=1}^n (\alpha_i e^{-K_{Si} D_S t}) \quad (7)$$

where α_i and K_{Si} are functions of Θ_{PS} . These n elements can be regarded as a pure mathematical series approximation or as a representation of a corresponding physical picture. The physical picture is

that element i consists of a total of a number of very small regions within the polymer particles. What these regions have in common is the same drying rate: They all desorb exponentially with a drying rate time constant $1/(K_{Si}D_S)$. The exponential desorption rate is what one gets mathematically when the desorption rate out through the remaining polymer layer is proportional to the concentration in the region that is being dried. Element i further contained a fraction of α_i of the total residue initially.

Similarly, Eq. (6) can be approximated by

$$E = \sum_{j=1}^m E_j = \sum_{j=1}^m (\alpha_j e^{-K_{Pj}D_P t}) \quad (8)$$

The drying rate per unit volume of polymer is given by

$$q_{\text{transp}} = -H_S \Delta p_0 \frac{dE}{dt} \quad (9)$$

where Δp_0 is the difference between actual initial partial pressure and the new external partial pressure. Combining Eqs. (7) and (9) gives

$$q_{\text{transp}} = D_S H_S \sum_{i=1}^n (\alpha_i K_{Si} \Delta p_i) \quad (10)$$

where

$$\Delta p_i = \Delta p_0 e^{-K_{Si}D_S t} \quad (11)$$

where Δp_i is the difference between the partial pressure of the i th element and the external pressure. Similarly, Eqs. (8) and (9) give

$$q_{\text{transp}} = D_P H_S \sum_{j=1}^m (\alpha_j K_{Pj} \Delta p_j) \quad (12)$$

Polymerization Process

Assuming that the catalyst is distributed among the elements of the polymer particles proportional to the amount of monomer in the elements at equilibrium, and the polymerization rate is proportional to the partial pressure in the elements, this rate is

$$\begin{aligned} q_{\text{pol}} &= k \sum_{i=1}^n [\alpha_i (p_{\text{ext}} - \Delta p_i)] q_{\text{pol}} \\ &= k \sum_{j=1}^m [\alpha_j (p_{\text{ext}} - \Delta p_j)] \quad (13) \end{aligned}$$

This polymerization rate must equal the transport rate of monomer from external to the particle, for each element.

The transport rate equation given in Eqs. (10) and (12) can be applied also in this case, with appropriate values of constants. A sign change must be made since now transport into and not out of the particle should be considered positive.

Combining the parts concerning element i in Eqs. (10) and (13) gives a means of calculating the effectiveness factor η for element i :

$$1 - \eta_i = \frac{\Delta p_i}{p_{\text{ext}}} = \frac{k}{D_S H_S K_{Si} + k} \quad (14)$$

and the total effectiveness factor η by

$$\eta = \sum_{i=1}^n (\alpha_i \eta_i) \quad (15)$$

The value of the polymerization rate constant k based on monomer partial pressure in the elements of polymer is not known. However, the polymerization rate constant k_{ext} based on external partial pressure of monomer can be directly measured. The relationship between k and k_{ext} is

$$\eta = \frac{k_{\text{ext}}}{k} \quad (16)$$

If $n = 1$, then Eqs. (14), (15), and (16) can be solved easily:

$$\eta = \frac{D_S H_S K_S - k_{\text{ext}}}{D_S H_S K_S} \quad (17)$$

Similarly,

$$1 - \eta_j = \frac{k}{D_P H_S K_{Pj} + k} \quad (18)$$

$$\eta = \sum_{j=1}^m (\alpha_j \eta_j) \quad (19)$$

If $m = 1$, then

$$\eta = \frac{D_S H_S K_P - k_{\text{ext}}}{D_P H_S K_P} \quad (20)$$

Table I Properties of PE Fluff

Particle size, weight median	1.0 mm
Polymer slab density	0.936 gm ³ cm ³
Specific surface, BET	0.43 m ² /g
Pore volume, Hg penetration ($r < 12 \mu\text{m}$) adjusted for polymer compressibility	0.22 cm ³ /g

APPLICATION

Drying Calculations

A master of science thesis by H. Bjørgum⁷ gives drying curves for removing hexene and octene monomers that are dissolved in the amorphous regions of a polyethylene (PE) fluff. The properties of this PE fluff are shown in Table I. The fluff had been prepared by the industrially important CrO_x/SiO₂ catalyst system.

Drying curves obtained were as shown in Figure 2. In the preceding section titled "Drying Process" was given a list of conditions to be fulfilled for applicability of Eqs. (5) and (6). For the conditions of drying given by Table I and Figure 2, it can be calculated that conditions 2, 3, and 4 were satisfied. Condition 1 must also be satisfied since these drying experiments were performed more than 100°C below the melting point of the rather crystalline polymer. Condition 5 is also reasonably satisfied, as can be seen from similar system.⁸

The solubility coefficient H_S of monomer is shown in Figure 3. The diffusion coefficient of monomer in PE is shown in Figure 4(a). The pore diffusion parameter D_P is shown in Figure 4(b). All three parameters and also later physical data are based on

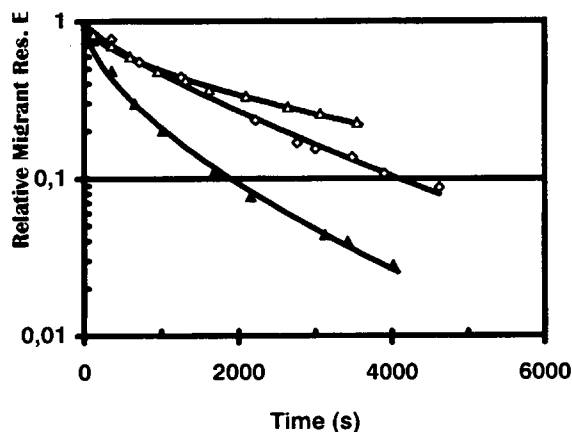


Figure 2 Drying curves: Polymer particles equilibrated with monomer, then from time zero monomer-free nitrogen around the fluff particles at a total pressure of 1 bar. Δ Hexene 3°C, \blacktriangle Hexene 21°C, \diamond Octene 21°C.

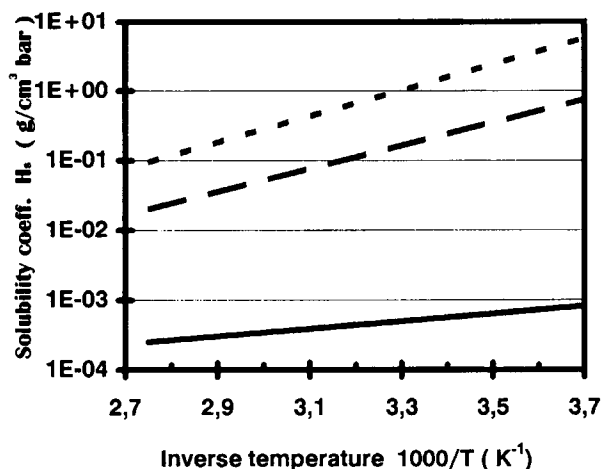


Figure 3 Solubility coefficient of monomer in PE. — Ethylene, — — hexene, octene.

examination of literature data,^{8,9,10,11,12} which are taken to be relevant for the monomers and PE used. Most lines are extrapolated to higher temperatures

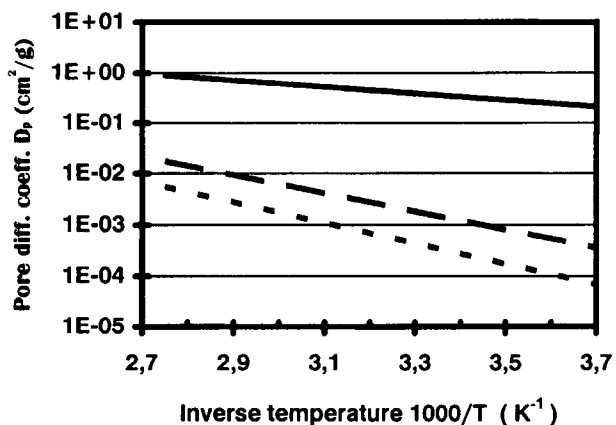
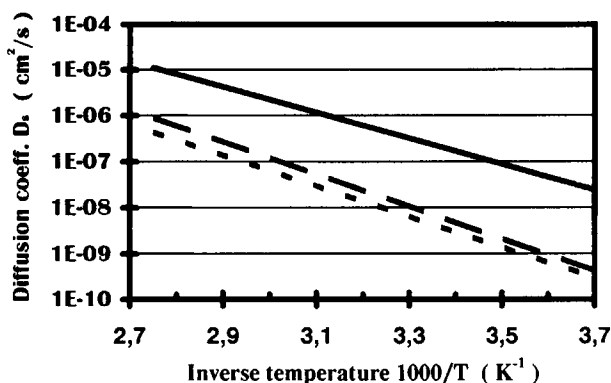


Figure 4 (a) Diffusion coefficient for monomer in PE phase. — Ethylene, — — hexene, octene; (b) pore diffusion coefficient for monomer in liquid butane (based on PE phase concentration). — Ethylene, — — hexene, octene.

than the experimental range. The data of Figure 2 and 4 have been used to compute the drying curves of Figure 5. Figure 5(a) is based on the dimensionless drying curve for polymer phase transport [Eq. (5)] and Figure 5(b) on the dimensionless drying curve for pore transport [Eq. (6)].

As can be seen, from neither Figure 5(a) nor 5(b) can a single general drying curve be obtained. The lower the value of Θ_{PS} is, the higher the curve in Figure 5(a) is, and the lower the curve in Figure 5(b) is. Hexene is more prone to polymer phase resistance than is octene. From Figure 5 it is seen that, with rather good approximation to the experimental curve, n and m can be taken as 1. The constants of Eqs. (7) and (8) are as shown in Table II.

Polymerization Calculations

As a basis for further calculation, additional data are given in Table III. The values for liquid butane

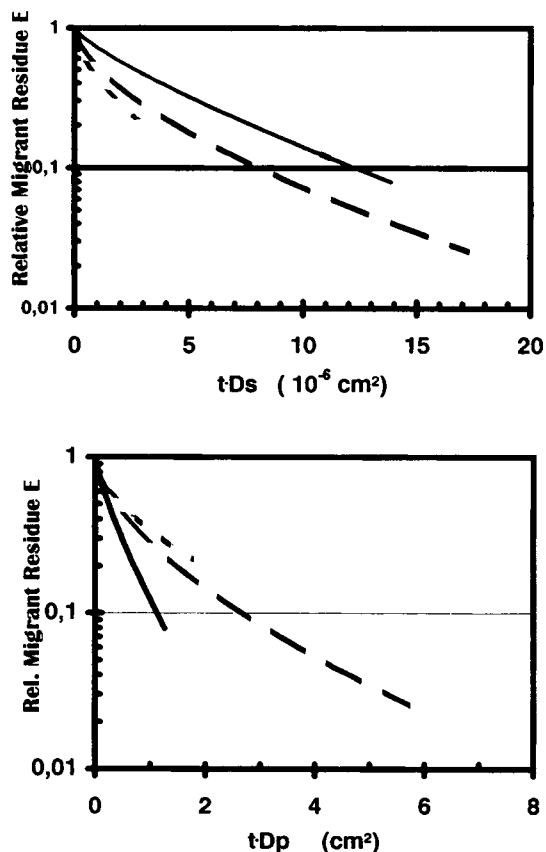


Figure 5 (a) Drying curves from Figure 1 transformed to form of Eq. (5). ----- Hexene 3°C, --- hexene 21°C, — octene 21°C; (b) drying curves from Figure 1 transformed to form of Eq. (6). ----- Hexene 3°C, --- hexene 21°C, — octene 21°C.

Table II Values of Constants of Eqs. (7) and (8) for $\Theta_{PS} = 90,000$ (Octene 21°C)

Constant	Dimension	Value
K_S	$\frac{1}{\text{cm}^2}$	$0.21 \cdot 10^6$
K_P	$\frac{1}{\text{cm}^2}$	2.1

are, as earlier values, based on literature data. The polymerization was actually performed in slurry. However, similar catalysts also polymerize in gas phase with a somewhat lower rate constant k_{ext} , and therefore a value of k_{ext} was introduced also for gas phase polymerization. The values for liquid butane are, as earlier data, based on literature data. D_P for slurry phase polymerization is calculated from Eqs. (1) and (3), with $D'_P = D_L$. Transport parameters Θ_{PS} for ethylene were calculated from Eq. (4), with basis in Figure 4.

Unfortunately, the curves of Figure 5 do not cover the range of transport parameter values for ethylene under polymerizing conditions. However, for both gas phase and slurry polymerization of ethylene, the following relationships (see Table III) exist:

$$K_S < 0.21 \cdot 10^6 \frac{1}{\text{cm}^2}$$

$$K_P > 2.1 \frac{1}{\text{cm}^2}$$

Introducing these into Eqs. (17) and (20) gives the results shown in Table IV. The results give efficiency factors lower than 1, indicating significant mass transfer resistance. Unfortunately, a very broad range of efficiency factors are satisfactory.

DISCUSSION

The idea of using drying data to achieve information about transport caused by chemical reaction is new, as well as the development of a unification theory for drying and gas phase polymerization and the theory that was developed for two-phase transport. The main uncertainties in the calculated values of Table IV are as follows:

1. The distribution of catalyst in the polymer particle may not be even. It is often assumed that the catalyst concentration in a given

Table III Polymerization Data

Parameter	Symbol	Dimension	Value
Polymerization rate constant (final), slurry phase	k_{ext}	$\frac{g}{cm^3 s bar}$	$5 \cdot 10^{-5}$
Polymerization rate constant (final), gas phase	k_{ext}	$\frac{g}{cm^3 s bar}$	$2 \cdot 10^{-5}$
Polymerization temperature	T	K	363
Diffusion coefficient of ethylene in liquid butane at 90°C	D_L	$\frac{cm^2}{s}$	$2.1 \cdot 10^{-4}$
Solubility coefficient of ethylene in butane	H_L	$\frac{g}{cm^3 bar}$	$2.5 \cdot 10^{-3}$
Pore phase diffusion coefficient based on liquid isobutane, 90°C (slurry phase polymerization)	D_P	$\frac{cm^2}{g}$	$2.1 \cdot 10^{-3}$
Transport parameter at 90°C for ethylene, with total pressure 20 bar (N ₂) in pores (gas phase polymerization)	Θ_{PS}	—	3500
Transport parameter at 90°C for ethylene with liquid butane in pores (slurry phase polymerization)	Θ_{PS}	—	190

element of polymer is inversely proportional to the yield of polymer in this element. The least accessible parts inside the polymer particle would have the highest catalyst concentration. On the other hand, Conner¹³ has shown that for some catalysts, the catalyst concentration is higher near the outer surface of the polymer particle.

2. The morphology of the polymer particles at polymerizing conditions could be different from the morphology after removing the polymer particles from the polymerization reactor.
3. The real diffusion coefficient of ethylene could be different from the value predicted at polymerizing conditions.

It is believed that the main uncertainty in this case is the distribution of catalyst.

The calculations done here do not include an additional potential mass transport limitation in the immediate vicinity of each submicroscopic catalyst fragment. In addition, the efficiency factor range calculation done here is relevant only for the end of the polymerization. The efficiency factor earlier during polymerization is probably different, due to other transport properties of the particles as well as

a different polymerization rate constant. However, the method might take into account different catalyst concentrations in the elements according to the element yield, if drying experiments are performed after various polymerization times.

The result that diffusion resistance can be important supports views based on computer modeling.^{3,4} Generally, however, experimenters seem to consider diffusion resistance not important,² as also can be seen from the widespread use of using kinetic equations on active site reactions for propagation and chain transfer with the (usually unmentioned) assumption of negligible mass transfer restriction. However, the catalytic systems studied differ widely and might behave differently.

CONCLUSION

A novel theory for the calculation of general migrant (monomer, cocatalyst, donor, poisons, solvents) mass transfer into or out of the polymer phase has been developed. It has been shown that the mass transfer depends on the dimensionless transport parameter Θ_{PS} developed here, which gives the competitiveness of pore phase versus polymer phase

Table IV Efficiency Factor η

	Minimum Value [Eq. (19)] (Exclusively Pore Phase Diffusion Control)	Maximum Value [Eq. (16)] (Exclusively Polymer Phase Diffusion Control)
Gas phase polymerization	0.17	0.97
Slurry phase polymerization	Zero	0.91

transport. For a specific polymer powder, a general mass transfer curve exists for each value of Θ_{PS} .

From drying data for a polyethylene powder, it has been shown that the efficiency factor of ethylene during the final stage of slurry polymerization of this powder can not be higher than 0.91. A very important assumption for this result is that the catalyst concentration through a polymer particle is either constant or is highest at the center of the particle.

<i>L</i>	Liquid
<i>P</i>	Pore
<i>S</i>	Solid (polymer phase)
ext	Externally particle
pol	Polymerization
transp	Transport

NOMENCLATURE

C (g/cm ³)	Concentration in polymer
D (cm ² /s)	Diffusion coefficient
E	Migrant residue above equilibrium value, relative to initial value above equilibrium value
H (g/cm ³ bar)	Solubility coefficient of gas
K (1/cm ²)	Transport rate constant
k (g/cm ³ s bar)	Polymerization rate constant
M (g/mol)	Molecular weight of migrant
p (bar)	Migrant partial pressure
q (g/cm ³ s)	Drying rate or polymerization rate per unit volume of particle
R (cm ³ bar/mol)	Gas constant
S	Equilibrium concentration of monomer in pore medium versus polymer phase
T (K)	Temperature
t (s)	Time
<i>Greek letters</i>	
α	Relative amount of migrant
η	Efficiency factor
Θ_{PS}	Transport parameter
<i>Subscripts</i>	
G	Gas
0	Initial value

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