Kinetics of Mass Transfer in the Melt Polycondensation of Poly(Ethylene Terephthalate)

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ABSTRACT

For a four-parameter reaction-mass transport model of melt polycondensation, the constants of polycondensation, thermolysis, and diffusion were determined by means of experiments in thin-layer polycondensation. Based on these constants, the convectional mass transport and efficient melt thickness in polycondensation systems under conditions of compelled mixing can be estimated. However, for stirred polycondensation systems a reaction-mass transfer model proves more suitable. The constants of polycondensation and thermolysis obtained by the diffusion model can be transferred to the reaction-mass transfer model. Thus, only the mass transfer coefficient has to be determined.

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1. INTRODUCTION

The macroscopic rate of polycondensation reactions depends on the reactivity of the reactants as well as on the mass transfer of the components. Whereas the reaction mechanisms of polycondensation and thermolysis in poly(alkylene terephthalate) melts have been investigated in detail (see, e.g., Ref. 1 and references therein), the possible mass transfer mechanisms, their dependence on the process variables, and their effect on the overall rate have scarcely been discussed. Obviously, this is mainly due to the interaction between mass transfer and chemical reactions, and particularly to the impossibility of considering these processes separately in experimental investigations. Because separate consideration of mass transfer in investigations of melt polycondensation reactions is impossible, experiments have to be carried out with model systems that take into account the transport phenomena.

In a series of communications we presented the results of investigations of mass transport by diffusion and convection in melt polycondensation. Based on a four-parameter model that accounted for polycondensation, thermolysis, diffusion, and convection as essential individual processes of polycondensation in polyester melts, these processes were described quantitatively in thin layers of the melt. We considered nonstirred [2] as well as stirred systems [3]. The determination of the model parameters requires investigation of the polycondensation reaction independent of time and location (different melt layer thickness) of the reaction. In a stirred reactor with an anchor agitator or mixer, the definitions of the local coordinates and the concentration gradient assumptions along these coordinates are necessarily arbitrary. However, the results presented in Ref. 3 prove the melt polycondensation model to be mostly valid also for agitated polycondensation systems. The coefficients of convective mixing as determined for polycondensation in stirred reactors and the specific area of interphases provide information about the magnitude of these macrokinetic reaction parameters.

The concept of a single-phase transport process involves undisturbed mass transport at the interface of the melt with a vapor atmosphere having zero glycol vapor pressure. This effect, due to a different external pressure, cannot be taken into account by this model.

For stirred polycondensation systems the reaction-diffusion-convection model can be replaced by a reaction-mass transfer model by ignoring the concentration gradient and using different diol concentrations at the interface. This model, however, cannot be based exclusively on processes taking place at the molecular level.

This paper presents the results obtained in modeling the polycondensation of poly(ethylene terephthalate) by the reaction-mass transfer concept and compares it with the diffusion model.

2. REACTIONS-MASS TRANSFER MODELS OF MELT POLYCONDENSATION

The polycondensation of bis-(ω-hydroxyalkylene)-terephthalate oligomers in thin melt layers can be most adequately described by a four-parameter polycondensation-thermolysis-diffusion-convection model:

$$[RD]_\tau = D[RD]_{xx} + C[RD]_x + \frac{1}{2}(k[OH]^2 - \frac{4k}{K}[E][RD]) \tag{1}$$

$$[OH]_\tau = -k[OH]^2 + \frac{4k}{K}[E][RD] + k_A[E] \tag{2}$$

$$[E]_\tau = \frac{1}{2}(k[OH]^2 - \frac{4k}{K}[E][RD] - k_A[E] \tag{3}$$

$$[COOH]_\tau = k_A - \frac{1}{\sigma}\int_0^\sigma [E](\tau,x)\,dx \tag{4}$$

In Eq. (2) and consequently in Eq. (10), the endgroups formed by thermolysis are, to simplify matters, considered to behave like hydroxyalkylester endgroups. The system of differential equations is subject to the following boundary conditions:

$$[RD](\tau,0) = 0 \tag{5}$$

$$D[RD]_x(\tau,\sigma) + C[RD](\tau,\sigma) = 0 \tag{6}$$

The local coordinate of the diffusion and convection flow extends between x = 0 (surface of the melt) and x = σ (bottom of the vessel):

$$0 \leq x \leq \sigma \tag{7}$$

The determination of the parameters is described in detail in Refs. 2 and 3.

By neglecting boundary condition (5), the effect of the second phase, i.e., the vapor phase, on mass transfer in the liquid phase can be taken into consideration. An inhomogeneous boundary condition of this kind (Eq. 8) could likewise be established in the form of Henry's

or Raoult's law. If the physicochemical relationships of the concentrations at the interface are not known, this interface concentration [RD]* can be estimated from appropriate experiments ($\overline{P}_n = f(\tau,\sigma,p)$ in combination with the determination of the parameters:

$$[RD](\tau,0) = [RD]^* \neq 0 \tag{8}$$

This approach, using the inhomogeneous boundary condition (8), is a compromise of the reaction-mass transfer model (Eqs. 9 to 12).

Mass transport by diffusion and convection is limited to quiescent or laminarly flowing liquids and melts, respectively. Turbulently agitated melts can formally be treated by the same approach. This relates, however, to macroscopic processes, e.g., the transport of turbulence clusters. The molecular diffusion coefficient was known (from determination of the parameters [1] and from experimental investigations with nonreactive model systems [4]). We therefore relinquished determination of effective diffusion coefficients under turbulent conditions and expressed the mixing efficiency by the coefficient of the convective mass transfer.

The reaction-mass transport model involving a transfer mechanism by diffusion, convection, or turbulent diffusion requires a homogeneous melt layer. However, in polycondensation experiments in glass vessels fitted with different stirrers, the melt was found to have bubbles throughout [10]. By supposing the pressure within the bubbles to be approximately the same as in the vapor atmosphere, the bubble formation can be considered to be an enlargement of the melt surface. Based on this consideration, the effective layer thickness and the volume-dependent contact surface were determined by a five-parameter optimization, as described in Ref. 3.

Adequate representation of polycondensation in stirred melts by the model expressed by Eqs. (1) to (4) is limited to a considerable degree by the concentration gradient and bubble formation. Mass transfer models based on mass transfer processes are independent of the kind and intensity of mass flow in the liquid phase as well as of its internal structure. Although different theoretical approaches for describing mass transfer from a liquid to gaseous phase have been supported by experimental data, we decided to apply the two-film theory because of its physicochemical evidence and mathematical convenience (see, e.g., Refs. 6 and 7).

$$[RD]_\tau = -\beta F([RD] - [RD]^*) + \frac{1}{2}(k[OH]^2 - \frac{4k}{K}[E][RD]) \tag{9}$$

$$[OH]_\tau = -k[OH]^2 - \frac{4k}{K}[E][RD] + k_A[E] \tag{10}$$

$$[E]_\tau = \frac{1}{2} (k[OH]^2 - \frac{4k}{K} [E][RD]) - k_A[E] \qquad (11)$$

$$[COOH]_\tau = k_A[E] \qquad (12)$$

where D = diffusion coefficient of diol
       C = coefficient of convective transport
       β = mass transfer coefficient
       F = specific contact surface
       k = rate constant of polycondensation
       k_A = rate constant of thermolysis
       [RD] = concentration of diol
       [RD] * = concentration of diol at the phase interface
       [E] = concentration of ester groups
       [OH] = concentration of hydroxyalkylester endgroups
       K = equilibrium constant
       σ = layer thickness of the melt
       x = local coordinate
       τ = time coordinate
       $[RD]_{\tau,x}$ = second derivation to τ or x

The mathematical treatment requires the following normalization in Eqs. (1)-(4) and (9)-(12):

$$[E]_0 + \frac{1}{2} ([OH]_0 + [COOH]_0) = 1 \qquad (13)$$

The interfacial concentration of the diol was calculated by Raoult's law, but its value can also be determined by model calculation if the model parameters are known, as indicated by Eq. (8) (see Section 4.1).

3. EXPERIMENTAL DATA FOR THE PARAMETER DETERMINATION IN THE MODEL EQUATIONS

Determination of the constants of the model equations requires kinetic investigations essentially dependent on the parameters affecting the mass transport. In order to investigate mass transport by diffusion and convection, polycondensation experiments with different layer thicknesses of the melt were carried out. The layer thickness

TABLE 1. $\overline{P}_n = f(\tau, p)$ of PETP Formation in a Stirred Reactor with an Anchor Stirrer. Volume of the Melt, 3640 cm^3; $\overline{P}_n$, $\tau_0 = 5.5$

τ, min	$\overline{P}_n$, Pa			
	60	130	400	1330
30	40.4	34.5	28.4	18.0
60	76.2	67.8	57.0	33.1
90	110.0	99.1	80.4	46.2
120	129.0	118.0	96.0	56.1
150	141.5	129.0	107.1	64.6
180	149.5	137.6	115.0	71.0

was exactly determined in the nonstirred thin layer of the melt. In polycondensation systems subjected to stirring, the layer thickness can be determined only approximately by the melt volume and the reactor geometry.

The experimental results obtained at constant external pressure (p < 50 Pa) with nonstirred thin layers were reported in Refs. 1 and 8, and those obtained by polycondensation experiments in a stirred reactor are reported in Ref. 5. Data on the pressure dependence of PETP formation in a stirred reactor are summarized in Table 1. The measurements were carried out in the presence of a catalyst-inhibitor combination consisting of 3×10^{-4} mol/mol $Mn(ac)_2$, 3×10^{-4} mol/mol $Sb(ac)_3$, and 6×10^{-4} mol/mol triphenylphosphate at 280°C. In the polycondensation experiments in thin layers (Fig. 1), a PETP prepolymer of $\overline{P}_n = 17.8$ with an initial carboxyl group content of $[COOH]_0 = 20$ μequiv/g was used. In both systems the decrease of the macroscopic polycondensation rate with increased pressure was easily identified by the change of $\overline{P}_n = f(\tau)$. The effect of a vacuum applied to a stirred reactor is more distinct.

4.   RESULTS OF MODEL CALCULATIONS

4.1.   Pressure Dependence of PETP Formation

Based on the parameters of the diffusion-convection model (Eqs. 1-4) listed in Table 2, the interface concentration of diol in thin-
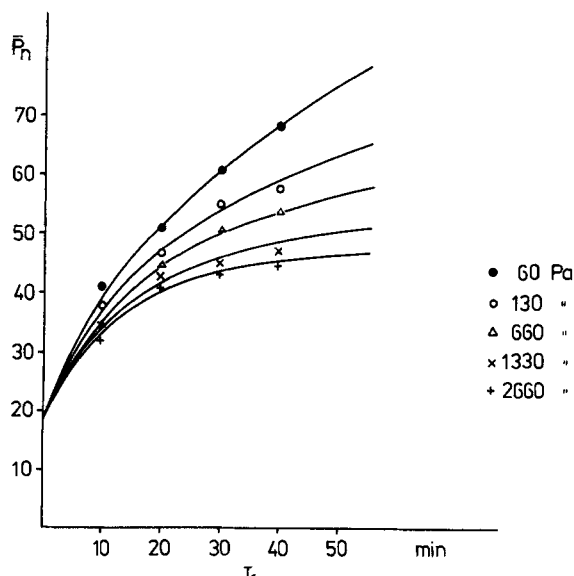
FIG. 1. $\bar{P}_n = f(\tau, p)$ of PETP formation in nonstirred melt layers. $T = 280°C$, $\sigma = 0.0185$. Full line: model-based calculation.

TABLE 2. Rate Constants and Transport Coefficients of PETP Formation in Nonstirred Melt Layer (calculated)

Catalyst	t, °C	$k \times 10^2$ g/mmol·s	$k_A \times 10^7$ s^{-1}	$D \times 10^5$ cm^2/s	$C \times 10^4$ cm/s
Catalyst-inhibitor combination	270	1.6	1.8	1.0	6.4
Catalyst-inhibitor combination	280	1.6	1.9	1.6	7.8
Catalyst-inhibitor combination	290	2.4	3.3	2.2	13.2
$Mn(ac)_2$	280	0.7	2.7	0.8	7.5
$Ti(OC_4H_9)_4$	280	6.7	5.1	2.2	8.8

layer polycondensation was determined by applying the inhomogeneous boundary condition (8). The parameters were calculated for $[RD](\tau,0)$ = 0 (Eq. 5) by using the experimental values indicated in Refs. 1, 3, and 8. Small deviations of the model parameters from the numerical values presented in Refs. 1, 3, and 8 are caused by the different mathematical techniques used (see Refs. 9 and 10). Figure 1 illustrates the degree of approximation obtained by applying the four-parameter diffusion-convection model in combination with boundary condition (8) at a layer thickness of $\sigma = 0.0185$ cm. In polycondensation experiments in thin melt layers, the interface concentration was found to rise with pressure (Table 3). The increase of $[RD]*$ with increasing layer thickness is caused by the small increase of $\overline{P}_n$ with increasing layer thickness. With respect to the equilibrium condition

$$[RD]_{Gl} = K \frac{[OH]^2}{[E]} \tag{14}$$

higher values of the equilibrium concentration $[RD]_{Gl}$ have to be considered in comparing τ_i because lower values of $\overline{P}_n$ correspond to higher endgroup concentrations. The dependence of diol concentration on molecular weight indicates that the melt system diol/polyester obeys Raoult's law even under polycondensation conditions, i.e. under conditions of high deviation from thermodynamic equilibrium.

In equilibrium investigations the validity of Raoult's law was repeatedly supported. In this way, for example, Fontana [11] succeeded in determining the equilibrium constant of PETP formation. Also, the relationship of the temperature dependence on the vapor pressure of glycol used in our calculations is indicated in Ref. 11.

Compared to the glycol concentration in the melt, the glycol concentration at the interface is low (see the concentration plot of glycol in the polycondensation-diffusion model in Ref. 6). Therefore, boundary condition (5), being a prerequisite for the diffusion-convection model, is met for thin melt layers at pressures of p < 5 Pa under our experimental conditions. With respect to polycondensation in a stirred reactor, the mass transfer approach (Eqs. 9-12) resulted in distinctly lower values of the interface concentration of diol (Tables 3 and 4). This may be due to the dynamics of the system which accelerates the desorption of glycol from the interface by improved gas exchange as compared with that in thin layer polycondensation.

4.2 Mass Transfer Coefficients of Ethylene Glycol in PETP Melts

In the mass transfer model (Eqs. 9-12) only the product βF can be approximated by model calculations because, at least for stirred

TABLE 3. Concentration of Ethylene Glycol at the Phase Boundary
of Thin Melt Layers

σ, cm	p, Pa (at [RD] * × 10³ mmol/g)				
	6	130	660	1330	2660
0.009	0.53	0.91	1.01	1.24	1.53
0.018	0.56	0.97	1.10	1.60	1.74
0.055	1.60	1.93	2.21	3.40	4.42
0.128	3.28	4.55	5.46	6.45	8.06

TABLE 4. Concentration of Ethylene Glycol at the Phase Boundary of
PETP Melts Subjected to Compelled Mixing

p, Pa	[RD] * × 10⁵ mmol/g
60	0.73
130	4.81
400	2.73
1330	10.27

autoclaves, no data are available for the extent of the mass transfer
area generated (see Section 4.3). Therefore, we applied the polyconden-
sation-mass transfer approach to nonstirred thin layers. In this case
the contact surface can be considered equal to the surface of the melt
layer. The approximation was carried out with respect to $\overline{P}_n$ values
in the melt layer, the mass transfer being assumed to equalize suffi-
ciently fast any difference in concentration within the layer. For this
special case the diffusion and mass transfer model were proved to be
equivalent [12].

   The mass transfer coefficients of ethylene glycol are independent
of the chemical reactivity of the system (Table 5). With the PETP/
catalyst systems investigated, which represent very different values of
$\overline{P}_n$ vs τ (Table 6 and experimental data in Ref. 1), equal β values were
obtained at 280°C. Thus, chemical reactions and mass transfer processes
are separated adequately by the mass transfer model investigated.

   As observed with diffusion coefficients [4], the mass transfer co-
efficients also decrease with increasing molecular weight of the alkane
diol. Table 7 indicates the average values of the mass transfer coeffi-

TABLE 5. Coefficients and Diffusion Interface of the Mass Transfer of Ethylene Glycol in PETP Melts

t, °C	Catalyst	$\beta \times 10^3$ cm/s	$(D/\beta) \times 10^3$ cm
270	Catalyst-inhibitor combination	4.1	2.4
280	Catalyst-inhibitor combination	5.4	3.0
290	Catalyst-inhibitor combination	8.4	2.6
280	$Mn(ac)_2$	4.5	2.1
280	$Ti(OC_4H_9)_4$	8.6	2.5

TABLE 6. Range of $\overline{P}_n$ Values for the Parameter Determination of the Polycondensation-Mass Transfer Model at $\sigma = 0.009$

Catalyst	$\overline{P}_n$ range
$Mn(ac)_2$	20.8-78.0
$Mn(ac)_2/Sb(ac)_3/(C_6H_5)_3PO_4$	18.2-117.7
$Ti(OC_4H_9)_4$	29.9-195.0

TABLE 7. Coefficients of Mass Transfer of Alkane Diols in Poly(Alkylene Terephthalate) Melts

Reaction system	t, °C	$\overline{\beta} \times 10^3$ cm/s	$\overline{D} \times 10^5$ cm^2/s
Ethylene glycol/PETP	280	6.0	2.0
Butane diol/PBTP	240	9.5	2.4
Hexane diol/PHMT	240	3.4	1.5
Decane diol/PDMT	240	2.2	0.9

cients. Based on the two-film theory of mass transfer, the "diffusion interface layers," in which the mass transport proceeds exclusively by molecular diffusion, can be determined. The diffusion interface layers are distinctly thinner than the melt layers achieved in our experiments.

4.3 Mass Transfer Area in the Polycondensation in Stirred Reactors

Experimental investigations of PETP melt polycondensation with specific catalysts and temperatures show the macrokinetics of the reaction to depend essentially on the contact surface. This is particularly obvious with polycondensation experiments in nonstirred melt layers, but results also from the dependence of the effective rate of polycondensation on the melt volume in the stirred reactor (see Refs. 3 and 5). In the continuous preparation method of polyesters in horizontal one- and two-shaft reactors (see, e.g., Refs. 13-16) or in a vertical cone reactor [17], comparatively large specific contact surfaces are generated by peculiarities of reactor construction and operation. The comparatively high macroscopic rate of polycondensation in stirred reactors with a small melt surface with respect to the volume indicates that the contact surface does not necessarily depend on reactor construction. Experimental investigations and visual observation of the melt suggest that, due to intensive bubble formation combined with high stability of the bubbles, the specific mass transfer area is considerably enlarged as compared with the geometrical melt surface area [18].

Based on the diffusion-convection model, the specific mass transfer area of melt polycondensation was determined by five-parameter optimization, taking into account the effective melt layer thickness in the stirred reactor [3].

The values of the mass transfer coefficient (Table 5) allow determination of the specific contact surface for the polycondensation-thermolysis-mass transfer model. As a consequence of mixing and bubble formation, the specific mass contact surface generated in the stirred reactor is more than one order of magnitude larger than the area calculated from the melt volume and reactor dimensions. The melt surface in the nonstirred 10-L laboratory reactor used in our experiments is 600 cm^2, corresponding to a specific mass transfer area of F_{static} 0.1-0.2 cm^{-1}. As compared with the diffusion model characterized by a specific mass transfer area ranging between 40 and 60 cm^2/cm^3 [3], the values ($F_{dynamic}$) resulting from the mass transfer model (Tables 8 and 9) are lower. Judged by a simple geometrical estimation of the volume ratio of the melt to the bubbles [18], the small contact surfaces resulting from the mass transfer model seem to be more reliable.

TABLE 8. Specific Contact Surface of Melt Polycondensation in a
Stirred Reactor. Catalyst-inhibitor combination, 280°C

Melt volume, cm^3	$F_{dynamic}$, cm^2/cm^3	F_{static}, cm^2/cm^3
2650	14.6	0.23
3640	11.3	0.11
4300	8.7	0.10

TABLE 9. Specific Contact Surface of Melt Polycondensation in a
Stirred Reactor and Dependence on the Catalyst

Catalyst	Melt volume, cm^3	$F_{dynamic}$, cm^2/cm^3
$Mn(ac)_2/Sb(ac)_3/(C_6H_5O)_3PO$	2650	14.6
$Ti(OC_4H_9)_4$	2650	28.0
$Mn(ac)_2/Sb(ac)_3/(C_6H_5O)_3PO$	3640	11.3
$Ti(OC_4H_9)_4$	3640	15.1

Since the specific mass transfer area is generated by both stirring
and evaporation, it depends on the reactivity of the reactants in the
system. Corresponding to the k and k_A values of PETP formation
catalyzed by titanium alkoxides (Table 2), these catalysts create the
largest contact surface.

Figure 2 illustrates the approximation attained by the mass trans-
fer model for the experimental values of $\overline{P}_n = f(\tau,p)$ indicated in
Table 1. The decrease of the macroscopic rate of polycondensation
with increasing pressure can only be ascribed to slower mass trans-
fer since the "chemical" rate of polycondensation is independent of
the pressure. In agreement with this conclusion, the values of the
product of the mass transfer coefficient and the contact surface at
increasing pressure, as obtained by model calculations, were found
to decrease (Table 10). The slow mass transfer is probably due to
decreasing values of β caused by increasing interface concentration
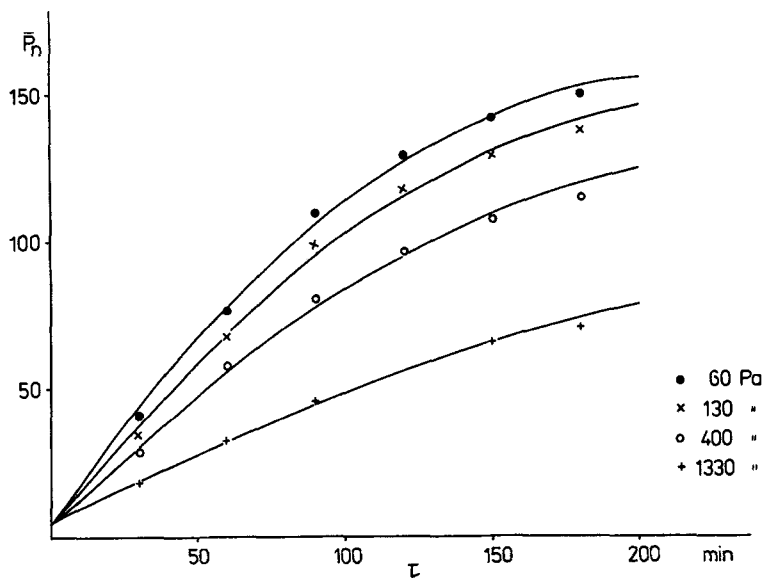and, therefore, of slower diffusion in the interface layer.

FIG. 2. $\overline{P}_n = f(\tau,p)$ of PETP formation in stirred reactor at T = 280°C. Full line: model-based calculation.

TABLE 10. βF Dependence on Pressure in Melt Polycondensation in a Stirred Reactor. Catalyst-inhibitor-combination, T = 280°C, V = 3640 cm³

Pressure, Pa	$\beta F \times 10^2 \ s^{-1}$
60	6.1
130	5.2
400	3.8
1330	1.8

5.   THE VALIDITY OF THE REACTION-MASS TRANSPORT MODELS

According to our experimental investigation and model calculations, an adequate model for melt polycondensation in thin, nonstirred melt layers at low pressure can be established. The defined geometry of the melt volume allowed us to fix and define the local coordinate. Based on special experimental techniques applicable to kinetic laboratory investigations, we succeeded in describing quantitatively how the macroscopic polycondensation process is dependent on the thickness of the melt layer by the polycondensation-thermolysis-diffusion-convection model. Two of the parameters of this model were verified by separate experiments. In investigations of the thermal degradation of poly(alkylene terephthales) combined with integral kinetic evaluation [19], the rate constants were found to agree with the values obtained by model calculations based on the four-parameter diffusion-convection model. Support was also achieved by another approach, independent of modeling, for the diffusion coefficient of diols in polyester melts. To this purpose we investigated the diffusion in nonreactive polyester/α,ω-dichloroalkane systems [4]. Additionally, the independence of the diffusion coefficient on viscosity, suggested by the model, was supported experimentally.

The behavior of continuous reactors generating thin films is under investigation. The application of the model presented to this type of reactor is possible.

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