Micro kinetics and mass transfer in poly(ethylene terephthalate) synthesis

Th. Rieckmann¹* and S. Völker²

¹University of Applied Sciences Cologne, Department of Chemical Engineering and Plant Design, Betzdorfer Str. 2, D-50679 Cologne
²University of Kassel, Institute of Thermal Engineering, Kurt-Wolters-Str. 3, D-34109 Kassel

Abstract

The polycondensation of PET through ester interchange is a process strongly limited by mass transport effects. Therefore, design and scale up of industrial PET plants require a detailed knowledge of micro and macro kinetics. In this work, a comprehensive model for the polycondensation of PET has been developed taking into account 1) kinetic data, 2) equilibrium data, 3) diffusion processes for the major by-products EG and water in the molten PET. The model was validated using own experimental data determined by thermogravimetric analysis. As a sample, so called “PET-prepolymer” was used. The kinetic parameters for the ester interchange reaction, for the water formation through esterification as well as for the most significant side reactions were taken from the literature. The mass transport was described using the classical diffusion equation according to Fick’s law and a modified Wilke-Chang diffusion model. Diffusion coefficients were then calculated as a function of temperature and degree of polycondensation to give a good explanation of the process phenomena.

Keywords: Polycondensation; PET; Kinetics; Mass transfer; Diffusion; Multivariate regression

1. Introduction

Poly(ethylene terephthalate) (PET) is a commodity product for many different applications. PET is processed to fibres, spanning the quality range from staple fibres to mono filaments with silk like characteristics and high performance technical yarns as well as to bottles, sheets and films. The PET market is increasing rapidly and will further be boosted by current developments of PET grades with high gas barrier properties and temperature stability suitable for the packaging of oxygen sensitive beverages and foods which require hot filling. (Rieckmann, 1995, Becker, et al. 1999).

Continuous processes of capacities from 60 tonne/d to 300 tonne/d are well established for the industrial production of PET. Nowadays, most of the polycondensation processes start with the monomers 1,2 ethanediol (EG) and terephthalic acid (TPA), incorporating co-monomers like isophthalic acid (IPA). The synthesis of PET requires two reaction steps (Gupta and Kumar, 1987, Ullmann, 1996). The first step is an esterification reaction, forming a so called prepolymer, and by-product water is removed via a column system. The second reaction step is polycondensation, which is a transesterification reaction that takes place in the melt phase. The low molecular weight product EG is removed from the melt using high vacuum. The melt viscosity increases rapidly with progressing polycondensation. As the transesterification reaction is a reversible equilibrium reaction, the macro kinetics of the whole polycondensation process become more and more limited by diffusion and mass transfer of the volatising EG molecules.

The reaction kinetics of the polycondensation process are still under investigation and are not unambiguously determined (Zimmerer et al., 1997, Kang et al., 1997, Ravindranath and Mashelkar, 1986 and 1984). The published data as they depend on the specific experimental procedures and the resulting kinetic parameters vary with the assumed kinetic model and the applied data fitting procedure. In the absence of a reliable model, reaction engineers are forced to scale-up established reactors in economically undesirable small steps. Additionally, the available reaction and mass transport data are insufficient for designing new reactor concepts with justifiable expenditure.

In an earlier work (Rieckmann et al., 1999), we have developed a mass transfer model by applying the penetration theory to the volatilisation of EG and water from molten PET. The mass transfer coefficients were described as functions of the degree of polycondensation (Fig. 1) respectively the molecular weight, the viscosity, as well as of the reaction temperature with dependencies according to the Wilke-Chang diffusion model. This reaction / mass transfer model describes the experimental data for thin polymer layers well, but

* Corresponding author. Fax: ++49-221-8275-2202 ; e-mail: thomas.rieckmann@fh-koeln.de
Th. Rieckmann and S. Völker, presented at ISCRE-16, Kraków 2000, also published in Chemical Engineering Science 56 (2001) 945-953

2. Methods

2.1. Samples

A sample of prepolymer from Acordis, Obernburg, Germany was taken from the esterifier output. The sample was prepared from TPA and EG to give ester and water. The ester was further transesterified to give an oligomer with an average length of 2.5 repeat units, and the sample was prepared from TPA and EG to give ester and water. No additional metal based esterification catalyst or polycondensation catalyst, as well as no further additives were added.

2.2. Thermogravimetric analysis

The TGA/DTA (STA) apparatus used in this work is the type STA 503 from Bähr GmbH, Germany. The maximum load of the TGA is 1000 mg with a measuring range of 200 mg and a maximum resolution of 1 µg. The TGA apparatus has a horizontal weighing beam, which generates an unusually low drag in the weighing direction and the effect of drag was further reduced by using helium as a low viscosity purge gas, thus avoiding significant corrections of the baseline. As all STA devices, the STA 503 is easy to calibrate by analysing significant corrections of the baseline. As all STA devices, the STA 503 is easy to calibrate by analysing

2.3. Numerical computation procedure and evaluation of model parameters

The crucible contents of the TGA are modelled as a dynamic system with distributed parameters. The material balance (see section 3) of the reaction system yields a set of twelve meshed partial differential equations (PDE) plus one equation for the retained mass. All equations and initial conditions are transposed 1) into a dimensionless form and 2) into a set of ordinary differential equations (ODE) and analysed by the finite differences technique.

\[
\frac{\partial u_{i,j}}{\partial t} = \left( \frac{u_{i,j-1} - 2u_{i,j} + u_{i,j+1}}{\Delta z^2} \right) + \Gamma_j, \quad (1)
\]

for \( i = 1, m \) functional group or compound, and \( j = 2, n-1 \) finite element.

**Boundary conditions**

Left boundary (bottom of crucible), \( j = 1 \),

\[
\frac{\partial u_{i,j}}{\partial t} = \left( -u_{i,j} + u_{i,j+1} \right) + \Gamma_j. \quad (2)
\]

Right boundary (open top of crucible, inert gas flow), \( j = n \),

\[
\frac{\partial u_{i,j}}{\partial t} = \left( u_{i,j-1} - 2u_{i,j} \right) + \Gamma_j. \quad (3)
\]

An adapted grid was used to save computation time, taking into account the spatial gradients at the right boundary are the steepest. By this technique, the control volume is cut into \( n_1 \) main intervals, afterwards the last interval (i.e. interval \( n_1 \)) is divided again into \( n_2 \) subintervals and so on (Fig. 2). Applying this procedure twice, a resolution at the right boundary of \( n_1^3 \) is achieved by solving \( 3n_1 - 2 \) ODEs only. Such for \( n_1 = 6 \), the total number of grid points calculates to 16, which means to solve 16 · 12 + 1 = 193 ODEs, with a spatial resolution at the right boundary of \( n_1^3 = 216 \). In case of equidistant grid points this would mean to solve 2593 ODEs.
The simultaneous numerical solution of the ODE system and the estimation of the kinetic data by the least squares (LSQ) method were done using Matlab (The MathWorks, Inc.). With Matlab the integrator ode15s and the optimisation routine fmins were implemented. Ode15s is a variable order solver based on the numerical differentiation formulas. Optionally, it uses the backward differentiation formulas (also known as Gear’s method); ode15s is a multi-step solver. The routine fmins uses a Nelder-Mead type Simplex search method.

The reaction and diffusion parameters of the polycondensation process have been fitted with Matlab, running the optimisation routine and the ODE solver simultaneously according to the technique of non-linear multivariate regression (Kaisersberger, 1991). The task of non-linear regression is the iterative calculation of the minimum sum of least squares. In case the multivariate regression technique is applied, the total LSQ yields into a sum of LSQ calculated with data from the different experimental runs.

\[ \text{LSQ} = \sum_{k=i}^{m} \sum_{i=1}^{n} w_k (y_{\text{exp},k,i} - y_{\text{mod},k,i})^2 \]  
(4)

with

\[ w_k = \frac{1}{y_{\text{exp,max}}^2 + y_{\text{exp,min}}^2} \]  
(5)

The experimental values \( y_{\text{exp,k,i}} \) are the normalised masses, \( y = m(T)/m_0(t=0) \) from TGA. The model values \( y_{\text{mod},k,i} \) result from the numerical solution of the respective ODEs. The multivariate analysis bases on the assumption that the kinetic and diffusion parameters have to be identical for all experimental conditions in the modelled parameter range. This constraint facilitates the choice of an appropriate model considerably and improves the model validity.

3. Kinetic model

The model for the PET formation takes into account 1) kinetic data, 2) equilibrium data, and 3) diffusion processes for the major by-products EG and water. The Flory postulate (Flory, 1953) was used for all reactions taking place during the formation of PET, which can be regarded as reactions between functional groups. The rate constants depend on temperature and some of them additionally on the concentration of acid groups. The mass transport of water and EG in the polymer melt is described applying the classical diffusion equation using Fick’s law.

In total, eleven reactions have been included, some of them being reversible reactions:

- transesterification  
- acetaldehyde formation  
- DEG formation  
- water from esterification  
- degradation of diester groups  
- transesterification of vinyl end groups

The compounds and functional groups considered in the reaction model are listed in Tab. 1. The complete set of modelled reactions is shown in Tab. 2 and covers reactions necessary for describing some of the important quality parameters established in PET production. Those quality parameters include the concentrations of carboxyl end groups (-COOH, influences hydrolysis stability), acetaldehyde (AA, for food packaging), diethylene glycol (DEG, influences dyeability) and vinyl groups (V, potential AA), as well as the degree of polycondensation, the average molecular weight (M_n), the intrinsic viscosity (I.V.), and the melt viscosity (η).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Component or functional group</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>ethylene glycol</td>
<td>HOCH₂CH₂OH</td>
</tr>
<tr>
<td>TPA</td>
<td>terephthalic acid</td>
<td>HOOC-CH₆-COOH</td>
</tr>
<tr>
<td>DEG</td>
<td>diethylene glycol</td>
<td>HO(CH₂)₂O(CH₂)₂OH</td>
</tr>
<tr>
<td>AA</td>
<td>acetaldehyde</td>
<td>CH₃CHO</td>
</tr>
<tr>
<td>W</td>
<td>water</td>
<td>H₂O</td>
</tr>
<tr>
<td>tEG</td>
<td>EG end group</td>
<td>R-OCH₂CH₂OH</td>
</tr>
<tr>
<td>bEG</td>
<td>EG repeat unit</td>
<td>R-OCH₂CH₂-O’</td>
</tr>
<tr>
<td>tTPA</td>
<td>TPA end group</td>
<td>R-OC-CH₆-COOH</td>
</tr>
<tr>
<td>bTPA</td>
<td>TPA repeat unit</td>
<td>R-OC-CH₂-CO-R’</td>
</tr>
<tr>
<td>tDEG</td>
<td>DEG end group</td>
<td>R-O(CH₂)₂O(CH₂)₂OH</td>
</tr>
<tr>
<td>bDEG</td>
<td>DEG repeat unit</td>
<td>R-O(CH₂)₂O(CH₂)₂-O’</td>
</tr>
<tr>
<td>tV</td>
<td>vinyl end group</td>
<td>R-OCH=CH₂</td>
</tr>
</tbody>
</table>

Equations of an Arrhenius type have been used for the temperature dependent rate constants. Furthermore, it has been assumed that the polycondensation and the esterification reactions (reactions 1; 6; 7; 8; 9) are acid catalysed and that the corresponding rate constants can be written as:

\[ k_i = k_{i0}c_{\text{acid}} \exp(-E_{a,i} / RT) \]  
(6)

with the concentration of acid groups \( c_{\text{acid}} \) being the sum of the concentrations of carboxylic end groups (tTPA) and carboxylic groups of the free acid (2·TPA). The kinetic parameters and equilibrium constants for the reactions are compiled in Tab. 3 together with the data source.
According to the Wilke-Chang model (an empirical modification of the Stokes-Einstein relation), the mutual diffusion coefficient of a component at very low concentrations in a solvent is proportional to the temperature and to the square root of the molecular weight as well as to the reciprocal of the viscosity of the solvent (Reid, 1988). This approach was modified, taking into account a temperature dependency according to the Arrhenius equation as well as a modified proportionality to the melt viscosity:

\[
D_{i,\text{PET}} = D_{0,i} \cdot \exp(-E_a/D_i / RT) \cdot M_i^{0.5} / \eta^{0.5}
\]  

(7)

The average molecular weight, \( M_n \), was calculated from the degree of polycondensation, \( x \). The correlation used for the calculation of the melt viscosity bases on own experimental data.

\[
\eta = \eta(I.V., T)
\]  

(8)

\[I.V. = 5 \cdot 10^{-4} \cdot M_i^{0.72}
\]  

(9)

\[M_n = 192 \cdot x + 62
\]  

(10)

The vapour pressure of the prepolymer (\( x = 2.5 \)) is very small at reaction conditions, therefore its volatilisation can be neglected. This assumption is due to observations made by one of us at a variety of runs with industrial batch polycondensation plants.

Tab. 3. Kinetic and equilibrium data

<table>
<thead>
<tr>
<th>No</th>
<th>( k_{i,0} )</th>
<th>( E_i/kJ/mol )</th>
<th>( k_i )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.364</td>
<td>74</td>
<td>0.5</td>
<td>Kang et al., 1997</td>
</tr>
<tr>
<td>2</td>
<td>8.32 \cdot 10^1</td>
<td>125</td>
<td>-</td>
<td>Ravindranath and Mashelkar, 1984</td>
</tr>
<tr>
<td>3-5</td>
<td>2.17 \cdot 10^6</td>
<td>125</td>
<td>2.5</td>
<td>Kang et al., 1997</td>
</tr>
<tr>
<td>6-7</td>
<td>4.68 \cdot 10^1</td>
<td>75</td>
<td>2.5</td>
<td>Kang et al., 1997</td>
</tr>
<tr>
<td>8-9</td>
<td>2.34 \cdot 10^1</td>
<td>75</td>
<td>1.25</td>
<td>Kang et al., 1997</td>
</tr>
<tr>
<td>10</td>
<td>7.2 \cdot 10^1</td>
<td>158</td>
<td>-</td>
<td>Ravindranath and Mashelkar, 1984</td>
</tr>
<tr>
<td>11</td>
<td>1.36 \cdot 10^3</td>
<td>77</td>
<td>-</td>
<td>Ravindranath and Mashelkar, 1984</td>
</tr>
</tbody>
</table>

4. Results

4.1 Thermogravimetric analysis of polycondensation

Examples of TGA results for different reaction temperatures and film thickness are shown in Fig. 3 and Fig. 4. The relative mass loss is plotted as a function of time under isothermal conditions.

Fig. 3 shows the influence of reaction temperature on the polycondensation process. The PET formation is accelerated considerably at higher reaction temperatures. Although high temperatures are desirable from a kinetic point of view, industrial PET plants are limited to maximum temperatures around 295 °C (in exceptional cases 305 °C) due to the onset of yellowing degradation reactions.

Fig. 4 confirms the well known phenomenon that the PET polycondensation is mass transport limited, even down to values for the film thickness of less than 0.5 mm. According to Zimmerer (1997), the kinetic regime shifts to reaction control at a film thickness well below 0.05 mm.

Fig. 3. TGA results for the PET polycondensation at \( T = 267; 287; \) and \( 307 \, ^\circ C \), \( h = 0.8 \, \text{mm} \)

Fig. 4. TGA results for the PET polycondensation at \( h=0.2 \, \text{mm}, T=287 \, ^\circ C, \text{no catalyst} \), \( h=0.8 \, \text{mm}, T=287 \, ^\circ C, \text{no catalyst} \), \( h=0.2 \, \text{mm}, T=307 \, ^\circ C, \text{no catalyst} \)

4.2. Micro kinetics and diffusion

As a first approach, kinetic data for the diffusion of EG in PET were taken from the literature (\( D_{\text{EG,PET}} (270 \, ^\circ C) = 1.7 \cdot 10^8 \) to \( 8.0 \cdot 10^{-10} \, \text{m}^2/\text{min} \). Raffler et al., 1985, Pell and Davis, 1973) and the diffusion
coefficients of EG and water were assumed to depend on the temperature only \( (D_{i,PET} = D_{i,T} \cdot T) \)

As an approximation, the diffusion coefficient for water was derived from \( D_{i,PET} \) assuming proportionality to the reciprocal of the molecular volume respectively the molecular weight. The results for this parameter set are compared to the experimental TGA data in Fig. 5. The predicted TGA mass losses are in the order of magnitude of the measured data. The deviations between predicted and experimental data should mainly be effected 1) by an underestimated contribution of the mass transport and 2) by an improper temperature dependency of the diffusion coefficients.

The overall kinetic regime is limited by the mass transport of EG and water. The mass transport resistance increases with progressing polycondensation. With a diffusion coefficient depending on temperature only, the model prediction for the quantitative mass loss can not be improved further. Particularly, the model predictions do not match the experimental data for higher degrees of polycondensation. With progressing polycondensation, the melt viscosity increases about 2 - 4 orders magnitude, which is expected to affect the diffusion coefficients.

Nevertheless, the model predictions for the quality parameters match the tendencies of parameter evolution of industrial production plants. Model predictions for selected PET quality parameters are shown in Figs. 7 - 10.

Fig. 5. Best fit assuming \( D_{i,PET} = D_{i,T} \cdot T \), with literature data listed in Tab. 3,
\( D_{T,EG} = 5.7 \cdot 10^{-11}, D_{T,W} = 2.0 \cdot 10^{-10} \text{m}^2/\text{min}/\text{K} \),
\( h = 0.2 (\odot); 0.8 (\odot); 2.5 (\triangle) \text{mm}, T = 267; 287; 307\degree \text{C} \)

Fig. 6. Best fit assuming \( D_i = D_{0,i} \exp(-E_a,D_i/RT) \)
\( k_{1,0} = 0.071 \text{ (m}^3/\text{mol})/\text{min}, E_{a_1} = 74 \text{ kJ/mol}; D_{0,PEG} = 0.087 \text{m}^2/\text{min}, D_{0,w} = 0.29 \text{m}^2/\text{min}, E_{a,LD} = 67.8 \text{kJ/mol}, h = 0.2(\odot); 0.8(\odot); 2.5(\triangle) \text{mm}, T = 267; 287; 307\degree \text{C} \)

Fig. 7. Concentration of COOH end groups (tTPA),
\( T = 287\degree \text{C}, h = 0.8 \text{ mm}, \text{parameter: spatial coordinate}, \text{top curve for } j = 1 \).

Fig. 8. DEG concentration (bDEG), \( T = 287\degree \text{C}, h = 0.8 \text{ mm}, \text{parameter: spatial coordinate}, \text{bottom curve for } j = 1 \). The concentrations of tDEG and free DEG are orders of magnitude smaller.
Fig. 9. Concentration of vinyl end groups (tV), T = 287°C, h = 0.8 mm, parameter: spatial coordinate, top curve for j = 1

Fig. 10. Degree of polycondensation (x), T = 287°C, h = 0.8 mm, parameter: spatial coordinate, top curve for j = 1

To improve the model validity, a dependency of the diffusion coefficient according to Eq. 7 was incorporated. In Fig. 11, results for the fit of experimental data at a constant film thickness and three different reaction temperatures are shown. Shape and curvature of the experimental data are described nicely by the modified diffusion model. For this data fit, the pre-exponential factor of the polycondensation (reaction 1) as well as the diffusion coefficients have been optimised.

Good agreement between model and experiment is easily achieved for single experiments or for data sets at constant film thickness and different reaction temperatures. The Arrhenius parameters of reaction 1; $D_{\text{EG},\text{PET}}$; and $D_{\text{w},\text{PET}}$ may be adjusted to specific values for each single experiment. In this case neither of the values obtained from fitting single data sets can describe the full experimental parameter range completely. This observation emphasizes the fact, that the non-linear multivariate regression is essential for the determination of kinetic parameters with comprehensive validity.

Consequently, nine experimental runs have been fitted simultaneously with h = 0.2; 0.8; 2.5 mm and T = 267; 287; 307 °C. Optimised parameters are the diffusion coefficients for EG respectively water as well as the pre-exponential factor and the activation energy of the polycondensation (reaction 1). The Arrhenius parameters $k_{i,0}$ and $E_{a,i}$ of all other reactions have been kept constant according to the data taken from literature (Tab. 3). The results are shown in Fig. 12, the optimised model parameters are displayed in Tab. 4.

Fig. 11. Best fit $D_i = D_{0,i} \exp(-E_{a,i} \cdot RT) \cdot M_0^{0.5} \cdot \eta^{0.5}$ fitted for data with h = 0.8(0) mm only, $k_{1,0} = 0.115$ (m³/mol)²/min, $E_{a,1} = 74.0$ kJ/mol; $D_{\text{EG},\text{PET}} = 0.202$ m²/min (mol/g)⁰.⁵ (Pa s)⁰.⁵; $D_{\text{w},\text{PET}} = 0.696$ m²/min (mol/g)⁰.⁵ (Pa s)⁰.⁵; $E_{a,\text{D}} = 103$ kJ/mol, T = 267; 287; 307°C, experimental data: symbols, model: lines.

Fig. 12. Best fit $D_i = D_{0,i} \exp(-E_{a,i} \cdot RT) \cdot M_0^{0.5} \cdot \eta^{0.5}$ T = 267; 287; 307 °C, h = 0.2(0); 0.8(0); 2.5(0) mm, experimental data: symbols, model: lines.

Tab. 4. Kinetic and mass transport parameters for the polycondensation of PET

<table>
<thead>
<tr>
<th>par. value</th>
<th>h = 0.2; 0.8; 2.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{1,0}$</td>
<td>0.089 (m³/mol)²/min</td>
</tr>
<tr>
<td>$E_{a,1}$</td>
<td>75.0 kJ/mol</td>
</tr>
<tr>
<td>$D_{0,\text{EG}}$</td>
<td>0.239 m²/min (mol/g)⁰.⁵ (Pa s)⁰.⁵</td>
</tr>
<tr>
<td>$D_{0,\text{w}}$</td>
<td>0.823 m²/min (mol/g)⁰.⁵ (Pa s)⁰.⁵</td>
</tr>
<tr>
<td>$E_{a,\text{D}}$</td>
<td>99.6 kJ/mol</td>
</tr>
</tbody>
</table>
With this model type, the experimental data with varying temperature and polymer layer thickness are predicted very satisfactorily. For very thin polymer layers the model predictions are not as accurate as those for higher film thickness. This may be due to the uncertainty with regard to the surface area which is expanded by wetting of the sample bin walls. This systematic error affects considerably only samples with very high surface area to volume ratios. At a temperature of 307 °C and a polymer layer thickness of 2.5 mm the influence of mass transport on the apparent reaction rate is overestimated. Most industrial PET reactors are operating well below 300 °C with polymer layers distinctly thicker than 0.2 mm. For this parameter range, our model yields excellent predictions of the polycondensation behaviour.

In industrial polycondensation reactors, the degree of polycondensation increases from \( x = 3 \) to values beyond \( x = 100 \) with approaching reaction. Thereby, the melt viscosity increases from \( \eta = 0.05 \) Pas to \( \eta = 350 \) Pas (at \( T = 290 \) °C, I.V. = 0.64 dL/g). Assuming the validity of the modified Wilke-Chang model over the whole viscosity range, the diffusion coefficients derived from our model would follow a trend with the degree of polycondensation as displayed for EG in Fig. 13.

![Fig. 13. Diffusion coefficient \( D_{\text{EG,PET}} \) in molten PET film as a function of the degree of polycondensation and \( T \).](image)

During the initial state of polycondensation, the diffusion coefficients vary distinctly with progressing reaction. For long chain polymers, the diffusion coefficients show an asymptotic behaviour, becoming less dependent of the chain length. This also has been suggested by molecular modelling approaches. A degree of polycondensation of \( x < 30 \) was achieved in the TGA experiments. In this parameter range, the diffusion of EG and water in the polymer melt is the rate determining step of the PET synthesis.

The side reactions influence the extent of the overall reaction significantly and can not be neglected. Their consideration is also essential for predicting the commercial quality parameters of PET. The kinetic parameters of the side reactions should receive further attention.

The multivariate regression comprises much stronger restrictions for deriving kinetic models than the classical approach. Therefore, inadequacies of the assumed kinetic model can be recognised much easier. The resulting kinetic parameters are valid over the whole investigated parameter range and should provide a more reliable data basis for design and scale-up.

### Notation

- \( c_i \): concentration of component or functional group \( i \), mol/m³
- \( c_{\text{acid}} \): concentration of R-COOH groups, mol/m³
- \( D_{\text{PET}} \): mutual diffusion coefficient, m²/min
- \( D_{0,i} \): constant in \( D_i = D_{0,i} \exp(-E_{i,PET}/RT) M_i^{0.5}/\eta^{0.5} \), m²/min (mol/g)⁰.⁵ (Pa·s)⁰.⁵
- \( D_{T,i} \): constant in \( D_{i,PET} = D_{T,i} T \), m²/min/K
- \( E_{a,i} \): activation energy, kJ/mol
- \( E_{a,D} \): activation energy, diffusion, kJ/mol
- \( h \): polymer film thickness, mm
- \( I.V. \): intrinsic viscosity, dL/g
- \( k_{i,o} \): coefficient of Arrhenius equation
- \( k_j \): equilibrium constant
- \( k_{\text{LSQ}} \): mass transfer coefficient, m/min
- \( M_i \): number average of molecular weight, g/mol
- \( n \): finite element, \( j=1...n \)
- \( R \): ideal gas constant, J/mol/K
- \( T \): temperature, °C, K
- \( w_k \): weight, in LSQ
- \( x \): degree of polycondensation
- \( z \): spatial dimension
- \( \Gamma_j \): reaction term, mol/(m³/min)
- \( \eta \): viscosity, Pa·s
References


Flory, P.J., (1953), Principles of polymer chemistry. Cornell University Press


Rieckmann, Th., (1994), Polycondensation and recycling of PET fibres and other PET waste by continuous processes. 5th Conference on Man-Made Fibres, Beijing

Rieckmann, Th., (1995), Recycling of PET food grade quality on a commercial scale. In Chemical Fibers International 45

Rieckmann, Th., Rösner, F., and Völker, S., (1999), Mass transfer and volatilization of small molecules from molten poly(ethylene terephthalate). ECCE2, Montpellier, France, October 5-7