

University of Groningen

Reaction kinetics of polybutylene terephthalate polycondensation reaction

Darda, P. J.; Hogendoorn, J. A.; Versteeg, G. F.; Souren, F.

Published in:
 AIChE Journal

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
 Publisher's PDF, also known as Version of record

Publication date:
 2005

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Darda, P. J., Hogendoorn, J. A., Versteeg, G. F., & Souren, F. (2005). Reaction kinetics of polybutylene terephthalate polycondensation reaction. *AIChE Journal*, 51(2), 622-630.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Reaction Kinetics of Polybutylene Terephthalate Polycondensation Reaction

P. J. Darda, J. A. Hogendoorn, and G. F. Versteeg

Design and Development of Industrial Processes, Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.

F. Souren

DSM Research, P.O.Box 18, 6160 MD, Geleen, The Netherlands.

DOI 10.1002/aic.10360

Published online January 14, 2005 in Wiley InterScience (www.interscience.wiley.com).

The kinetics of the forward polycondensation reaction of polybutylene terephthalate (PBT) has been investigated using thermogravimetric analysis (TGA). PBT - prepolymer with an initial degree of polymerization of 5.5 was used as starting material. The PBT prepolymer was prepared from dimethyl terephthalate (DMT), and 1,4 - butanediol with 470 ppm wt (with respect to DMT) of tetrabutoxytitanate as catalyst. The process conditions in the TGA were such that the weight loss curves obtained from the TGA could be correlated uniquely and directly to the forward polycondensation reaction kinetics due to the absence of (1) mass transfer limitations in the removal of 1,4 butanediol from the melt, and (2) degradation reactions. It is shown that in the temperature range of 230–270°C, the forward polycondensation reaction can be expressed using second-order kinetics in terms of the hydroxyl end group concentration of the PBT polymer. © 2005 American Institute of Chemical Engineers AIChE J, 51: 622–630, 2005

Keywords: kinetics, polybutylene terephthalate, polycondensation, thermogravimetry

Introduction

Polybutylene terephthalate (PBT) is a thermoplastic elastomer used extensively as an engineering plastic. PBT has excellent mechanical and processing properties and is, therefore, used in the electronics and automotive industry, and also in consumer goods and films. Industrial production of polyesters like PBT proceeds via a condensation reaction and is carried out industrially in two steps: (1) prepolymerization, and (2) polycondensation.

During the prepolymerization step, monomers, such as dimethyl terephthalate (DMT), or terephthalic acid (PTA) undergo esterification reactions with diols like 1,4 butanediol (BDO) (in case of PBT) to form oligomers. Prepolymerization is carried out in a series of stirred reactors giving a prepolymer

with a degree of polymerization ranging from 4 – 10. The prepolymer reacts further to obtain high degrees of polymerization (≈ 100) during the actual polycondensation reaction. In this step the oligomers (with hydroxyl end groups, E_{OH}) formed during prepolymerization react giving diester groups (Z) with liberation of BDO (Figure 1).

The polycondensation reaction is highly reversible and, hence, removal via devolatilization of the volatile products, in this case the diol from the reaction mixture is an important factor in industrial reactors. Industrially, the polycondensation reaction is carried out between 230 – 240 °C using rotating disc contactors (RDC). RDCs provide a relatively large interfacial area, and are operated under vacuum of ≈ 1 mbar to enable rapid devolatilization in order to speed up the polycondensation process.¹ For the RDCs, calculations show that the forward polycondensation reaction can enhance the devolatilization mass-transfer rate with enhancement factors ranging from 1.5 – 5. Details of the mass-transfer calculations for computing enhancement factors will be presented in a forthcoming publica-

Correspondence concerning this article should be addressed to G. F. Versteeg at g.f.versteeg@ct.utwente.nl.

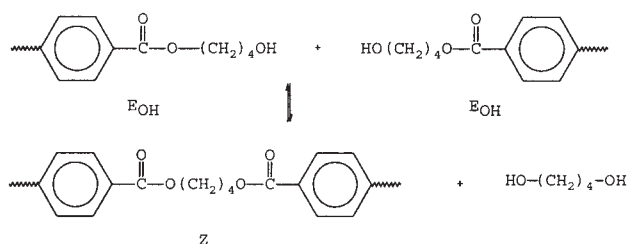


Figure 1. Polycondensation of PBT.

tion. In case of novel polycondensation reactors—like spinning disc contactors (SDC),² the mass-transfer coefficient is expected to be much higher than those typically encountered in RDCs. This means that the influence of the kinetics to the overall polycondensation devolatilization rate should not be neglected for the current RDCs and future SDCs. Therefore, in this study the kinetics of the forward polycondensation reaction of PBT has been studied.

To determine the rate constant for the forward polycondensation reaction for polyesters like poly(ethylene terephthalate) (PET), researchers have used various experimental methods like sealed tube experiments, semi-batch reactors,⁴ thin stagnant films,⁵ and thermogravimetric analysis.^{6,7,8} Pilati et al.⁹ have used model molecules to quantify the kinetics of the PBT polycondensation reaction.

In this study, we choose the method of thermogravimetric analysis because of its simplicity, the possibility to eliminate mass transfer resistances, direct applicability to the PBT polycondensation reaction and accuracy. Since thermogravimetric analysis can detect small changes in weight, the weight lost by the prepolymer during the polycondensation reaction is directly related to the forward rate of the polycondensation reaction as long as (1) internal and external mass-transfer limitations of BDO can be neglected, and (2) degradation/side reactions occur to a negligible extent. A summary of the application of thermogravimetric analysis for the determination of the rate constant in the formation of PET and polyethylene naphthanate (PEN) is shown in Table 1. The kinetics as reported in literature for PET and PEN have all been obtained in the presence of

mass-transfer limitations, although attempts have been made to correct for this.^{6,7,8} This study has first focused on the determination of process conditions for which the removal of BDO from the melt is not limiting the conversion rate anymore, that is, conditions for which the internal and external mass transfer resistances for the removal of BDO from the melt can be neglected. This has been realized by using very small quantities of prepolymer (to eliminate internal mass-transfer limitations) and high nitrogen gas flows (to eliminate external mass-transfer limitations). Once these conditions have been fulfilled and degradations reactions do not occur to any considerable extent, it is possible to derive the intrinsic forward polycondensation reaction kinetics directly and uniquely from the TGA results.

Experimental

Materials

The PBT prepolymer used in this kinetic study of the forward polycondensation reaction was prepared in a batch reactor as also used by the same authors for studying the equilibrium of this reaction.¹⁰ 440.7 g of DMT was prepolymerized with 257 g of BDO. Tetrabutoxytitanate (TBT) was used as catalyst in an amount of 0.207 g (470 ppm wt with respect to DMT). The prepolymerization stage was carried out at a pressure of 1 bar with a temperature rising from 110 – 235 °C in 120 min. In the second stage, polycondensation was carried out at a constant BDO partial pressure of 100 mbar at a temperature of 235 °C until the torque measurement system of the batch reactor indicated a constant value. The PBT prepolymer was finally removed from the bottom of the batch reactor by applying nitrogen overpressure at the top of the reactor. A detailed description of the experimental setup of the batch reactor is presented in Darda et al.¹⁰ The expected degree of polymerization obtained with this procedure is in the range of 4–10. Analysis of the prepolymer using different methods (see Appendix, and also reference¹⁰) made clear that the degree of polymerization of the prepolymer was equal to 5.4, the hydroxyl end group concentration 1.55 mole kg_{melt}⁻¹ (titration), and

Table 1. Thermogravimetric Analysis Applied to Study Kinetics of Polycondensation Processes for PET and PEN

Polyester	Temperature Range °C	Order of Forward Reaction with Respect to Reacting End Groups	Forward Polycondensation Rate Constant at 280°C	Activation Energy kJ mole ⁻¹	Remarks
PET, Spühler, Zimmerer and Renken ⁷	260–300	2	$5 \cdot 10^{-7} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	67	Various weights of prepolymer used for kinetic analysis using method of moments
PEN, Zimmerer, Amhred, Zierer and Renken ⁸	240–300	2	$3.5 \cdot 10^{-7} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	100	Mass transfer and kinetic constant described together by one lumped parameter—effective rate constant
PET, Rieckmann and Völker ⁶	267, 287, 307	3	$1.22 \cdot 10^{-10} \text{ m}^6 \text{ mol}^{-2} \text{ s}^{-1}$	75	Mass transfer coefficient and rate constant were estimated from weight loss data

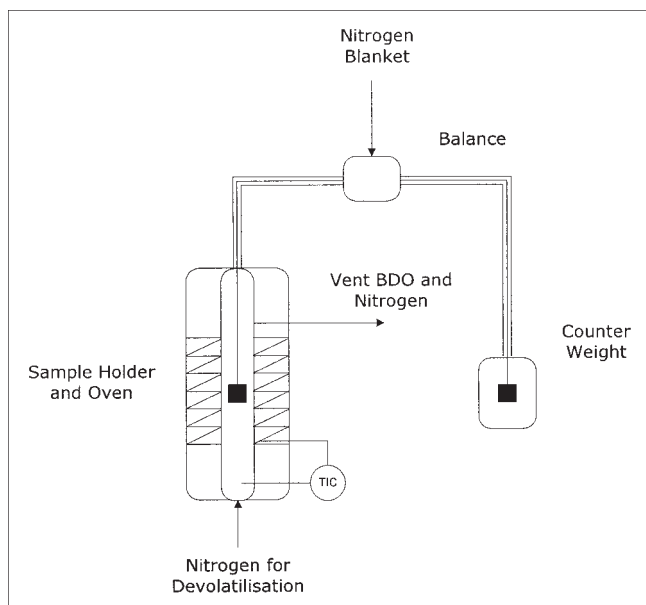


Figure 2. Setup of the TGA for studying the PBT polycondensation reaction kinetics.

the carboxylic end group concentration equal to $1.42 \cdot 10^{-4}$ mole $\text{kg}_{\text{melt}}^{-1}$ (also titration).

Thermogravimetric Analysis

The Thermogravimetric Analyzer (TGA) used for the determination of the polycondensation kinetics was a SETARAM B 85 Balance. The TGA (Figure 2) has a maximum load of 10 g, and an absolute sensitivity of ± 10 micrograms. The output of the TGA is a voltage signal. The TGA voltage signal was calibrated using standard weights ranging from 2 – 100 mg. The TGA consists of a balance across which the sample holder and the counter weight are hung. The sample holder is hung in a cylindrical oven maintained at a prescribed temperature, in this case ranging from 230 – 270 °C.

During the polycondensation reaction butanediol (BDO) is released. In the TGA nitrogen was used to remove devolatilized BDO from the PBT prepolymer reaction mixture. Nitrogen entered from the bottom of the sealed oven, carried away the BDO released from the polycondensation reaction and was subsequently vented. The top section of the balance was maintained under a nitrogen blanket, to force the reaction gases to leave through the vent. Mass-flow controllers regulated the flow of nitrogen into the oven and the flow of nitrogen that was used as blanket. The counter weight was placed in an enclosure to avoid the surrounding airflow affecting the reading of the TGA. A data acquisition system was used to log the dynamic voltage readings from which the weight of the TGA sample could be deducted.

In the TGA experiments, the amount of PBT prepolymer used ranged from 1 – 30 mg. In a typical TGA experiment, the oven was switched on and brought to the prescribed temperature. A thermocouple present below the sample holder indicated the temperature. A temperature controller that regulates the current flowing through a heating coil maintained the temperature inside the oven. Once the oven reached the desired

temperature, the nitrogen flow to the oven, and the nitrogen flow used for blanketing the balance were switched on at prescribed flow rates using mass flow controllers.

In order to get a blank reading of a sample holder, an empty sample holder was introduced in the oven. The two sample holders used in the TGA experiments are shown in Figure 3. The deeper sample holder (DSH) could hold PBT prepolymer amounts up to about 30 mg. For experimenting with small amounts of PBT prepolymer (down to ± 1 mg) a relatively flat sample holder was used (FSH). The sample holders were made of glass and could be used at temperatures up to 300 °C.

The readings corresponding to the empty sample holder gave a blank reference reading for the TGA. The sample holder was then removed from the oven, allowed to cool down to room-temperature and filled with the desired amount of PBT prepolymer. The filled sample holder was then hung back in the TGA and the oven (that was already at the desired reaction temperature). The difference between the blank reading and the initial reading of the filled sample holder represented the initial weight of PBT prepolymer. A blank reading was performed for each experiment to take into account the effect of the actual nitrogen flow and temperature as used during the experiment on the readings.

Relation between dynamic weight loss and forward reaction kinetics introduction

The relation between the TGA weight loss as a function of time and the forward polycondensation kinetics can be established if the rate of the polycondensation reaction can be correlated to the amount of hydroxyl end groups present in the PBT melt at any given instant. In the Appendix, the details of the PBT polycondensation reaction, and the relation between the weight loss of BDO and the hydroxyl end group concentration are described. During a TGA experiment, the weight of the prepolymer decreases because of the loss of volatile BDO from the prepolymer reactive melt. BDO coming from the PBT melt can stem from two sources:

(1) BDO initially present in the prepolymer: During the prepolymerization reactions of BDO with DMT a molar excess of BDO is used. Depending on the prepolymerization pressure, temperature and molecular weight of the prepolymer, some of the physically dissolved BDO is still present in the prepolymer at the beginning of the TGA experiment. The amount of physically dissolved BDO can be accounted for in the TGA

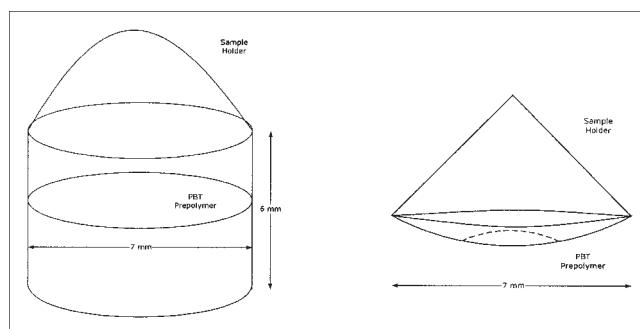


Figure 3. Two sample holders used in the in the TGA experiments.

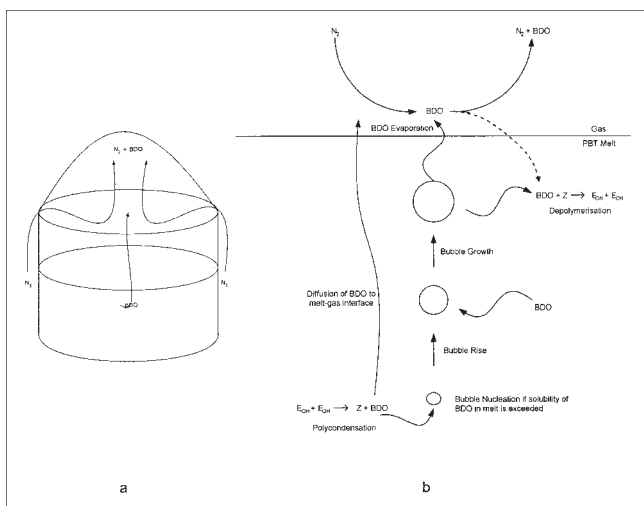


Figure 4. BDO related processes that can occur in sample holder during TGA experiments.

The goal is to realize process conditions in which only the polycondensation forward reaction determines the BDO removal rate.

experiments if this initial amount of BDO is known (See Appendix).

(2) BDO generated by the polycondensation reaction: During the PBT polycondensation reaction, two hydroxyl end groups of the prepolymer with an average degree of polymerization i (PBT i -mers) react reversibly to give a PBT $2i+1$ -mer and BDO: $E_{OH} + E_{OH} \leftrightarrow Z + BDO \uparrow$.

In the TGA a PBT prepolymer sample is subjected to a temperature above its melting point (≥ 230 °C) so that melt polycondensation occurs. Since the polycondensation reaction is highly reversible the removal of BDO from the melt is very important to prevent that BDO can react back with Z units and generate hydroxyl end groups. The intrinsic forward reaction kinetics can be derived if (1) BDO is removed directly and completely from the reactive melt once it is formed by the forward reaction, and (2) degradation reactions do not occur to any measurable extent. The fulfillment of these conditions are validated in the first part of the experimental program.

Background Internal and external mass-transfer resistances

In order to relate the TGA dynamic weight loss directly to the forward polycondensation reaction rate various mass transfer resistances that can occur during melt polycondensation have to be eliminated. When PBT prepolymer is present in a sample holder and is subjected to a temperature higher than 230 °C, the following (mass-transfer related) phenomena induced by the forward reaction can occur (Figure 4a and 4b).

- (1) Diffusion of BDO to melt-gas interface;
- (2) Nucleation of BDO bubbles in the melt;
- (3) Growth of BDO bubbles by diffusion of BDO from melt to gas in bubbles or surface of melt layer;
- (4) Rise of BDO bubbles to gas - PBT melt interface;
- (5) Depolymerization of PBT by BDO in melt (that is, backward polycondensation reaction);
- (6) Evaporation of BDO at gas - PBT melt interface;

- (7) Removal and carryover of BDO by nitrogen;
- (8) Dissolution of BDO back in the PBT melt.

Conditions to link the dynamic weight loss to the forward reaction kinetics

In order to ensure that the dynamic TGA weight loss corresponds uniquely, and directly to the forward polycondensation reaction rate, the following conditions must, thus, be satisfied:

(1) The weight loss caused by the initially present physically dissolved BDO is over and has been accounted for.

(2) The carrier nitrogen flow rate must be high enough to carry away all BDO evaporated from the melt, avoiding BDO to re-dissolve in the melt (that is, gas phase interface partial pressure of BDO must be near zero).

(3) The melt layer should be small enough to ensure that the BDO mass transfer rate by diffusion can be higher than the BDO generation rate from the forward polycondensation reaction (that is, the concentration of BDO in the melt should be near zero).

(4) The weight loss should reach a constant value at (near) complete conversion of the hydroxyl end groups. This is because the main degradation reactions (that is, diester scission and hydroxyl end group scission) are irreversible and lead to the formation of 1, 3 - Butadiene and Tetrahydrofuran,¹⁰ which are both volatile and on their occurrence a continuous weight loss should occur.

If condition 2 and 3 are fulfilled, the depolymerization (“backward”) reaction of BDO with the polymer will not occur because there will be a negligible concentration of BDO available in the melt. Also, since BDO will be removed virtually instantaneously from the melt, the forward reaction rate will be rate determining for the weight lost as a function of time if conditions 1 and 4 are also fulfilled. It seems logical to assume that condition 1 is satisfied once condition 2 and 3 are fulfilled as the amount of *initially* present physically dissolved BDO is relatively low (around 1 wt %, see appendix). If condition 2 and 3 are satisfied, the forward polycondensation kinetics is controlling the (dimensionless) dynamic weight loss of the prepolymer sample, so the initial amount of prepolymer and the nitrogen flow should not have any influence on the (dimensionless) TGA experimental results. The fulfillment of the earlier conditions 2, 3, and the absence of degradation reactions (condition 4) have been verified experimentally in the next section.

Results and Discussion

Preliminary devolatilization curves for determination required process conditions

In order to have a common basis of comparison for various TGA experiments the weight loss during the experiments was defined as

$$\% W_{L,t}^{Total} = \left(\frac{W_0^{Total} - W_t^{Total}}{W_0^{Total}} \right) 100 \quad (1)$$

Where W_0 and W_t were the initial and instantaneous weights of the PBT prepolymer sample, respectively.

During preliminary testing TGA weight loss curves as a function of time were obtained for 23 mg of PBT prepoly-

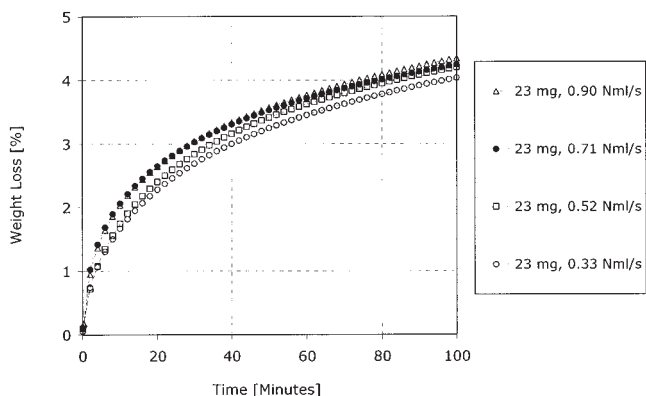


Figure 5. TGA results at various nitrogen flows at polycondensation temperature of 240 °C (The devolatilization curves represent the total weight lost during the polycondensation experiments).

mer placed in a deep sample holder (Figure 3, left picture). The temperature during PBT devolatilization was maintained at 240 °C. The carrier nitrogen flow rate was systematically increased from 0.33 to 0.90 Nmls⁻¹ to study the effect of the nitrogen flow rate on the BDO devolatilization rate (Figure 5). The BDO devolatilization rate increased, when increasing the nitrogen flow from 0.33 – 0.52 – 0.71 Nmls⁻¹. This indicated that for devolatilization in the range of carrier nitrogen flow rates of 0.33 – 0.71 Nmls⁻¹, the BDO gas-phase interface concentration was still not negligible. However, the devolatilization curves for 0.71 and 0.90 Nmls⁻¹ coincided indicating that a gas phase resistance was absent and the gas-melt interface concentration of BDO negligible, so condition 2 was fulfilled.

In order to investigate the effect of the amount of prepolymer used on the dimensionless weight loss curves, experiments were carried with varying amounts of PBT prepolymer ranging from 0.7 – 31.9 mg (Figure 6). Devolatilization experiments with 20 and 31.9 mg were done using deep sample holders (Figure 3, left), and for lower weights of initial prepolymer (6.3, 1.5 and 0.7 mg) the shallow sample holders (Figure 3, right) were used. During all these experiments, the temperature in the TGA oven was maintained at 230 °C, and the carrier nitrogen flow was maintained at 0.90 Nmls⁻¹ to ensure that external mass transfer was not limiting the BDO removal (condition 2).

The results obtained for various initial PBT prepolymer weights are shown in Figure 6. As the amount of PBT prepolymer was reduced from 31.9 to 1.5 mg, the dimensionless BDO devolatilization rate increased, meaning that BDO was not instantaneously removed from the melt and, consequently, condition 3 was not yet satisfied. On further reducing the amount of prepolymer from 1.5 mg to 0.7 mg of the rate of devolatilization was within the experimental accuracy, identical to the results of the 1.5 mg of experiment. The near coincidence of the devolatilization curves for 0.7 and 1.5 mg of prepolymer demonstrated that below 1.5 mg of prepolymer weight, the amount of prepolymer (and, thus, the mass transfer of BDO in the melt) did not influence the effective rate of devolatilization anymore, and besides, condition 2, also condition 3 was now fulfilled.

Thus, above a carrier nitrogen flow rate of 0.90 Nmls⁻¹ and below 1.5 mg of prepolymer weight, the removal of BDO from the melt and externally via nitrogen does not influence the results anymore, and condition 2 and 3 are fulfilled. The devolatilization curves then simply represent the intrinsic forward reaction kinetics of the forward PBT polycondensation reaction if condition 4 is also satisfied. Since both the degradation reactions are irreversible and lead to volatile products, on their occurrence PBT prepolymer would have lost weight continuously. Devolatilization curves for 0.7 and 1.5 mg of prepolymer (Figure 6) show that after about 40 min the total weight loss reached a constant value of about 8%. In the presence of degradation reactions the weight loss would have increased continuously. Hence, it can be concluded that the degradation reactions are negligible for the performed experimental conditions and duration of the experiment and condition 4 is also fulfilled.

In order to attribute the percentage total weight loss correctly to the polycondensation reaction rate, the amount of BDO stemming from the polycondensation reaction has to be distinguished from the initial weight loss caused by the initially present physically dissolved BDO in the starting PBT prepolymer (=1.1 wt %, see Appendix)

$$\%W_{L,t}^{\text{Chemical}} = \%W_{L,t}^{\text{Total}} - \%W_L^{\text{Physical}} = \%W_{L,t}^{\text{Total}} - 1.1\% \quad (2)$$

This dynamic chemical weight loss has been used in the actual determination of the forward polycondensation kinetics.

Determination of forward polycondensation kinetics

Devolatilization experiments to measure the kinetics of the forward polycondensation reaction were performed using 1 mg of prepolymer, a carrier nitrogen flow rate of 0.90 Nmls⁻¹, and the shallow sample holder (see Figure 3, right) to fulfill conditions 1–5. The, thus, obtained chemical weight loss curves are shown in Figure 7. In order to quantify the rate constant for the forward polycondensation reaction, the reaction was as-

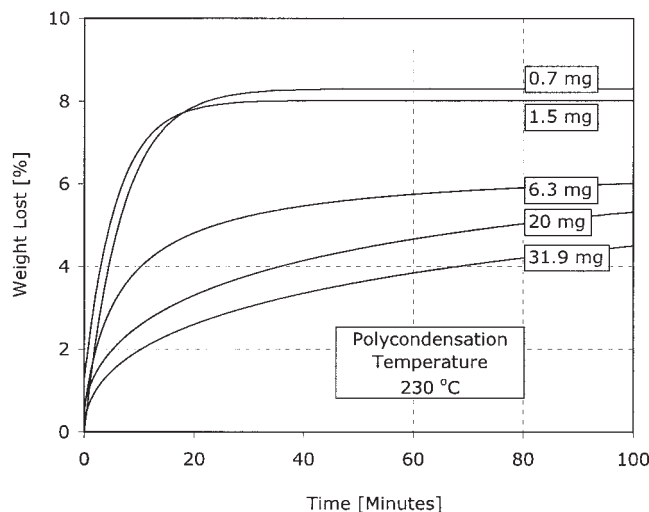


Figure 6. Devolatilization curves for TGA using various amounts of prepolymer at a polycondensation temperature of 230 °C.

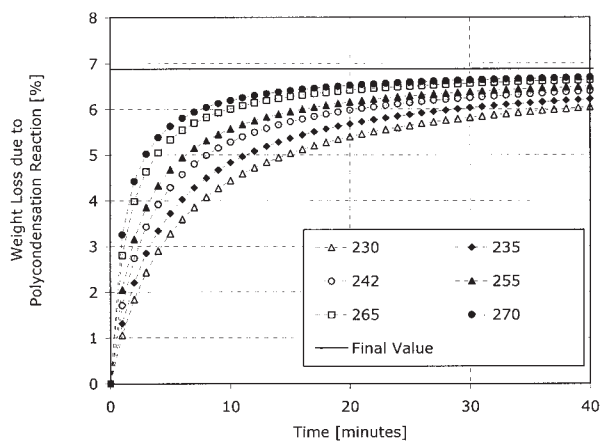


Figure 7. Chemical weight loss due to polycondensation reaction for various polycondensation temperatures (expressed in °C).

sumed to follow second-order kinetics.³ The rate of the reaction is then expressed by

$$R_Z = kC_{EOH,t}^2 \text{ mole kg}_{\text{melt}}^{-1} \text{ s}^{-1} \quad (3)$$

The rate of the depletion of hydroxyl end group concentration is given as

$$\frac{dC_{EOH,t}}{dt} = -2R_Z = -2kC_{EOH,t}^2 \quad (4)$$

Integrating the rate equation yields the time-dependent equation for the hydroxyl end group concentration as

$$\frac{1}{C_{EOH,t}} = \frac{1}{C_{EOH,0}} + 2kt \quad (5)$$

Using the final chemical weight loss of 6.9% the initial hydroxyl end group concentration can be calculated to be 1.53 mole kg_{melt}⁻¹ (see Appendix). Equation 5 can be rearranged to (see Appendix)

$$\frac{1}{C_{EOH,t}} = \frac{100 - \%W_{L,t}^{\text{Chemical}}}{100C_{EOH,0} - \frac{2}{0.09} \%W_{L,t}^{\text{Chemical}}} \quad (6)$$

Combining Eq. 5 and 6 gives the cumulative TGA chemical weight loss as a function of the initial hydroxyl end group concentration, second-order rate constant and time

$$\%W_{L,t}^{\text{Chemical}} = \frac{100C_{EOH,0}(2k)t}{\left(\frac{2}{0.09} \frac{1}{C_{EOH,0}}\right) + \left(\frac{2(2k)t}{0.09}\right) - 1} \quad (7)$$

An example of the experimental chemical weight loss and fitted weight loss is given in Figure 8. Figure 8 shows that the experimental chemical weight loss and second-order fitted

chemical weight loss match well. This seems to confirm the second-order kinetics assumption in terms of hydroxyl end group concentration for the forward polycondensation reaction.

The second-order kinetic rate expression was used to interpret the experimental data at various temperatures. The results for the second-order rate constant are given in Figure 9. To determine the activation energy and pre-exponential factor of the Arrhenius equation, $\ln k$ was plotted against $1/T$, where T is the temperature in K (Figure 9). The second-order rate expression for the forward polycondensation reaction can be given by

$$R_{EOH} = -2kC_{EOH,t}^2 = -1.15 \cdot 10^6 e^{-(84500/RT)} C_{EOH,t}^2 \text{ mole kg}_{\text{melt}}^{-1} \text{ s}^{-1} \quad (8)$$

The activation energy of 84.5 kJ mole⁻¹ obtained from this study compares reasonably well with the activation energy of the PET polycondensation reaction,^{6,7} although the absolute value of the forward reaction rate constant as found in this study is higher than the ones previously found for PET (up to a factor of ~100). The reason for this might be twofold: first the use and/or difference in catalyst (in the study of Rieckmann and Völker⁶ no catalyst was used, and in the study of Sphüler, Zimmerer and Renken⁷ a different (antimony) catalyst was used), and second, in the other studies -the authors of the respective articles also admit this- mass transfer limitations still play a role, and most probably have affected the determination of the rate constant, resulting in a too low reaction rate constant. In order to compare the currently obtained second-order rate constant for PBT melt polycondensation with the solid-state postcondensation (SSPC) second-order rate constant, the graph of $\ln k$ against $1/T$ was extended till 190 °C. The rate constant for the SSPC process, although lower than suggested by the melt polycondensation rate equation, does not differ substantially from this line (Figure 9). The difference in the value of the rate constant of SSPC, and that of this TGA experiments can be explained by the prevailing mass transfer limitations during the SSPC study, which are even more likely to occur than during melt polymerization.

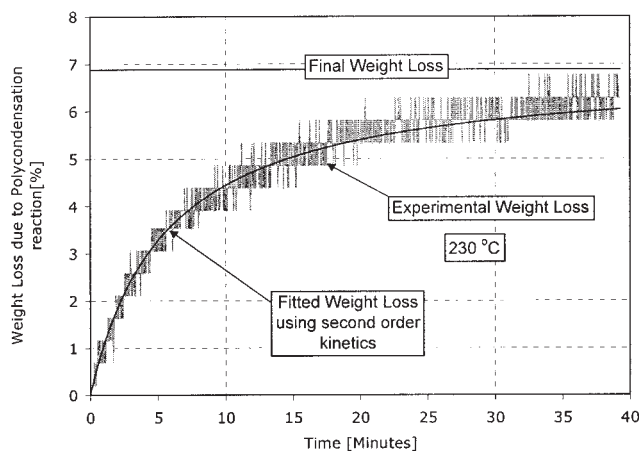


Figure 8. Chemical weight loss fitted to second-order polycondensation kinetics at a temperature of $T = 230$ °C, (with a rate constant of $9.23 \cdot 10^{-4} \text{ kg}_{\text{melt}}^{-1} \text{ s}^{-1}$).

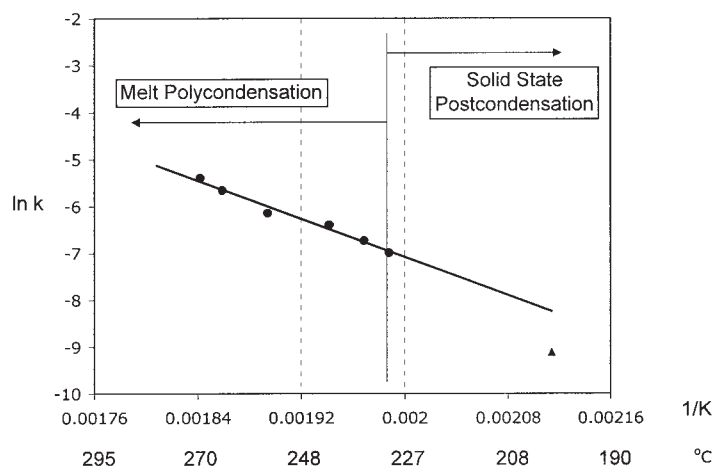


Figure 9. Arrhenius plot for the PBT Polycondensation reaction (▲ represents the rate constant for solid state post condensation (data supplied by DSM, Geleen, The Netherlands))

Conclusions

The intrinsic forward kinetics of the PBT polycondensation reaction has been studied using thermogravimetric analysis. First, an operating regime of the TGA was established in which mass transfer of BDO in the melt and from the melt was fast enough to assume a (near) zero concentration of the BDO in the prepolymer melt. Second, a correction for the initial amount of physically dissolved BDO in the prepolymer was applied. After also checking for the absence of degradation reactions, it was possible to uniquely link the observed time-dependent weight loss to the forward reaction rate of the polycondensation reaction. It appeared that the data could be well described using a second-order forward polycondensation reaction

$$R_{EOH} = -2kC_{EOH,t}^2 = -1.15 \cdot 10^6 e^{-(84500/RT)} C_{EOH,t}^2 \text{ mole kg}_{\text{melt}}^{-1} \text{ s}^{-1}$$

$$k = k_0 e^{-(E_a/RT)} = 5.73 \cdot 10^5 e^{-(84500/RT)} \text{ kg}_{\text{melt}} \text{ mole}^{-1} \text{ s}^{-1}$$

The activation energy of the forward polycondensation reaction was found to be 84.5 kJ mole⁻¹, which is in reasonably good agreement with the activation energy of the PET polycondensation reaction of ~70 kJ mole⁻¹ as previously reported in literature.^{6,7}

Notation

- C_{EOH} = concentration of EOH in PBT - BDO melt, mole kg_{melt}⁻¹
- $C_{EOH,0}$ = Initial hydroxyl end group concentration mole kg_{melt}⁻¹
- $C_{EOH,t}$ = hydroxyl end group concentration at any given time instant t mole kg_{melt}⁻¹
- C_{PBT} = Concentration of PBT in PBT - BDO melt, mole kg_{melt}⁻¹
- C_Z = Concentration of Z in PBT - BDO melt, mole kg_{melt}⁻¹
- i = Average degree of polymerization of PBT, mole kg_{melt}⁻¹
- k = Forward polycondensation rate constant, kg_{melt} mole⁻¹ s⁻¹
- k_0 = Pre - exponential factor in Arrhenius equation for forward polycondensation reaction, kg_{melt} mole⁻¹ s⁻¹
- MW_{BDO} = BDO molecular weight, kg mole⁻¹
- Mn = Number-average molecular weight of PBT, gram mole⁻¹
- MW_{EOH} = Molecular weight of a pair of hydroxyl end groups, gram mole⁻¹
- MW_Z = Molecular weight of the single unit of repeating diester group, gram mole⁻¹

- $N_{EOH,0}$ = Number of moles of hydroxyl end groups present initially in the PBT prepolymer sample
- $N_{EOH,t}$ = Number of moles of hydroxyl end groups in the PBT - prepolymer sample present at time t
- P_{BDO} = BDO partial pressure, mbar
- P_{BDO}^s = BDO saturated vapor pressure, mbar
- R_{EOH} = Rate of formation of hydroxyl end group EOH, mole kg_{melt}⁻¹ s⁻¹
- R_Z = Rate of formation of repeating diester group Z, mole kg_{melt}⁻¹ s⁻¹
- T = Polycondensation temperature, K
- t = Polycondensation reaction time, s
- \hat{V}_{BDO} = molar volume of BDO, m³ mole⁻¹
- \hat{V}_{EOH} = Molar volume of hydroxyl end group in PBT, m³ mole⁻¹
- \hat{V}_{PBT} = Molar volume of complete PBT molecule, m³ mole⁻¹
- \hat{V}_Z = Molar volume of repeating diester group in PBT, m³ mole⁻¹
- W_0 = Initial weight of PBT prepolymer sample, mg
- W_t = Weight of PBT prepolymer sample at any given time instant t , mg
- % W_L = Percentage weight loss
- % $W_{L,t}$ = Percent age weight loss of PBT prepolymer sample at any given time instant t
- X_{BDO} = BDO mass fraction in PBT - BDO melt
- x_{PBT} = Mass fraction of PBT in PBT - BDO melt

Literature Cited

- Cheong SI, Choi KY. Modeling of continuous rotating disk polycondensation reactor for the synthesis of thermoplastic polyesters. *J. Appl. Polym. Sci.* 1996;61:763.
- Burns JR, C. Ramshaw C, Jachuck RJ. Measurement of liquid film thickness and determination of spin - up radius on a rotating disc using electrical resistance technique. *Chem.Eng.Sc.i.* 2003;58:2245.
- Challa G. Formation of P.E.T by Ester Interchange. *Makromol. Chem.* 1960;38:138.
- Tomita K. Studies of the Formation of P.E.T.: 1. Propagation and Degradation Reactions in the Polycondensation of bis (2-Hydroxyethyl) Terephthalate. *Polymer.* 1973;14:50.
- Pell TM, Davis TG. Diffusion and Reaction in Polyester Melts. *J.Polym.Sci.Polym. Phys. Ed.*, 1973;11:1671.
- Rieckmann T, Völker S. Micro - kinetics and mass transfer in poly (ethylene terephthalate) synthesis. *Chem. Eng. Sci.* 2001;56:945.
- Spühler C, Zimmerer W, Renken A. Microgravimetric determination of polycondensation kinetics. *DECHEMA Monographs*, 1998;134: 587.
- Zimmerer W, Amhred E, Zierer D, Renken A. The influence of mass transfer on polycondensation kinetics. *ECCEI, Florence.* 1997.
- Pilati R, Manaresi P, Fortunato B, Munari A, Passalacqua V. Formation of poly(butylene) terephthalate: Growing reactions studied by model molecules. *Polymer.* 1981;22:799.

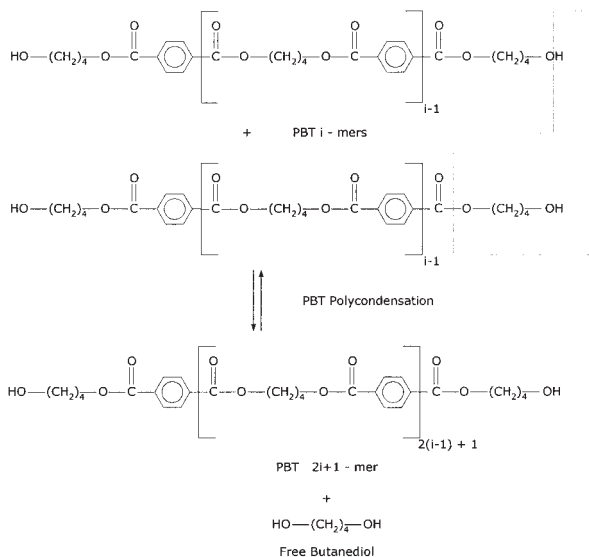


Figure A1. PBT polycondensation reaction.

10. Darda PJ, Hogendoorn JA, Molenkamp T, Versteeg GF. Determination of PBT polycondensation reaction equilibrium constant. In polymer reaction engineering V, macromolecular symposia 1, Wiley-VCH, Weinheim, 2004:275-291.

Appendix

Relation between degree of polymerization and hydroxyl end group concentration

In a PBT melt with DP of i , PBT chains of varying length are present. However, in this case the concept of an average degree (DP) of polymerization has been used to study the polycondensation reaction rate. This means that all PBT chains are assumed to have the same length as suggested by the DP.

PBT chains with a DP of i (PBT _{i}) consist of $i - 1$ PBT repeating units (Z) and two hydroxyl end groups. The two hydroxyl end groups (E_{OH}) consist of one benzene ring and two groups, as shown in Figure A1. The number averaged molecular weight of PBT is given by the sum of the molecular weights of $i - 1$, Z groups ($Mw_Z = 220 \text{ gram mole}^{-1}$) and two E_{OH} end groups ($Mw_{E_{OH}} = 310 \text{ gram mole}^{-1}$).

$$Mn = 220(i - 1) + 310 \quad (\text{A1})$$

The concentrations of PBT, Z, and E_{OH} are normally expressed in terms of moles of species present per kg of melt. If the mass fraction of PBT chains in the melt (x_{PBT}) is known then the PBT concentration in mole $\text{kg}_{\text{melt}}^{-1}$ can be deduced. The concentration of PBT is given by the expression

$$C_{PBT} = \frac{1000x_{PBT}}{220(i - 1) + 310} \quad (\text{A2})$$

Since every mole of PBT chain consist of $i - 1$ moles of Z and two moles of E_{OH} , the concentration of Z and E_{OH} is, respectively given by

$$C_Z = \frac{1000x_{PBT}(i - 1)}{220(i - 1) + 310} \quad (\text{A3})$$

$$C_{E_{OH}} = \frac{2000x_{PBT}}{220(i - 1) + 310} \quad (\text{A4})$$

This means that once the initial concentration of hydroxyl groups is known the initial DP can be calculated using Eq. A4.

Determination of initial concentration of hydroxyl end groups from experimental results

The forward polycondensation reaction proceeds by the reaction of hydroxyl end groups to give the PBT diester linkages (Z groups). Every mole of BDO formed corresponds to two moles of hydroxyl end groups reacted and one mole of diester linkages formed. With increasing number of diester linkages and decreasing hydroxyl end group concentration, the degree of polymerization of PBT also increases. If for the forward polycondensation reaction: $E_{OH} + E_{OH} \rightarrow Z + BDO \uparrow$, the initial number of moles of hydroxyl end groups is known ($N_{E_{OH},0}$), the number of moles of hydroxyl end group at any given time instant ($N_{E_{OH},t}$) can be calculated from the chemical weight lost by the melt using

$$N_{E_{OH},t} = N_{E_{OH},0} - \frac{2}{0.09} (W_0^{\text{Chemical}} - W_t^{\text{Chemical}}) \quad (\text{A5})$$

Where 0.09 kg/mole is the molecular weight of BDO. The term $2/0.09 (W_0^{\text{Chemical}} - W_t^{\text{Chemical}})$ corresponds to twice the number of moles of BDO lost by the prepolymer during devolatilization - which is the same as the number of moles of hydroxyl end groups reacted when the PBT prepolymer weight decreases from an initial value to the dynamic value. The concentration of hydroxyl end groups at any time instant ($C_{E_{OH},t}$) expressed in $\text{mol/kg}_{\text{melt}}$ is obtained by dividing the dynamic number of moles of hydroxyl end groups by the weight of PBT prepolymer at that instant

$$C_{E_{OH},t} = \frac{N_{E_{OH},t}}{W_t^{\text{Chemical}}} \quad (\text{A6})$$

Substituting the value of $N_{E_{OH},t}$ from Eq. A5 yields

$$C_{E_{OH},t} = \frac{N_{E_{OH},0} - \frac{2}{0.09} (W_0^{\text{Chemical}} - W_t^{\text{Chemical}})}{W_t^{\text{Chemical}}} \quad (\text{A7})$$

$C_{E_{OH},t}$ can then be rewritten as

$$C_{E_{OH},t} = \frac{N_{E_{OH},0}}{W_0^{\text{Chemical}}} \left(\frac{W_0^{\text{Chemical}}}{W_t^{\text{Chemical}}} \right) - \frac{2}{0.09} \left(\frac{W_0^{\text{Chemical}} - W_t^{\text{Chemical}}}{W_0^{\text{Chemical}}} \right) \left(\frac{W_0^{\text{Chemical}}}{W_t^{\text{Chemical}}} \right) \quad (\text{A8})$$

Which yields the relation between, $C_{E_{OH},t}$, $C_{E_{OH},0}$ and $\% W_{L,t}^{\text{Chemical}}$ - the TGA percentage chemical weight loss:

$$C_{E_{OH},t} = \frac{C_{E_{OH},0} - \frac{2}{0.09} \left(\frac{\% W_{L,t}^{Chemical}}{100} \right)}{1 - \left(\frac{\% W_{L,t}^{Chemical}}{100} \right)} \quad (A9)$$

At near 100% conversion of the forward polycondensation reaction virtually all hydroxyl end groups are consumed in the PBT melt. As the total observed weight loss was 8.0% during the experiments (independent on temperature) and the initial weight fraction of BDO was 1.1% (see later), the final chemical weight loss can be determined at 6.9% for a (near) complete

consumption of hydroxyl end groups. This means that for near 100% conversion Eq. A9 can be written as

$$0 = \frac{C_{E_{OH},0} - \frac{2}{0.09} \left(\frac{6.9}{100} \right)}{1 - \left(\frac{6.9}{100} \right)} \quad (A10)$$

This yields an initial hydroxyl end group concentration of 1.53 moles $\text{kg}_{\text{melt}}^{-1}$.

On the basis of the Flory–Huggins theory, it is possible to estimate the amount of BDO physically “dissolved” in the initial prepolymer using the following equation.¹⁰

$$x_{BDO} = \frac{P_{BDO}}{P_{BDO}^s \exp \left[\chi + \left(1 - \frac{\hat{V}_{BDO}}{(i-1)\hat{V}_Z + 2\hat{V}_{EOH}} \right) \right] \left(\frac{0.22i + 0.09}{0.09} \frac{\hat{V}_{BDO}}{(i-1)\hat{V}_Z + 2\hat{V}_{EOH}} \right)} \quad (A11)$$

For the conditions of the preparation of the prepolymer, this results in $x_{BDO} = 0.011$ wt % and $x_{PBT} = 0.99$ wt %. Using relation A4 for the hydroxyl end group concentration, the initial degree of polymerization is calculated to be 5.5, and the initial diester group concentration is calculated to be 3.42 mole $\text{kg}_{\text{melt}}^{-1}$ using relation A3.

(Chemical) Analysis starting material

Using dilute viscosimetry, DSM determined the initial degree of polymerization of the starting material to be 5.4,

which is well in line with DP as determined in the previous paragraph. DSM also determined the hydroxyl end group concentration and carboxylic end group concentration for the prepolymer, and these were equal to 1.55 (titration procedure) and $1.42 \cdot 10^{-4}$ mole $\text{kg}_{\text{melt}}^{-1}$ (titration procedure), respectively.

Manuscript received Jan. 5, 2004, and revision received June 24, 2004.