

The Synthesis of Poly(butylene terephthalate) from Terephthalic Acid, Part I: The Influence of Terephthalic Acid on the Tetrahydrofuran Formation

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ABSTRACT: An in depth study is performed on the origin of and influences on the formation of tetrahydrofuran (THF) during the first stage of the terephthalic acid (TPA) based synthesis of poly(butylene terephthalate) (PBT). Although many improvements on the synthesis process of PBT have been reported in literature to suppress this undesired side reaction, only few studies reported on the actual mechanism of the THF formation, which is not completely understood. Low molecular weight compounds

have been used to model the side reactions occurring during the polymerization reaction. It could be concluded that, in contrast to previous reportage, only the THF formation from the monomer, 1,4-butanediol, is directly influenced by the use of TPA as a starting material for the production of PBT. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2435–2444, 2009

Key words: polyesters; synthesis; esterification

INTRODUCTION

Poly(butylene terephthalate), PBT, was introduced commercially in 1970, 17 years after poly(ethylene terephthalate), PET. It easily obtained its place in the engineering plastic market with a current annual world production exceeding 800 ktonnes. PBT owes its success to its fast crystallization rate compared to PET, which makes it suitable for injection molding applications.¹ Nowadays, a broad range of pure and modified PBT grades are available, as well as a whole spectrum of PBT blends that are widely applied in the automotive and electric/electronic industries.² PBT is generally prepared by a relatively expensive polycondensation of dimethyl terephthalate (DMT) and 1,4-butanediol (BD), accompanied by the production of significant amounts (14 ktonnes per annum) of tetrahydrofuran (THF) as a side product.^{1,2} Hence, synthesizing PBT via a less expensive and more atom efficient route would imply a major economic advantage.

Various studies on the synthesis of PBT from terephthalic acid (TPA) and BD as a cheaper alterna-

tive for the DMT-based process have been reported.^{3–6} The major drawback of the TPA-based route and the main reason the DMT-based route is still used in most commercial plants is that approximately twice the amount of tetrahydrofuran (THF) is formed as a waste product, when TPA instead of DMT is used as a monomer for the synthesis of PBT. Consequently, to make the TPA-based synthesis of PBT more lucrative than the currently used DMT process, it is essential to reduce the amount of THF formed during the polymerization process.⁷

A lot of research has already been performed to decrease the amount of THF formed during the polymerization for both the DMT and TPA route to PBT by means of optimizing the process conditions (temperature, monomer ratio, set off of the second stage, continuous processes), the use of new catalyst mixtures and the addition of organic and inorganic salts.^{3–6,8–13} In spite of the results and conclusions of all these studies, many questions remain unanswered and some assumptions concerning the mechanism of the THF formation during PBT synthesis are still unproven.

Here we report on the different processes that result in THF formation during the first stage of the polycondensation of PBT. To simulate the conditions during the first stage of the PBT synthesis as accurately as possible, 3-chlorobenzoic acid (3-CIBA), with a pK_a and a Hammett- σ value very

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similar to that of TPA, was used as a monofunctional model for TPA and methyl 3-chlorobenzoate (3-CIBM) was used as a monofunctional model for DMT.

EXPERIMENTAL

General considerations

3-chlorobenzoic acid (3-CIBA), 4-chlorobenzoic acid (4-CIBA), and 3-chlorobenzoyl chloride were used as received from VWR International B.V. (Amsterdam, The Netherlands). Butanediol (BD), methyl 3-chlorobenzoate (3-CIBM), and titanium tetra n-butoxide ($\text{Ti}(\text{O}i\text{Bu})_4$) were purchased from Acros Organics (Geel, Belgium). Benzoic acid (BA), 2,4,6-trichlorobenzoic acid (2,4,6- Cl_3BA) and 2,6-dichlorobenzoic acid (2,6- Cl_2BA) were obtained from Sigma Aldrich (Zwijndrecht, The Netherlands). All chemicals were used without further purification. Both 4-hydroxybutyl 3-chlorobenzoate (HBB) and butane-1,4-diyl bis(3-chlorobenzoate) (BDB) were synthesized according to literature procedures.¹⁴ Sample preparation was carried out in a Braun MG-150 GI glove box. ^1H -NMR spectra were recorded on a Varian Gemini-2000 300 MHz NMR-spectrometer or a Varian Mercury-Vx 400 MHz NMR-spectrometer. GC measurements were performed using a Hewlett-Packard 5890 series II apparatus containing an Ultra 1, silicone type of column (25 m \times 0.32 mm) and a flame ionization detector (FID).

Model reactions

In the glove box 24 mm \times 150 mm threaded glass reaction vessels were charged with the reagents and closed with gas-tight PTFE caps. In a typical reaction, 3-CIBA (1.0 g, 6.0 mmol) and BD (0.58 g, 6.0 mmol) and 0.1 mol % $\text{Ti}(\text{O}i\text{Bu})_4$ catalyst were used. Outside the glove box, the vessels were placed in an electrically heated aluminum block of the reactor (STEM 10 place Omni-Reactor Station) and were heated to $180^\circ\text{C} \pm 0.5^\circ\text{C}$. The tops of the reaction vessels were cooled with a water-cooled condenser lit. The reaction mixture was stirred at 500 rpm using magnetic stirrer bars. After set reaction times,

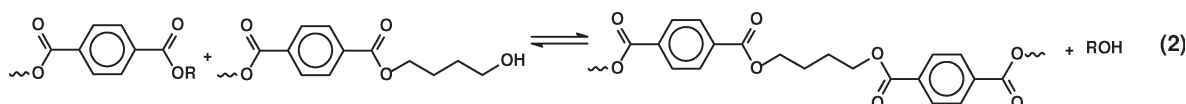
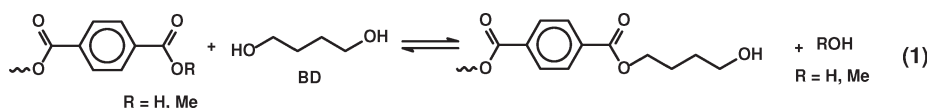
the samples were removed from the heating block and cooled in an ice bath. The first sample was drawn when the reaction mixture reached 180°C (an average time of 30 minutes).

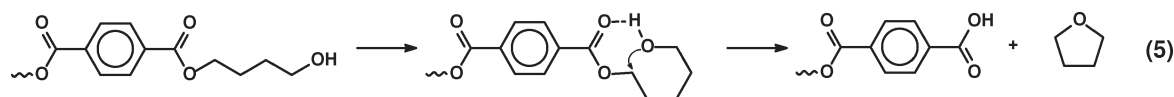
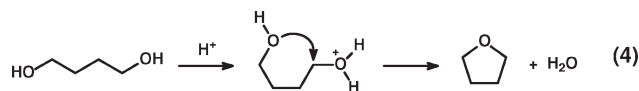
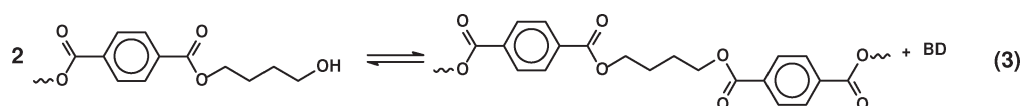
Sample analysis

The conversion of acid was determined using ^1H NMR (chloroform- d_1) by the comparison of the integral of the *ortho*-protons of the benzene ring of 3-CIBA (resp. 8.04 ppm and 7.96–7.92 ppm) with the integral of the corresponding protons of the formed esters (respectively 7.99 ppm and 7.92–7.88 ppm). The ratio of HBB : BDB was determined from the integration of the α -protons of the ester bond (4.44–4.33 ppm). As the *ortho*-protons of the benzene ring of 3-CIBM are not distinguishable from the ones of HBB and BDB, the conversion of the methyl ester was determined by comparison of the integration of the α -protons of the ester bond (4.44–4.33 ppm) with the signal for the protons of BD and HBB next to the hydroxyl functionality (3.72–3.67 ppm for HBB and 3.68–3.63 ppm for BD, respectively). Low concentrations of 3-CIBA were determined by titration of a methanol solution of the reaction mixture with a 0.02 N solution of NaOH in methanol with bromothymol blue as an indicator. The THF content of the reaction mixtures was determined by gas chromatography (GC).

RESULTS AND DISCUSSION

PBT is synthesized via melt polymerization in a two-step process. During the first step DMT or TPA is reacted with an excess of BD at atmospheric pressure to afford oligomers containing hydroxybutyl ester end-groups. In the second stage of the reaction vacuum is applied, and the temperature is raised to remove the excess of BD, resulting in high molecular weight product eqs. (1)–(3).² There is basically no difference in the second stage of the polymerization process between the TPA- and DMT-based routes. To study the differences between both routes, therefore, we only need to look at the first stage of the polymerization process.





One of the most convenient ways to study the (trans)esterification and THF formation is by using monofunctional models for TPA and DMT, although there are certain limitations. For example, the model compounds are completely soluble in the reaction medium at the temperatures commonly used for the first stage of the polymerization process (150–210°C), whereas TPA is not. If only the dissolved fraction of TPA is able to react, it should be assumed that the dissolution of TPA is not the rate-limiting step in the polycondensation process. As we will demonstrate later, this is not the case. Another point of concern is the reactivity of the model compound. In most of the previously reported model studies on the first step of the PBT synthesis benzoic acid (BA) is used as a monofunctional model molecule for TPA.^{14–20} Since it is believed that THF formation out of BD is acid-catalyzed, the pK_a of the carboxylic acid used as TPA-model is very important. This was also recognized by Banach et al.,⁹ who chose based on Hammett- σ values, 4-chlorobenzoic acid (4-CIBA) as a monofunctional model substrate for TPA. Although this choice implied an improvement with respect to benzoic acid, the pK_a and Hammett- σ value of 4-CIBA still deviate considerably from the values of TPA (3.75 and 0.45, respectively). The pK_a and Hammett- σ value of 3-chlorobenzoic acid (3-CIBA : 3.83 and 0.37, respectively) are considerably closer to TPA than the corresponding values of 4-CIBA.²¹ Hence, in consideration of the electronic effects of the substituents on the benzene ring, the 3-CIBA should be an even more realistic model in terms of chemical reactivity than the 4-CIBA. This was confirmed by an experiment where the three monofunctional acids, BA, 4CIBA, and 3-CIBA, were reacted separately with one equivalent of BD (with or without 0.1 mol % $\text{Ti}(\text{O}i\text{Bu})_4$), which showed that 3-CIBA was consumed considerably faster than the other two carboxylic acids. Despite the limitations the used model systems have, they proved to be very useful to get more insight in the processes governing the THF formation during the PBT synthesis.

There are two reactions responsible for the THF formation during the synthesis of PBT. While acid-catalyzed dehydration of BD to THF is the major source of THF in the TPA-based process, both the DMT- and TPA-based processes can undergo backbiting of the hydroxybutyl end groups of the polymer to form an acid end group and THF [eqs. (4) and (5)]. To understand the process of THF formation during the PBT synthesis better and to find a way to minimize this undesired side reaction, it is important to first investigate the different factors influencing the two reactions shown in eqs. (4) and (5) independently.

THF from the dehydration of BD

The dehydration of BD is generally described in literature as an acid-catalyzed S_N2 reaction,^{1–3,15,22,23} which already explains why more THF is formed in the TPA-based route to PBT than when the dimethyl ester is used [eqs. (4) and (5)]. The acidic monomer insuperably catalyzes the THF formation from the co-monomer, BD. In the absence of an acid, practically no THF is formed when BD is heated for 300 minutes at 180°C. Likewise and in accordance with the literature, it was found that the polymerization catalyst $\text{Ti}(\text{O}i\text{Bu})_4$ has no significant influence on the THF formation from BD.¹⁵ When a catalytic amount (3 mol %) of a strong Brønsted acid like H_2SO_4 was added, after 5 hours at 180°C the major part (89 mol %) of the BD was dehydrated to THF. Conversely, 3 mol % of the weak acid 3-CIBA only afforded small quantities of THF (2.8 mol %) for the same reaction time and temperature. Notwithstanding the fact that dissolution of TPA in the reaction mixture is relatively slow, a considerably larger amount of the weak acid is expected to be present throughout the major part of the reaction, which is assumed to have a significant impact on the total amount of THF formed. To verify this assumption, the influence of the addition of an equimolar amount of weak Brønsted acid to BD, was studied. For this experiment, two bulky carboxylic acids (2,6-

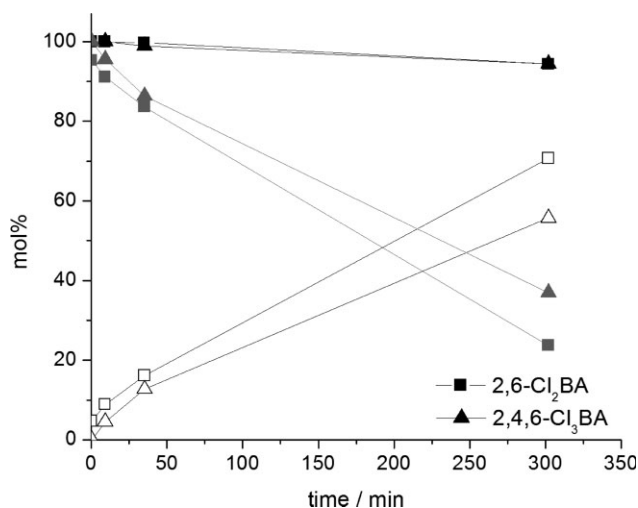


Figure 1 Mole fraction of 2,6-Cl₂BA, 2,4,6-Cl₃BA (both solid black symbols), BD (gray symbols), and THF (open symbols) with time for the reaction of BD in the presence of 1 equivalent of either 2,6-Cl₂BA (squares) or 2,4,6-Cl₃BA (triangles) at 180°C.

dichlorobenzoic acid (2,6-Cl₂BA) and 2,4,6-trichlorobenzoic acid (2,4,6-Cl₃BA)) were chosen that have an acidity comparable to 3-CIBA but are almost incapable to react with BD since the nucleophilic attack is impeded by steric hindrance caused by the ortho-chloro substituents. Figure 1 shows that only 6 mol % of both acids have reacted with BD after 300 minutes, whereas 55 and 70 mol % of the original amount of BD has been converted to THF for 2,6-Cl₂BA and 2,4,6-Cl₃BA, respectively. This high amount of THF clearly demonstrates that for weak acids the concentration affects the rate of BD dehydration. Hence, it is important that during the PBT synthesis TPA is esterified with BD as fast as possible. As expected, addition of 3 mol % of methyl 3-chloro-benzoate (3-CIBM), the monofunctional model molecule for DMT, to BD afforded practically the same amount of THF than without its addition, indicating that indeed an acid is required to catalyze the formation of THF from BD. Consequently, for the DMT-based process to PBT, this reaction will initially hardly play a role.

The formation of THF from BD is unavoidable when TPA is used for the synthesis of PBT. To decrease the formation of this undesired byproduct, an optimization of the reaction parameters, influencing the kinetics of this side reaction and of the polycondensation reaction, is the only way to success.

THF from the cyclization of the hydroxybutyl end groups

The hydroxybutyl end-groups of the polymer chains form the second source of THF during the synthesis of PBT [eq. (5)]. Whether or not this backbiting pro-

cess is an acid-catalyzed reaction is still a matter of debate.^{1-4,15,23} To assess its mechanism we studied the backbiting reaction during a transesterification reaction of 4-hydroxybutyl 3-chlorobenzoate (HBB) in both the absence and presence of Ti(OBu)₄ as transesterification catalyst (Figure 2). The amount of 3-CIBA produced during the titanium-catalyzed reaction is significantly lower than the amount of THF formed and stays more or less constant throughout the reaction, which demonstrates that Ti(OBu)₄ effectively catalyzes the esterification reactions of 3-CIBA with BD or HBB [eqs. (1) and (2)]. Unfortunately, this makes it impossible to determine whether the THF originates from HBB or BD as small quantities of 3-CIBA and BD are continuously present in the reaction medium. In the absence of

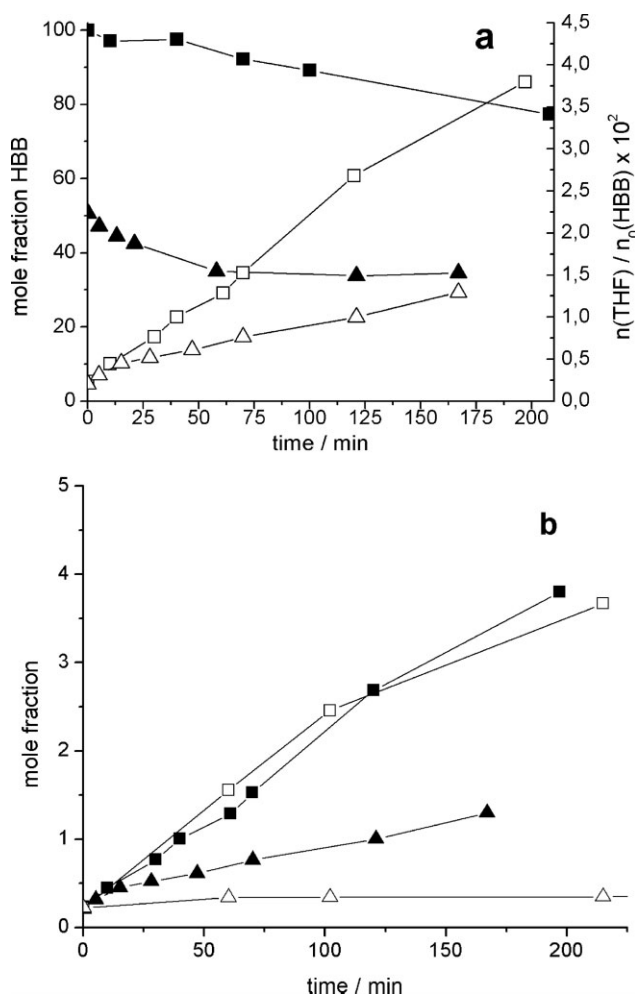


Figure 2 Decrease of the mole fraction of HBB (solid symbols) and increase of the mole fraction of THF with respect to HBB (n = number of moles) (open symbols) in time during the heating of HBB to 180°C in the presence of 0.1 mol % of Ti(OBu)₄ (▲ and Δ) and without catalyst (■ and □) (a) and the increase of the mole fraction of 3-CIBA (open symbols) and THF (solid symbols) for the same reaction, again in the presence of 0.1 mol % of Ti(OBu)₄ (▲ and Δ) and without catalyst (■ and □) (b).

Ti(OBu)₄, 3CIBA and THF are formed in equimolar amounts, and their formation seems to follow a linear trend according to eq. (5). This is an indication that the THF formed originates solely from backbiting of HBB.

It is not inconceivable that the THF formation by backbiting of the hydroxybutyl end groups takes place both by an acid-catalyzed and by a noncatalyzed mechanism. Proving the existence of one mechanism, does not rule out the presence of the other. To demonstrate the existence of the acid-catalyzed THF formation mechanism from HBB, the latter has to be heated in the presence of an acid while transesterification affording BD, the second source of THF, should be prevented. To achieve this, instead of HBB, a mixture of HBB and a 10-fold excess of butane-1,4-diyl-bis(3-chloro-benzoate) (BDB) was used. According to Le Chatelier's principle, the equilibrium of eq. (3) will then strongly shift to the left. This reaction was performed both with and without an equimolar amount of 2,6-dichloro-benzoic acid (2,6-Cl₂BA) with respect to HBB. The results presented in Figure 3 show that, due to the excess of BDB present in the reaction mixture, for both reactions only a small quantity of BD is formed. In spite of the addition of 1 equivalent of 2,6-Cl₂BA to HBB, the amount of THF increased with only a factor 2.5 in comparison with the same reaction carried out in the absence of 2,6-Cl₂BA (Figure 3). This increase is negligible when it is compared with the effect of the addition of 1 equivalent of 2,6-Cl₂BA to BD: after 300 minutes, 70% of the original amount of BD is converted to THF. It is even possible to assign the relatively small extra amount of THF formed (1.5 mol % after 240 minutes) completely to the acid-catalyzed dehydration of the little amount of BD still present in the reaction mixture. Consequently, from this result (Figure 3) it can be concluded that the acid-catalyzed backbiting reaction of the hydroxybutyl end groups is negligible and that during PBT synthesis the production of THF from the hydroxybutyl ends will almost completely proceed via a nonacid-catalyzed backbiting mechanism.

Although the acid-catalyzed backbiting reaction of HBB is not observed in the experiments previously described, it is a mistake to assume that this reaction does not exist at all. It could be argued that the THF formation from the protonated HBB would be even more easily compared with the backbiting reaction from the unprotonated ester, as the α -carbon of the latter is less electrophilic. Since 3-CIBA is a relatively weak acid, the fraction of protonated ester is very small compared with the neutral HBB. Hence, the statistical probability that the neutral HBB will form THF via the cyclic intermediate as proposed by Pilati et al.¹⁵ [eq. (5)] is considerably higher than the probability that it will happen via the protonated ester,

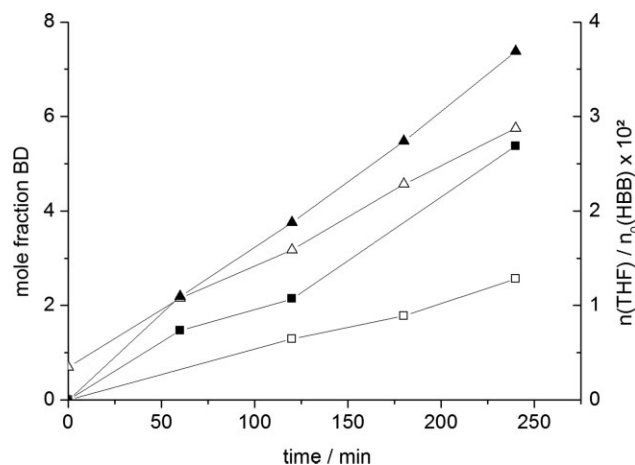


Figure 3 Formation of BD (solid symbols) and THF (open symbols) as a function of time during the heating of HBB + 10 BDB at 180°C without catalyst (■ and □) and in the presence of 1 equivalent of 2,6-Cl₂BA (▲ and △).

even though the latter would possibly form THF more easily.

BD dehydration versus HBB backbiting to THF

In the next section the importance of both routes to THF formation during the DMT- and TPA-based process to PBT will be discussed on the basis of model reactions. Figure 4(a) shows the decrease of 3-CIBA and BD as a result of esterification and the formation of THF in time. The decrease of BD is not equal to that of 3-CIBA, as the reactions displayed in eqs. (2) and (3) start to play a role as soon as HBB is formed. In the beginning of the reaction, the rate of THF formation is high. This is in particular due to the acid-catalyzed dehydration of BD. After approximately 50 minutes, 80% of the original amount of 3-CIBA was converted, and the rate of THF formation starts slowing down. From that moment on, the curve shows a linear increase in time and HBB becomes the main source of THF [eq. (5)]. Even after all 3-CIBA was converted (150 minutes), THF continues to be formed via the backbiting process eq. (5).

To study the DMT-based synthesis of PBT, 3-CIBM was used as a model compound for DMT and was reacted with BD to study the difference in THF formation in comparison with the model for the TPA-based process. The titanium-catalyzed transesterification of the methyl ester is a very fast reaction [Fig. 4(b)]. Most of the 3-CIBM has already reacted before the carousel-reactor reached 180°C. In spite of the high reaction rate, not all the 3-CIBM was converted as the reaction vials are closed, and methanol is not completely removed from the reaction mixture, and equilibrium was reached after approximately 25 minutes. As there is almost no acid

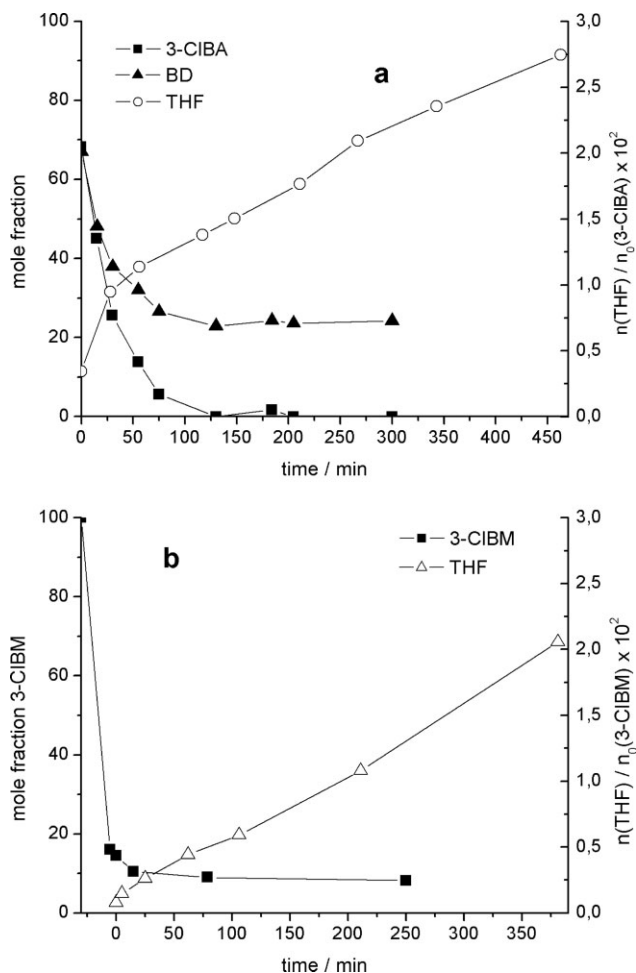


Figure 4 (a) Mole fraction of 3-CIBA (■), BD (▲) and mol % of THF (○) with respect to 3-CIBA in time during the heating of 3-CIBA + BD at 180°C in the presence of 0.1 mol % of $\text{Ti}(\text{OBu})_4$. (b) Mole fraction of 3-CIBM (■) and mol % of THF (Δ) with respect to 3-CIBM in time during the heating of 3-CIBM + BD at 180°C in the presence of 0.1 mol % of $\text{Ti}(\text{OBu})_4$.

present, the backbiting of the hydroxybutyl ends of HBB will form practically all THF.

Figure 5 displays the esterification of 3CBA with BA. It is clear that not all the 3CIBA has been converted to the ester before the rate of the acid-catalyzed THF formation, i.e., the dehydration of BD, starts to decrease. More specifically, when approximately 80 mol % of 3CIBA has reacted with BD or HBB, almost all THF will be formed via the nonacid-catalyzed backbiting of the hydroxybutyl groups of HBB.

It was already concluded for eq. (1) that the THF formation after 50 minutes, when most of the 3-CIBA has reacted with either BD or HBB, originates from HBB. When a linear curve is fitted through the data points after this reaction time (Fig. 5), one can shift this straight line to the origin and label it as the approximate THF formation from HBB for eq. (5).

When this line is subtracted from the original curve for the total amount of THF measured for this reaction, it results in the contribution of the acid catalysis to the THF formation (THF from BD) of this model reaction for the synthesis of PBT from TPA (Figure 5). Hence, to minimize the THF formation via the acid-catalyzed dehydration of BD, it is important that 3-CIBA and BD itself react away as fast as possible. As this slope is dependent on the actual concentration of HBB, the inclination of the shifted curve is a function of both the rate of transesterification and esterification. Consequently, it can be concluded that the applied catalyst for the synthesis of PBT has an indirect influence on the amount of THF formed during the synthesis process, as the rate of the main reactions (esterification and transesterification) influence the rate of the side reactions. For the TPA-based synthesis route, it is important that the catalytic system accelerates both the esterification and transesterification reactions, contrary to the DMT-based process where only transesterification reactions take place.

Influence of temperature, catalyst concentration, and the 3-CIBA : BD ratio

The amount of THF formed during PBT synthesis can be tailored by changing the process conditions. As in all chemical processes, temperature is an important variable in melt polymerizations. Since the various reactions and side reactions during the first stage of PBT synthesis are influenced differently by temperature changes (dependent on the order of the reactions), by changing the temperature, the rate of each reaction is affected independently.

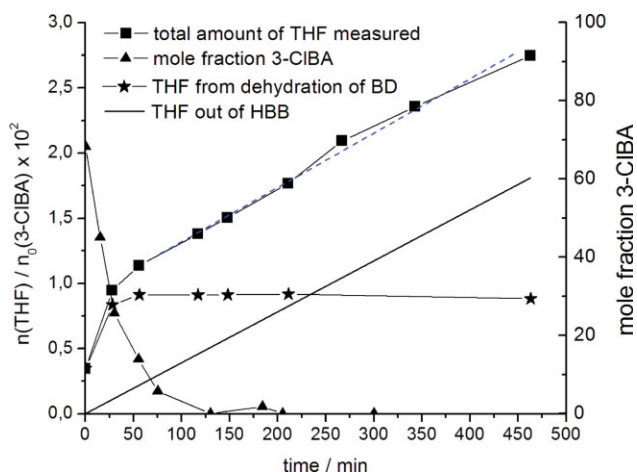


Figure 5 Measured mole fraction of 3-CIBA (▲) and THF (■) plus calculated mole fraction of THF from HBB and calculated mole fraction THF from BD (*) in time by heating 3-CIBA + BD at 180°C in the presence of 0.1 mol % of $\text{Ti}(\text{OBu})_4$.

TABLE I
The Apparent Activation Energies (E_{act}) for the Model Reactions of the First Stage of the TPA-Based Route to PBT and for the THF Formation During these Reactions. These Reactions were Performed in the Presence of 0.1 mol % $Ti(OBu)_4$

Model reaction	$E_{act}/kJ\ mol^{-1}$	E_{act} for the THF formation ^a /kJ mol^{-1}
3-CIBA + BD	69	23
3-CIBA + HBB	69	13
HBB + HBB	19	165

^a For the THF formation, only the experimental data points of the first 30 minutes of the reaction were fitted to calculate the activation energies. Consequently, the value for the activation energy of reaction 3CIBA + BD is in approximation the activation energy of the dehydration of BD, whereas for the reaction HBB + HBB the value represents the activation energy of the backbiting reaction of HBB.

Consequently, it would be interesting to study the influence of temperature during the first stage, more specifically to determine its effect on the total amount of THF formed during this part of the process. For this purpose, the model reactions for the TPA-based route to PBT [eqs. (1)–(5)] were performed at five different temperatures between 160 and 200°C in the presence of 0.1 mol % of $Ti(OBu)_4$. From these experiments, it was possible to get an impression of the activation energies of these reactions. The experimental data were fitted mathematically in Origin, and the slope of these curves was calculated for reaction time = 0. The apparent activation energies were then obtained from the Arrhenius plots of the different reactions using the values of the direction coefficients ($r_a|_0$) as the rate constants k_0 . Since the values in Table I were obtained in a semiquantitative way as described above, only the relative difference between the obtained activation energies of the different reactions will be discussed.

It is clear that the titanium-catalyzed transesterification reaction of the TPA-based polymerization of PBT (i.e., HBB + HBB) has a significantly lower energy barrier than the two esterification reactions (respectively, 3-CIBA + BD and 3-CIBA + HBB). Hence, due to the substantial difference between the activation energies of these reactions, the first stage of the polymerization process will require longer reaction times, as the clearing of the reaction mixture is only achieved when practically all carboxylic acid end groups have reacted. As discussed before, in view of the acid-catalyzed dehydration of BD, it is important to convert the acid end groups of the polymer as fast as possible as well. Similarly, as in the second stage of the polymerization reaction carboxylic acid groups are formed by either the backbiting of a hydroxybutyl end group or by (ther-

mal) degradation reactions, it will be difficult to avoid the formation of these end groups by further polycondensation. On the other hand, there are also some advantages linked to the fact that the transesterification of the hydroxybutyl end groups is faster than the two esterification reactions of this process. Building up the molecular weight of the PBT will proceed more easily, as in the first stage an excess of BD is used. A second advantage is that in the first stage less THF will be formed by the backbiting of the hydroxybutyl end groups (this side reaction is first order in the concentration of these end groups). Finally, it could be expected that due to the extreme low solubility of TPA in the reaction mixture during synthesis of PBT, the difference between the reaction rates of the different reactions will be even larger. From Table I it is observed that there is practically no difference between the two esterification reactions of the first stage of the polymerization process. However, 3-CIBA will react twice as fast with BD as with HBB, as the latter has only one hydroxyl group. From the activation energies for the THF formation in Table I for 3-CIBA + BD and HBB + HBB, it is clear that the THF formation from BD proceeds more easily than from HBB (as long as there is a substantial amount of 3-CIBA present). Again, this indicates the importance of converting the carboxylic acid groups as fast as possible (as BD will be present in the reaction mixture throughout the whole polymerization process).

Different kinetic studies were already published by Pilati et al.¹⁴ and Hsu and Choi,^{16,24} with the aim of obtaining information on the reaction orders and the mechanism of the $Ti(OBu)_4$ -catalyzed model reactions for the synthesis of PBT. Darda et al.²⁵ determined the PBT polycondensation equilibrium constant starting from a PBT prepolymer (degree of polymerization (DP) = 12.7), heated in a batch reactor to 255°C. The same group recently studied the reaction kinetics of the forward polycondensation reaction of PBT by thermogravimetric analysis. For this reaction, they found an activation energy of 84.5 kJ mol^{-1} ($[Ti(OBu)_4] = 470\ ppm$).²⁶ In a study on the side reactions in PBT synthesis, Pilati and coworkers found an activation energy of 121.4 kJ mol^{-1} for the THF formation when 4-hydroxybutyl benzoate was heated at different temperatures without the addition of a catalyst.²⁷ This value is in good agreement with the value of 116.8 kJ mol^{-1} that Lum²⁸ found for the activation energy for the THF formation during PBT synthesis and in reasonable agreement with the result for the THF formation from HBB (Table I).

Apart from studying the kinetics and the mechanism of the THF formation, at the end it is of importance to use this information to minimize the total amount of THF formed at the end of the

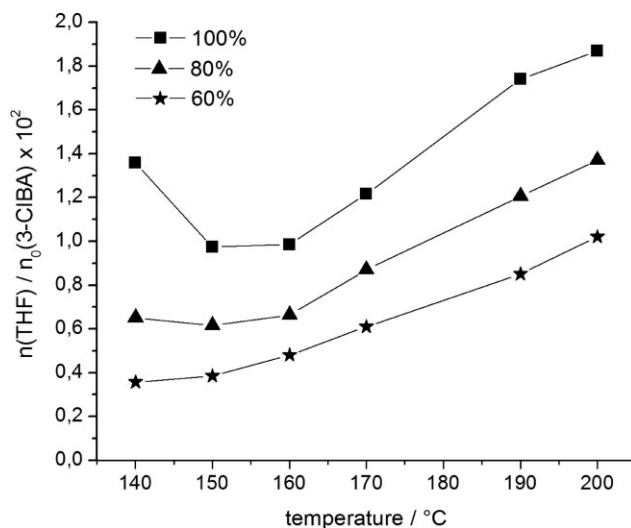


Figure 6 Mole fraction of THF with respect to 3-CIBA (n = number of moles) at different mol % conversion of 3-CIBA (■ 100, ▲ 80, and * 60%) vs. temperature for the reaction of 3-CIBA + BD in the presence of 0.1 mol % of $\text{Ti}(\text{O}i\text{Bu})_4$.

polymerization process. From determining the activation energies of the different (side) reactions during the preparation of PBT (vide supra), it is clear that a change in temperature will have a different influence on each of these reactions. There is a distinct minimum noticeable in the amount of THF, formed at full conversion of the model reaction of the first stage of the polymerization process (3-CIBA + BD), between 150 and 160°C (Fig. 6).

An increase of temperature proves to be disadvantageous for the amount of THF formed during the first stage of the TPA-based synthesis of PBT, as temperature increases the rate of the THF formation more than it expedites the polymerization reaction (temperature >150°C). The overall rate of the conversion of the carboxylic acid groups with time is fast at the beginning of the reaction. Near the end of the first stage, however, this rate decreases. Contrary to this, the THF formation from the hydroxybutyl end groups will increase with the increasing concentration of these groups. At temperatures below 150°C, the total amount of THF produced at 100% conversion of the acid groups will increase as well as it takes too long to reach complete conversion. From these data, it can be concluded that it would be favorable to start the polymerization reactions at lower temperatures than generally applied for this process (which are as high as 210°C). Similar to the first stage, lower temperatures are more profitable for suppressing the side reaction in the second stage. However, for the melt polymerization of PBT, it is impossible to work at temperatures below 230°C. Solid state polymerization (SSP) (at temperatures just below the melting point) is a good method to

build up the molecular weight of the polymer chains without too much THF formation. As less backbiting and degradation reactions occur via SSP, the end product will contain less carboxylic acid end groups, which is favorable for the hydrolytic stability of the polymer and the THF formation during processing.

Figure 7 shows the amount of THF produced for the model reaction (1) at the moment when all 3-CIBA has been converted for different concentrations of the $\text{Ti}(\text{O}i\text{Bu})_4$ catalyst. From the curve it is clear that for higher catalyst concentrations, the amount of this side product is suppressed. This is the result of a higher rate of the (trans)esterification reactions, as $\text{Ti}(\text{O}i\text{Bu})_4$ has no direct influence on the THF formation. The consumption rate of 3-CIBA and BD and the concentration of HBB govern the amount of side product formed [eqs. (4) and (5)].

An excess of BD will also result in shorter reaction times, by forcing the reaction equilibrium in reaction (1) towards the products. Nevertheless, more THF is formed, primarily by the backbiting of HBB, as the concentration of this ester will increase during the reaction because of the higher excess of BD (both by shifting the equilibrium of reactions (2) and (3)), as well as by the dehydration of BD. Unfortunately, due to the increased rate of the backbiting of the hydroxybutyl end groups, the higher excess of BD initially added to the polymerization process is not only disadvantageous for the TPA based process but also when DMT is used as a monomer, in contrast to what Yurramendi et al.²² have described. Nevertheless, in the polymerization process an excess of this BD is always needed, not only to force the

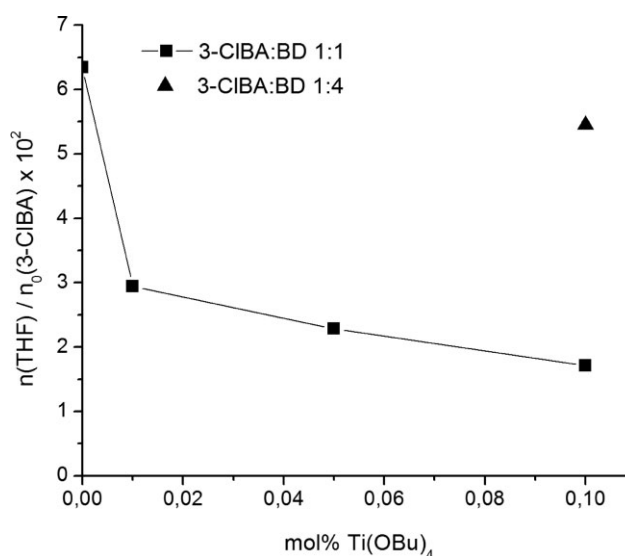


Figure 7 Mole fraction of THF with respect to 3-CIBA (n = number of moles) at 100% conversion of 3-CIBA by heating of 3-CIBA + BD at 180°C in the presence of different concentrations of $\text{Ti}(\text{O}i\text{Bu})_4$ (■ 1 : 1 and ▲ 1 : 4 3-CIBA : BD ratio).

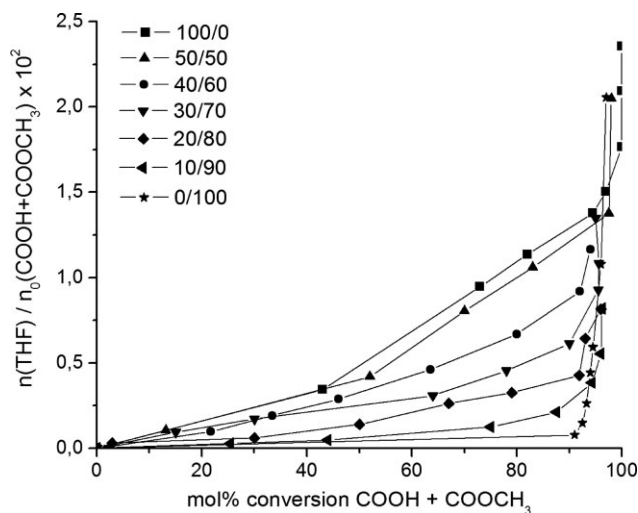


Figure 8 Mole fraction of THF vs. conversion of $[-\text{COOH}] + [-\text{COOCH}_3]$ by heating different ratios of 3-CIBA : 3-CIBM + BD at 180°C in the presence of 0.1 mol % of $\text{Ti}(\text{OBu})_4$ (n = number of moles) (■ 100/0, ▲ 50/50, ● 40/60, ▼ 30/70, ◆ 20/80, ◀ 10/90 and * 0/100 3-CIBA/3-CIBM).

reaction in the first stage to completion in an acceptable time but also to compensate for the loss of BD moieties by transformation into THF. A higher excess of the diol will also result in higher hydroxybutyl end groups during the first stage of the polymerization process. As the transesterification of these end groups is faster than the esterification of the carboxylic acid end groups in the TPA-based process or faster than the transesterification of the methylester end groups in the DMT-based process, the rate of the overall polymerization process will increase by a higher hydroxybutyl end group concentration in the reaction mixture.^{4,7} Consequently, it is clear why it is important to optimize the initial BD : TPA ratio.

Mixtures of 3-CIBA and 3-CIBM

It was observed in Figure 5 that, already before all acid was converted, the formation of THF in time started to slow down during the reaction of 3-CIBA with BD. Due to the fact that 3-CIBA is a weak acid in BD, the rate of THF formation from BD decreases significantly for low concentrations of 3-CIBA. As a model for the polymerization of BD with a mixture of TPA and DMT, it would be interesting to investigate how much 3-CIBA can be added to 3-CIBM in the reaction with BD, before the amount of THF formed reaches the same level as when only 3-CIBA is used. The reaction of 3-CIBM with BD [0/100 in Fig. 8; Fig. 4(b)] is very fast. Practically, all THF is formed out of HBB and most of it near the end of the reaction when the concentration of HBB is the

highest. The mole fraction of THF increases more rapidly for higher conversions as the rates of the transesterification reactions gradually decrease in time, while the production of THF continues [Fig. 4(b)] at approximately the same rate (the reaction does not reach 100% conversion, as methanol was not released from the reaction vessel, *vide supra*). The curve for the formation of THF in the reaction of 3-CIBA with BD (100/0 in Fig. 8) increases significantly stronger than the 0/100 between 0 and 80% conversion. This “extra” amount of THF can be explained by two contributions: it was already observed that the acid-catalyzed dehydration of BD is fast in the beginning of the reaction. Hence, the major part of the THF formation originates from this reaction. A second reason why more THF is formed is the fact that titanium is a better transesterification catalyst than an esterification catalyst for these model reactions. Hence, the overall reaction of the TPA-based model is slower than the DMT-based model. Consequently, in the TPA-based system, HBB has more time to produce THF. When 10% of the methyl ester is replaced by 3-CIBA (10/90, Fig. 8), the THF formation does not increase dramatically in comparison with the 0/100-curve. This proves in fact that the addition of 10% of this weak acid hardly catalyzes the dehydration of BD. It even takes up to 50 mol % of 3-CIBA to induce as much THF formation as in the 100/0 reaction. Summarizing, the partial replacement of DMT by TPA in PBT synthesis could possibly lead to the production of a cheaper product: less THF is formed compared with the TPA-based process, and a part of the DMT is substituted by a cheaper monomer.

CONCLUSIONS

3-CIBA was used as monofunctional model compound for TPA to facilitate the study of the THF formation during the first stage of the polymerization process of PBT. In agreement with the Hammett-relationship, this molecule proved to be a better model for TPA than BA and 4-CIBA. THF is practically completely produced by two reaction paths, i.e., the acid-catalyzed dehydration of BD and the backbiting of the hydroxybutyl end groups of the polymer. Acid-catalyzed hydrolysis of BD becomes the most important source of the extra amount of THF in PBT synthesis when using TPA as an alternative to DMT. For the production of THF from hydroxybutyl end groups of the polymer, it can be concluded that the presence of an equimolar amount of a weak acid in the reaction mixture is insufficient to observe the acid-catalyzed contribution from this molecule. Hence, TPA will have no significant catalytic effect on the THF formation from the hydroxybutyl end groups of the polymer.

The THF formation during these model reactions indicates the importance of the rapid conversion of the carboxylic acid groups during the first stage of the TPA-based polymerization process and the fast transesterification as well to decrease the concentration of hydroxybutyl end groups, the second precursor for the production of THF.

It was also concluded that an increase of the reaction temperature and the excess of BD in the polymerization process and a decrease of the catalyst concentration are disadvantageous for the THF formation.

Finally, mixtures of 3-CIBA and 3-CIBM were reacted with BD to investigate how strong the influence of the acid on the THF formation is, and hence to determine the relative importance of the dehydration of BD compared with that of the backbiting reaction of HBB to THF. From these experiments, it was concluded that for ratios 3-CIBA : 3-CIBM lower than one, less THF is produced and considerably shorter reaction times are required compared with the model for the TPA-based route to PBT. Consequently, the partial replacement of DMT by the cheaper TPA in PBT synthesis offers a possible alternative for a less expensive product.

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