

# The Synthesis of Poly(butylene terephthalate) from Terephthalic Acid, Part II: Assessment of the First Stage of the Polymerization Process

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**ABSTRACT:** The production of poly(butylene terephthalate) (PBT) struggles with the formation of substantial amounts of tetrahydrofuran (THF). When PBT is synthesized from terephthalic acid (TPA) instead of dimethyl terephthalate (DMT), even more THF is formed, mainly during the first stage of the melt polymerization process. Although a lot of literature reports on the existence of this side reaction in both processes, to the best of our knowledge, a comparison, which reveals the importance of the

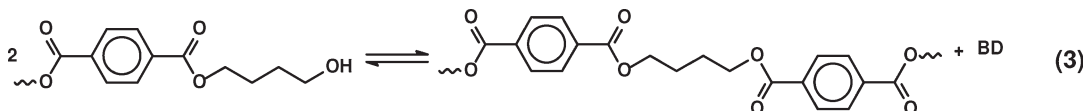
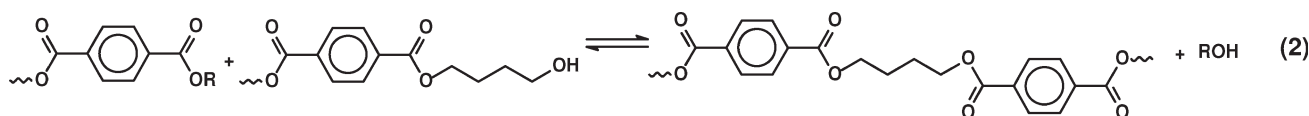
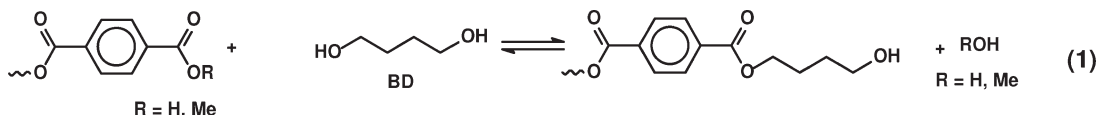
acidity and insolubility of TPA on the THF formation, was never described. Finally, an interesting study was performed on the THF formation during the synthesis of PBT from mixtures of DMT and TPA as well as from the completely soluble monomethyl terephthalate (MMT). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2427–2434, 2009

**Key words:** polyesters; esterification; synthesis; melt; step-growth polymerization

## INTRODUCTION

Poly(butylene terephthalate) (PBT) is an important engineering plastic, with an annual world production exceeding 800,000 tons. It is widely applied for injection molded components in the automotive industry and the electric/electronic industries.<sup>1,2</sup> Generally, PBT is produced via a two-step melt polymerization of dimethyl terephthalate (DMT) and 1,4-butanediol (BD). It would, however, be much more favorable from an economic point of view to produce PBT via the esterification of the cheaper terephthalic acid (TPA) and BD [eqs. (1)–(3)]. For the commercial production of the

major part of the other poly(alkylene terephthalates), i.e., poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT), the use of TPA has already been implemented.<sup>3</sup> Unfortunately, the synthesis of PBT has to contend with the formation of relatively large amounts of tetrahydrofuran (THF) as an undesired side product.<sup>1,2</sup> Moreover, the amount of THF formed during the synthesis of PBT out of TPA, is more than 100% higher compared with the DMT-based process. Consequently, the profit of using the cheaper TPA for the production of PBT as an alternative for DMT is limited due to the increase of the THF formation.



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From our previous work on a model study of the TPA- and DMT-based synthesis of PBT,<sup>4</sup> it could be concluded that besides the amount, also the origin of the production of THF differs for both processes. It was found that this undesired side product is

produced via two different reactions. The monomer, BD, is able to dehydrate to THF in the presence of a Brønsted acid. Consequently, this side reaction is substantially enhanced when TPA is used as a starting material for the PBT synthesis. Secondly, the formed hydroxybutyl end groups of the intermediate products obtained during the polymerization reaction can form THF as well via a so-called backbiting mechanism. It was demonstrated that this reaction is not influenced by the presence of a weak acid, like TPA. Practically all the THF formed during the first stage of the polymerization process of PBT out of DMT originates from this backbiting reaction. Although the same reaction also takes place during the first stage of the TPA-based route, the acid-catalyzed dehydration of BD forms a significant additional contribution to the amount of THF produced. Obviously, similar acid-catalyzed side reactions are not encountered during the TPA-based synthesis of either PET or PTT.

However, the major dissimilarity between the model compound 3-chloro-benzoic acid (3-CIBA) and the monomer TPA in the esterification reaction with BD, is the low solubility of the diacid in the reaction medium. However, if the rate of dissolution of TPA in the medium is higher than the rate of esterification of these monomers, the overall rate of the polymerization process will not be affected by the insolubility of TPA. Moreover, irrespective of the rate of dissolution, as long as undissolved TPA is present, substantially less carboxylic acid groups will be accessible in the reaction mixture, leading to a lower amount of catalyst for the acid-catalyzed dehydration of BD. On the other hand, if the dissolution of TPA in the melt is a rate-limiting process, the latter advantage is most probably lost as it will take longer to esterify all the carboxylic acid end groups.

Although many articles have already been published on both the TPA-based and the DMT-based route to PBT (both on the polymerization process and on the THF formation),<sup>1,2,4-42</sup> literature that describes a comparison between the two processes is, to the best of our knowledge, lacking. Interestingly, it was already observed from the model reactions that it is possible to gain a lot of information by performing a comparative study on the first stage of both polymerization routes.<sup>4</sup> Furthermore, the acquired knowledge on the mechanism of the THF formation collected by the model study was used in this work to comprehend the experimental data obtained for this side reaction during the synthesis of the polymer. Finally, also the influence of the poor solubility of TPA on the THF formation is studied.

## EXPERIMENTAL

### General considerations

TPA and DMT were used as received from Acros Organics and Merck, respectively. BD (VWR Interna-

tional B.V., Amsterdam, The Netherlands, >99%) was distilled and stored on molsieves before use. Titanium tetrabutoxide ( $\text{Ti}(\text{OBu})_4$ ) and mono-methyl terephthalate (MMT) were purchased from Acros Organics (Geel, Belgium) and used without further purification.

### Polymerization reactions

Both stages of the melt polymerization of PBT were performed in a single 250 mL stainless steel stirred tank reactor. An example of a typical polymerization reaction is described hereafter. TPA (116.23 g; 0.70 mol) and a 0.7 equiv. excess of BD (107.52 g; 1.19 mol) were charged into the reactor together with 500 ppm of  $\text{Ti}(\text{OBu})_4$  with respect to TPA. A flow of argon was purged over the reaction mixture to avoid oxidative side reactions and to facilitate the removal of the volatiles. The oil-circulator temperature was set at 230°C and the stirrer speed at 58 rpm. The  $\text{H}_2\text{O}$  and THF were collected in a calibrated burette and samples were taken at regular volume-intervals.

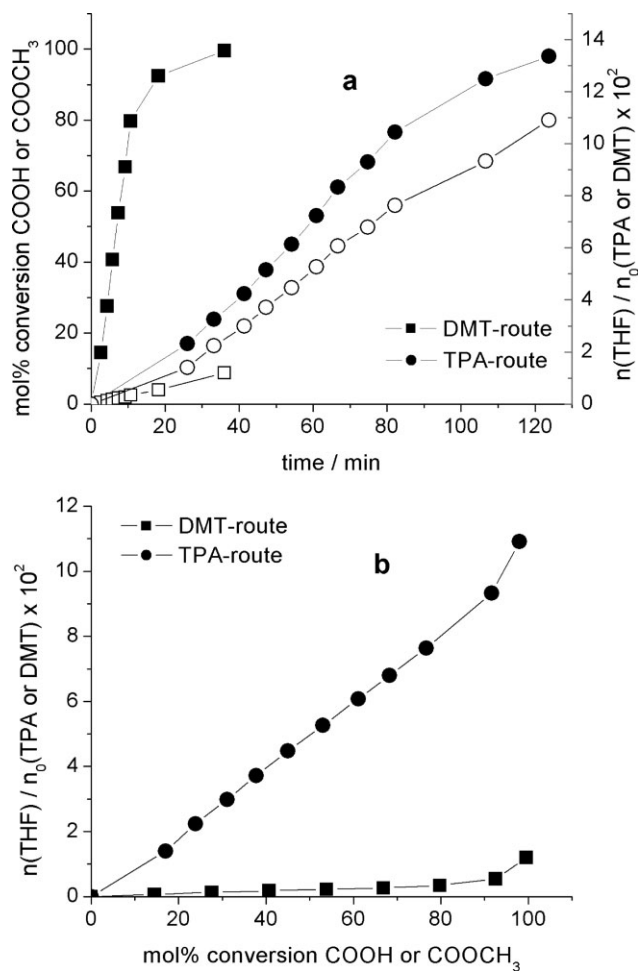
### Sample analysis

Conversion of the first stage of the polymerization reaction was determined by analyzing the composition of the fractions of the volatiles collected at the bottom of the Dean-Stark set-up by gas chromatography (GC). Two different GC-set-ups were used. The Chrompack CP9000 GC, equipped with a Chrompack capillary column (CP-Volamine 30 m  $\times$  0.32 mm id) and a FID detector, was used to determine the concentration of the different volatile organic components collected for polymerizations using DMT as a monomer. A second GC, a Chrompack CP9001, equipped with a capillary column from Alltech (AT-WAX 30 m  $\times$  0.53 mm id  $\times$  1.0  $\mu\text{m}$  stationary phase thickness) and two detectors in series (a TCD and a FID detector respectively), was used to measure the volatile components produced during the polymerization reactions where TPA was used as a monomer. The samples were diluted with either methanol or ethanol. Toluene was used as an external standard.

## RESULTS AND DISCUSSION

### Comparison of the TPA- and the DMT-based route to PBT

A study was performed by reacting both TPA and DMT with BD in the presence of  $\text{Ti}(\text{OBu})_4$  under the same reaction conditions. However, it should be noted that the applied reaction conditions, as described in the experimental, have not been optimized for both processes separately. Moreover, in practice, different conditions should be used for



**Figure 1** Comparison between the TPA-based (●) and the DMT-based synthesis (■) of PBT. TPA and DMT are reacted with a 0.7 equiv. excess of BD in the presence of  $\text{Ti}(\text{O}i\text{Bu})_4$  (850 ppm). Mol % conversion of the carboxylic acid groups or methylester groups, respectively, in time (●, a), mole fraction of THF with respect to either TPA or DMT ( $n$  = number of moles) in time (○, a) and mole fraction of THF vs. mol % conversion (b).

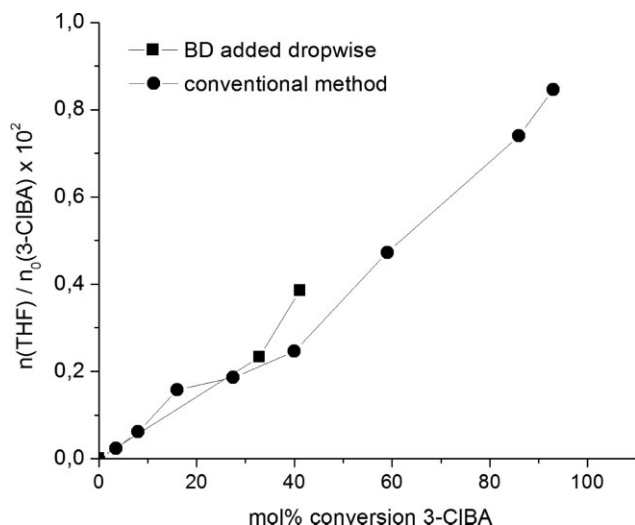
the two routes to suppress the amount of THF produced as much as possible.

From Figure 1(a) it is clear that there is a distinct difference in reaction rate for the complete esterification of TPA compared with the transesterification of DMT. The observed difference for these rates is in agreement with the rates of the model reactions of these two routes to PBT reported in our previous work.<sup>4</sup> Using monofunctional model components, it was shown that the intrinsic reaction rate of transesterification is higher than of the esterification. Besides, the poor solubility of TPA will even strengthen this difference. It will be demonstrated further on that indeed the dissolution of TPA is a rate-limiting process in this route. This is possibly the major cause of the difference in reaction time of the TPA and the DMT process.

A second observation from both graphs in Figure 1 is that the total amount of THF formed during these polymerization reactions is, as expected, considerably higher for the TPA-based polymerization (10.9 mol % vs. 1.2 mol % for the DMT-route). It should be noted that besides the obvious source of THF, i.e., the acid-catalyzed THF formation from BD, there is a second reason why more of this side product is formed via this route. Due to the slow dissolution of TPA, BD, and HBB end groups will be present in excess for a longer time than during the DMT-based process, which results in a higher total amount of THF. However, because of the abovementioned difference between the rate of the esterification reactions and the transesterification of the hydroxybutyl end groups, the concentration of these groups in the reaction mixture will possibly be somewhat lower in the TPA-based process. Consequently, the rate of the backbiting reaction to THF will also be somewhat lower compared with the DMT-based polymerization.

During the model reaction performed for the first stage of the TPA-based polymerization process of PBT, a high rate of THF formation was observed in the beginning of the reaction due to the acid-catalyzed formation of THF from BD.<sup>4</sup> Interestingly, during the major part of the actual polymerization reaction, the rate at which THF is formed is more or less constant in time [Fig. 1(a)]. It is possible to explain this apparent discrepancy between the model and the polymerization reaction by the fact that, as TPA is practically insoluble in the reaction mixture, the concentration carboxylic acid groups dissolved in the melt is maintained at a low, yet more or less constant level. Hence, the insolubility of TPA will decrease the dehydration rate of BD, but unfortunately, the same insolubility and dissolution rate retard the esterification process, which leads to a higher amount of THF formed at the end of the first stage for the TPA-based process compared with the DMT based-process. As discussed before, the results of the model reactions revealed that the THF formation observed for the DMT-based route in Figure 1(b) originates practically completely from the backbiting of the hydroxybutyl end groups formed during this process.

In the TPA-based synthesis of PBT, an excess of BD is always used, not only to speed up the first stage of the reaction but also to compensate for the loss of BD by its transformation into THF. As a considerable amount of THF is formed by the acid-catalyzed dehydration of BD during this process, and, moreover, as a higher excess of this monomer induces an increase of the production of THF,<sup>4</sup> it could be reasoned that adding this monomer dropwise to the diacid could possibly suppress this side reaction. Unfortunately, an exploratory model experiment



**Figure 2** Evolution of the mole fraction of THF formed with respect to 3-CIBA ( $n$  = number of moles) with the conversion of 3-CIBA in reaction with BD (1 : 1) at 160°C. Comparison between the dropwise addition of BD to 3-CIBA ■ and adding the reactants together at the start of the reaction (conventional method ●).

with 3-CIBA and BD shows no improvement compared with the conventional method (Fig. 2). Furthermore, due to the poor solubility of TPA and its high melting point, adding BD dropwise to this monomer will be ineffective in practice.

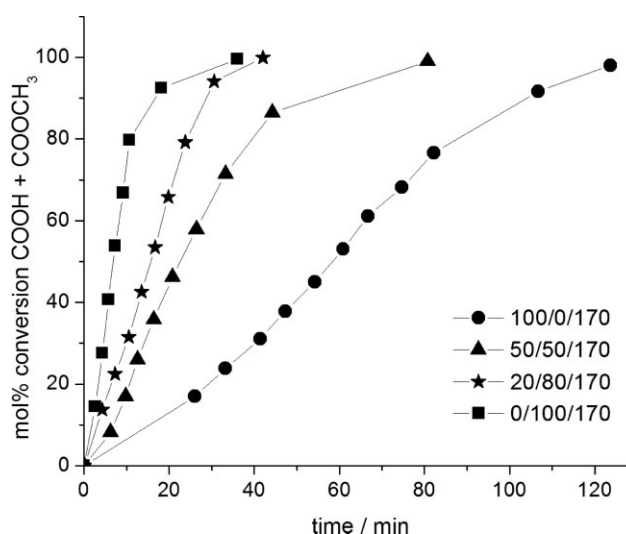
It can generally be concluded that it is practically impossible to suppress the amount of THF produced during the first stage of the TPA-based synthesis of PBT to the level of the DMT-based process, because of two major drawbacks in this system. A first and evident reason is that, as an acid is used as a monomer, BD will dehydrate to THF via an acid-catalyzed mechanism. A second reason is the extremely low solubility of TPA.

### Mixtures of TPA and DMT

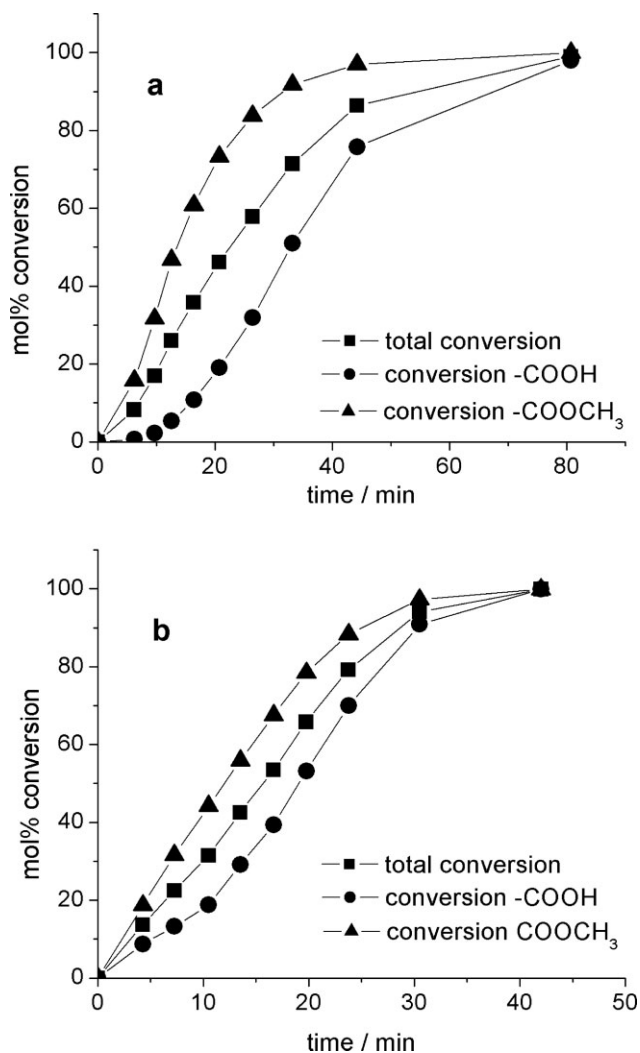
Model reactions for the synthesis of PBT using mixtures of 3-CIBA and Methyl 3-chloro-benzoate (3-CIBM) in combination with BD were performed in previous work to investigate the influence of the amount of acid in the reaction mixture on the THF formation.<sup>4</sup> It was found that mixtures of 3-CIBA and 3-CIBM in a ratio below one produced less THF compared with the esterification reaction using exclusively 3-CIBA. When more than 50% 3-CIBA was used, the amount of THF was comparable to the case where 100% 3-CIBA was applied. Moreover, for a COOH/COOCH<sub>3</sub> ratio below 0.25, it was concluded that PBT synthesized from such a mixture might lead to a less expensive product compared with the DMT-based route, as only a relatively small extra amount of THF is formed for these mixtures

and a substantial part of the DMT is replaced by the cheaper TPA. To verify the results obtained for the model system, polymerizations using mixtures of TPA and DMT were carried out. The only difference of the polymerization reaction compared with the model reactions is again the limited solubility of TPA in the melt.

This very low solubility, amongst other factors, has a relative large effect on the reaction time (Fig. 3), as already observed for the comparison made between TPA and DMT in the previous section. The lower the content of TPA in the TPA/DMT mixture, the better it dissolves in the reaction mixture during the first stage, as TPA is better soluble in a melt of DMT and BD than in BD alone.<sup>43</sup> Furthermore, the relative rate of the conversion of the carboxylic acid groups and the rate at which the methylesters are transesterified in the 20/80/170 (TPA/DMT/BD) mixture are also substantially closer together compared with these rates in the 50/50/170 mixture (Fig. 4). The total conversion is defined here as the sum of the relative conversions of the carboxylic acid groups of TPA and the methylester groups of DMT. In contrast to the clearing point (when the reaction mixture becomes homogeneous) observed during the TPA-based process (at the very end of the first stage, when practically all carboxylic acid groups of TPA have been converted), the 50/50/170 mixture already clears when 76 mol % of the acid groups has been converted, and the 20/80/170 even clears at 70 mol % conversion. Hence, it takes only 4 minutes more to complete the first stage for the 20/80/170 mixture compared with



**Figure 3** Comparison between the polymerization reactions of mixtures of TPA, DMT with BD (ratio TPA : DMT : BD ● 100 : 0 : 170, ▲ 50 : 50 : 170, ★ 20 : 80 : 170 and ■ 0 : 100 : 170) in the presence of 850 ppm Ti(OBu)<sub>4</sub>. Mol % conversion of the carboxylic acid groups and the methyl ester groups with time.

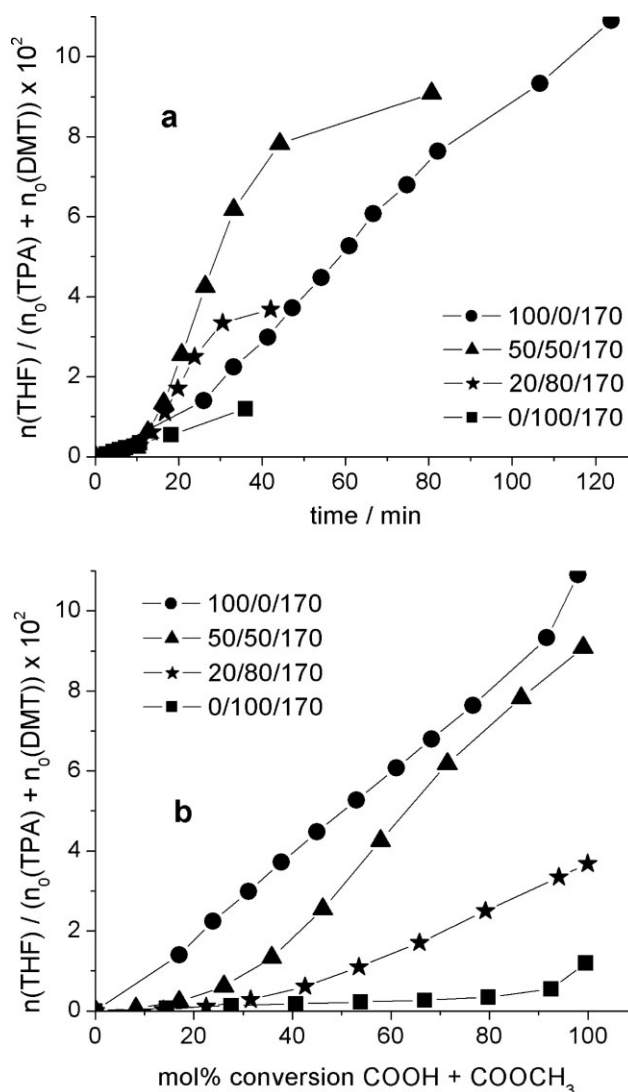


**Figure 4** Mol % conversion in time of the carboxylic acid groups (●), methylester groups (▲) and the total conversion (■) of the polymerization reaction of the 50/50/170 (TPA/DMT/BD) mixture (a) and the 20/80/170 mixture (b) in the presence of 850 ppm Ti(OBu)<sub>4</sub>.

the DMT-based polymerization, an additional time, which is lower than expected from the initial content of TPA in the mixture.

Figure 5(a) depicts the molar percentage of THF formed during the synthesis of PBT using different TPA/DMT mixtures. From the slope of the different curves, although it is observed that there is a significant difference in the rate of THF formation, there is no consistent correlation between this rate and the TPA-content of the mixture. This suggests that more than one variable is exerting an important influence on this side reaction. Despite the fact that the 100/0/170 (TPA/DMT/BD) polymerization contains more acid compared with the 50/50/170 mixture, the rate of the production of THF during the polymerization of the latter is considerably higher (at least up till 80% conversion). This can reasonably be explained by the higher solubility of the carboxylic

acid groups in the melt of the 50/50/170 mixture compared with the TPA route to PBT. However, although this effect should be even more pronounced for the 20/80/170 mixture, a lower rate of THF formation is found for this mixture compared with the 50/50/170 polymerization. As it was seen for the model study that the rate of THF formation already started slowing down when 80% of 3-CIBA has been converted, it is likely that the decrease in acid-catalyzed dehydration of BD due to the lower concentration of acid in this mixture counter balances the higher solubility of the carboxylic acid groups. As already discussed before, practically all the THF formed during the fully DMT-based 0/100/170 reaction originates from the hydroxybutyl end groups.



**Figure 5** Comparison between the polymerization reactions of mixtures of TPA, DMT with BD (ratio TPA : DMT : BD ● 100 : 0 : 170, ▲ 50 : 50 : 170, \* 20 : 80 : 170 and ■ 0 : 100 : 170) in the presence of 850 ppm Ti(OBu)<sub>4</sub>. Mol % THF with respect to TPA + DMT ( $n$  = number of moles) in time (a) and mol % THF vs. mol % conversion (b).

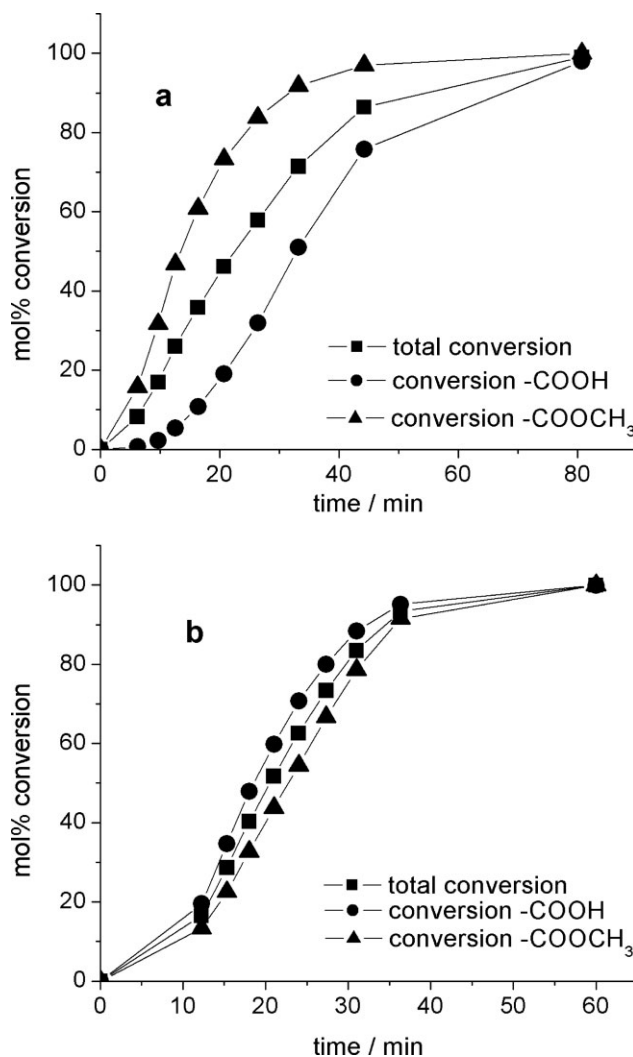
Figure 5(b) is very similar to the corresponding graph plotted for the model reactions on the corresponding mixtures.<sup>4</sup> In contrast to the model system, the poor solubility of TPA results in a lower amount of THF being produced at the end of the first stage for the 50/50/170 mixture than for the TPA-based reaction. As observed before, the increased solubility of TPA in the 50/50 TPA-DMT mixture compared with the process using exclusively TPA has an effect on both the rate of esterification of TPA and on the rate of THF formation. Hence, as the amount of THF at the end of the first stage is lower for the 50/50/170 mixture, it can be concluded that, with respect to the THF formation, the dissolution of TPA has a decisive influence on the rate of the esterification process.

Whether a mixture of TPA and DMT could lead to a cheaper product depends on the profit made by substituting a part of the more expensive DMT by TPA relative to the loss made due to the additional formation of THF and the longer reaction times.

### Monomethyl terephthalate

In the previous sections, it has been demonstrated that the extremely low solubility of TPA in the reaction mixture has a major influence on the TPA-based polymerization. To investigate the effect of the dissolution of the carboxylic acid groups, both on the rate at which these groups are converted and on the amount of THF produced, the synthesis of PBT from monomethyl terephthalate (MMT) and BD was compared with the reaction of a 50/50 mixture of TPA and DMT with BD. The reactivity of both the carboxylic acid groups and the methyl ester groups of MMT are identical with those of TPA and DMT, respectively (the Hammett parameters of COOH and COOCH<sub>3</sub> are the same).<sup>44</sup> As concluded from earlier results, the insolubility has two opposite effects with respect to the THF formation. The amount of THF will increase, as longer reaction times are required to complete the first stage. On the other hand, THF formation is suppressed from the cyclization of BD (as less acid is dissolved in the reaction medium) and possibly from the backbiting of the hydroxybutyl end groups (as the difference between the esterification and transesterification rate is possibly enlarged). In this section, it will be investigated which of both effects is most important.

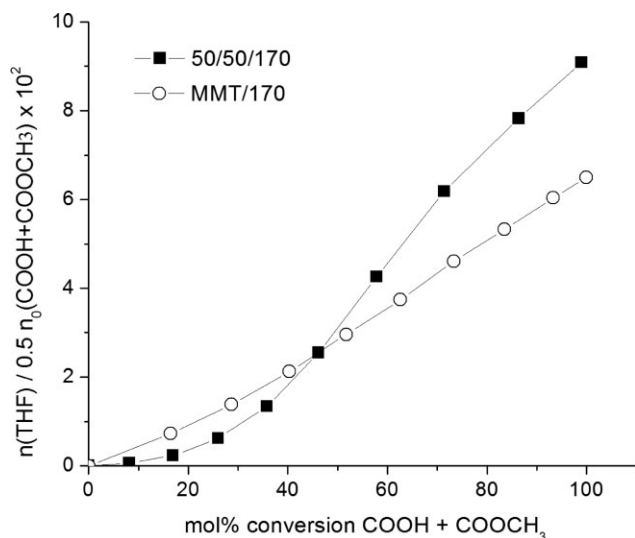
As expected, there is a distinct difference between the two polymerization reactions depicted in Figure 6. As MMT is completely soluble in the reaction mixture, the concentration of carboxylic acid groups available for esterification is higher than for the 50/50/170 DMT/TPA/BD mixture. Besides the fact that the reaction with MMT reduces the reaction time with 25%, the relative esterification rate of the carboxylic



**Figure 6** Mol % conversion in time of the carboxylic acid groups (●), the methylester groups (▲) and the total conversion (■) of the polymerization reaction of the 50/50/170 DMT/TPA/BD mixture (a) and the reaction of MMT with BD (0.7 molar excess) (b) both in the presence of 850 ppm Ti(OBu)<sub>4</sub>.

acid groups is also higher for MMT. At 50% conversion, 58% of the acid groups of MMT have already reacted, whereas in the DMT/TPA mixture only 22% have been esterified.

In Figure 7, the molar percentage of THF formed is plotted against the combined conversion of the acid and methylester functionalities. More THF is formed in the beginning of the reaction both from BD and from the hydroxybutyl end groups when MMT is used as a starting material for PBT synthesis. As the acid groups are converted faster relative to the methylester groups, less BD will be dehydrated to THF near the end of this stage. Moreover, THF formation from the hydroxybutyl end groups will be reduced as well by the shorter reaction times for the reaction where MMT is used. At the end of the first stage, when the reaction medium is



**Figure 7** Comparison between the polymerization reaction of the 50/50/170 DMT/TPA/BD mixture (■) and the reaction of MMT (○) with BD (0,7 excess) both in the presence of 850 ppm Ti(OBu)<sub>4</sub>. Mole fraction of THF with respect to COOH + COOCH<sub>3</sub> ( $n$  = number of moles) vs. mol % conversion.

completely homogeneous, almost 30% less THF is produced. Hence, it can be concluded that the slow dissolution of TPA in BD, which obviously slows down the esterification process, significantly contributes to the enhanced THF formation in the TPA-based PBT formation. By adding some DMT or MMT as comonomer, the solubility of TPA seems to increase significantly compared with neat BD, which increases the esterification rate and leads to a reduction of the formation of THF.

## CONCLUSION

Using the knowledge obtained from model studies on the formation of THF during the synthesis of PBT described in previous work and the influence of various parameters on this side reaction, the formation of THF was analogously investigated during the first stage of the polymerization reaction of TPA and DMT with BD. Performing these model reactions proved to be very useful to understand and analyze the results obtained for THF formation during the different polymerization reactions. Moreover, from the good agreement between the model experiments and the synthesis of PBT, with respect to the reaction rates, the choice of 3-CIBA as a model compound for TPA turned out to be an important improvement in comparison with the previously reported model reactions on the synthesis of PBT.

With respect to the synthesis of PBT from the diacid, the main difference with the model study is the poor solubility of TPA in the reaction mixture. Although it was observed that, due to the small frac-

tion of dissolved TPA, the rate of THF formation was suppressed (both from BD and from the hydroxybutyl end groups), the slow dissolution of TPA proved to be rate limiting for the esterification process as well, resulting in a disadvantageous effect on the final amount of THF produced during the first stage of the polymerization.

As it is generally understood, the use of TPA as a monomer for the synthesis of PBT induces the acid-catalyzed dehydration of BD to THF. Due to the large difference in completion time of the conversion of all carboxylic acid groups compared with the methylester groups during the DMT-based process, the formation of THF from the backbiting of the hydroxybutyl end groups becomes important as well.

Finally, it can also be concluded that mixtures consisting of a TPA : DMT ratio of about 20 : 80 exhibit only slightly longer polymerization times and a marginal increase in THF formation compared with the process using exclusively DMT, while 20 mol % of the more expensive DMT has been replaced by the diacid. By staying under a critical amount of acidic monomer in the reaction mixture and increasing the solubility of TPA in the TPA-DMT mixture (which is also influenced by its particle size), the use of such mixtures could possibly lead to the production of a more competitive resin from an economical viewpoint. Furthermore, MMT is also an intermediate in the Witten-process in the synthesis of DMT out of para-xylene and reduces the THF formation with 40% compared with the TPA-based synthesis of PBT.<sup>45</sup> Consequently, similar to TPA, this monomer could be a possible cheaper alternative for the synthesis of PBT out of DMT as well.

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