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New catalysts for poly(butylene terephthalate) synthesis. Part 3: effect of phosphate co-catalysts

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Abstract

An exhaustive study of the co-catalytic activity of phosphates on titanium and titanium/hafnium based catalytic systems in poly(butylene terephthalate) synthesis was conducted in order to investigate any improvement in the process and/or in the properties of the final polymer with respect to the industrially used titanium based catalyst. Small scale polymerisation and subsequent scale up in higher capacity reactors showed a strong co-catalytic effect of phosphates. A screening on model compounds showed NaH_2PO_4 to be the most active co-catalyst. The co-catalysts had a stronger effect on titanium with respect to hafnium. Decreases in polymerisation time and tetrahydrofuran formation were observed, which in turn can improve the productivity of the whole process. Moreover, the use of phosphate improved the thermal stability of the final polymers.

Keywords: Poly(butylene terephthalate); Co-catalyst; Phosphate

1. Introduction

Poly(butylene terephthalate) (PBT) is an important thermoplastic polyester widely used, either alone or in blends with other thermoplastics, in a wide array of engineering applications. Current PBT industrial production is based on the reaction of dimethyl terephthalate with 1,4-butanediol, catalysed by an organotitanate (e.g. titanium(IV) tetrabutoxide) [1,2]. Side reactions can occur at the high temperatures used, producing carboxylic acid end-groups, which affect the thermal stability of the final product, and waste 1,4-butanediol through conversion to unrecoverable by-products (e.g. tetrahydrofuran, THF) [3–8]. In order to suppress side reactions, phosphorous compounds are generally used as modifiers of polycondensation catalysts in the synthesis of poly(ethylene terephthalate) (PET) [2]. These co-catalysts increase the thermal stability and whiteness of PET [9–11]. Moreover, Kamatani [12] reported an increase in polymerisation kinetics when a phosphorous compound was added to Zn(II), Co(II), Mn(II) and to Sb(III) based catalysts in PET synthesis. Two patents [13,14] reported that the addition of a phosphate based co-catalyst to the titanium based catalyst led to a higher polymerisation rate also in PBT synthesis. In particular, these patents claim that the addition of NaH_2PO_4 and KH_2PO_4 gives rise to a 30% increase in the polycondensation rate. However, no information is provided on the thermal stability of the final polymers and THF formation with these catalytic systems. To the best of our knowledge, no paper reports a study of the effect of phosphorous compounds in the synthesis of PBT.

We have recently reported that the addition of acetylacetonates of hafnium and lanthanides to titanates leads to an increase in the kinetics of both stages in PBT polymerisation [15–18]. Yamamoto et al. [19–22] recently reported the high catalytic activity of Hf(IV) based catalyst in ester condensation reactions and in polyester synthesis, also claiming that hafnium based catalyst is hydrolitically more stable than titanium based catalyst and should be useful as an environmentally and industrially ideal condensation

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catalyst. Therefore, the aim of this work was the study of the effect of phosphates on titanium and on titanium–hafnium based catalytic systems in PBT synthesis. In this paper we report the screening of several phosphorous based co-catalysts (conducted both on model compounds and on full polymerisation), the measurements of the amount of THF formed and the study of the thermal properties of the PBT obtained. A detailed study of the involved catalytic mechanism by ^{31}P NMR and FTIR analyses will be presented in a following paper.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT) (purchased from Aussapol, Italy), 1,4-butanediol (BD) (from Aldrich Chemicals), were high purity products and were used as received without any further purification. Hafnium(IV) acetylacetonate was synthesised according to the literature [15]. Titanium(IV) tetrabutoxide (TBT) (purchased from Aldrich) was distilled under reduced pressure twice and stored in closed bottles under nitrogen at 0 °C.

Sodium phosphate, potassium phosphate, sodium hydrogenphosphate, potassium hydrogenphosphate, sodium dihydrogenphosphate, potassium dihydrogenphosphate, lithium dihydrogenphosphate, phosphoric acid (all from Aldrich Chemicals) were high purity products and were used as received without any further purification. Bis(hydroxybutyl terephthalate) (BHBT) was synthesised according with the method described in the literature [15].

2.2. Small scale catalyst screening procedure

A typical catalyst screening experiment was conducted as follow: 2.00 g of BHBT were placed in a glass tube (15 cm long, 2 cm internal diameter) provided with a stopcock. The catalysts were then added keeping the total amount of catalyst equal to 1.59 mmol/(mol of terephthalic units) (mmol/mol$_{TPU}$). The reactions were conducted for 25 min at 235 °C under dynamic vacuum (1 mbar). The trans-esterification reaction extent was determined by measuring the degree of polymerisation (DP) by ^{1}H NMR spectroscopy with a method previously reported [15]. The samples were dissolved in a $CDCl_3/CF_3COOD$ 4:1 (v/v) mixture immediately before recording the spectra in order to avoid the esterification reaction between hydroxyl terminal groups of PBT and CF_3COOD. Three replicates have been conducted for each catalyst composition.

2.3. Micro-pilot plant polymerisation procedure

Micro-pilot plant polymerisations were carried out by using a two-stage process in a 1.8 l stainless steel batch reactor equipped with a paddle stirrer (driven at 30 rpm) and a strain-gauge sensor mounted on the stirrer shaft in order to monitor the viscosity of the reaction melt (and indirectly the increase in PBT molecular weight) during the polymerisation. Two condensers in series (the first water-cooled and the second liquid nitrogen-cooled) were connected to the reactor to collect volatile products during the first and second stages. A typical polymerisation procedure is described below.

First stage: BD (458 g; 5.09 mol) and DMT (705 g; 3.63 mol) were loaded (BD/DMT ratio 1.4:1) into the reactor and then heated at atmospheric pressure under stirring to 150 °C. At this temperature, the catalyst (0.81 mmol/mol$_{TPU}$) and the co-catalyst were introduced into the reactor. The reaction temperature was increased from 150 to 215 °C at a heating rate of 3 °C min^{-1}. Volatile products (methanol and THF) were distilled off from the reactor, condensed in the water-cooled condenser and were collected in a graduated cylinder. The starting time for the first stage was taken when the first drop of liquid was collected in the water-cooled condenser. The temperature was then kept at 215 °C until 95% (corresponding to 275 ml) of the theoretical amount of methanol was distilled off. The distilled volume was recorded versus time as an indicator of the catalytic activity during the first stage and distillate samples were analysed by GC in order to measure the methanol/THF ratio and thus the rate of THF formation.

Second stage: the internal pressure was slowly reduced from atmospheric pressure down to 1 mbar in 20 min. At the same time the temperature of the reaction melt was increased to 245 °C and kept at this temperature until the end of the polymerisation. The starting time for the second stage was taken when the minimum pressure was reached. The second stage was stopped when no further significant increase in strain gauge signal was detected. The amount of THF formed during the second stage was evaluated by GC analysis of the distillate collected in the liquid nitrogen-cooled condenser.

2.4. Instrumental

^{1}H NMR analysis was performed on a Varian Gemini System 300 MHz instrument by using a $CDCl_3$ /CF_3COOD mixture (4:1 v/v) as solvent and tetramethylsilane (TMS) as reference.

Gel permeation chromatography (GPC) analysis was performed by using a 1,1,1,3,3,3-hexafluoro-2-propanol/-chloroform/methylene chloride (5:75:20 v/v) mixture as eluent (elution rate of 0.8 ml min^{-1}) on a HP 1100 Series apparatus equipped with a PL gel 5 μm Mixed-C column and a UV detector. Calibration was performed using polystyrene standards.

THF and methanol quantification was performed by GC analysis on a HP 6890 Series employing a 30 m (ID 0.53 mm, film thickness 1.0 μm) Zebron ZB-Wax column and *n*-butanol as an internal standard.

Intrinsic viscosity (IV) measurements were carried out on a Ubbelhode viscometer at 30.0 °C using a phenol/1,1,2,2-tetrachloroethane (60:40 by weight) mixture.

Differential scanning calorimetry (DSC) analysis was performed using a Perkin–Elmer DSC7 with a scanning rate of 20 °C min^{-1}. The thermal transitions have been measured in the second heating scan in order to eliminate previous thermal history. The isothermal crystallization have been measured after melting the polymer at 260 °C and cooling at 100 °C min^{-1} to 200 °C. The instrument was calibrated with high purity standards (indium and phenantrene). Dry nitrogen was used as purge gas.

The thermogravimetric analyses (TGA) were performed using a Perkin–Elmer TGA7 apparatus in air (gas flow 40 ml min^{-1}) at 10 °C min^{-1} heating rate, from 25 to 800 °C.

3. Results and discussion

The manufacture of PBT is generally performed in two steps. In the first step, named ester interchange (EI), DMT and BD are reacted (BD/DMT molar ratio of 1.4) while distilling off the resulting methanol and obtaining an oligomer mixture that mainly contains OH end-groups. The second step, named trans-esterification (TE) or polycondensation stage, is performed at 245 °C under dynamic vacuum in order to eliminate the excess glycol. In a previous paper [15] we have showed that BHBT is a good model system to compare the TE rate for the different catalytic systems because it does not contain methoxy or COOH end-groups.

3.1. Small scale catalyst screening

The comparison of the catalytic activities have been conducted by measuring the DP by ^{1}H NMR analysis with the procedure previously reported [15]. The phosphate/catalyst molar ratio used in this first screening was 4 according with the data reported in the literature [13,14]. The main results of the screening are presented in Table 1.

In the case of TBT/phosphate catalytic systems, the highest DP value was obtained using NaH_2PO_4 followed by KH_2PO_4. In particular, the addition of NaH_2PO_4 increased the DP by more than three times compared to the catalytic system containing only titanium. Significant differences were observed among different sodium phosphates: the DP observed for Na_3PO_4 was one third of that for NaH_2PO_4. On the contrary only a small difference was observed among the different potassium phosphates. In agreement with the results reported by Fortunato et al. [23], phosphoric acid acts as catalyst inhibitor. The reasons for these different catalytic behaviour are under investigation by ^{31}P NMR and FTIR analysis and the results will be reported in a following paper. NaH_2PO_4 and KH_2PO_4 were the best co-catalysts also when one half of the titanium was substituted with hafnium. A slight increase in DP was observed for the mixed Ti/Hf/phosphate system compared to the correspondent titanium/phosphate system due to the synergistic effect we have already reported on the Ti/Hf catalytic systems [15]. However, this increase was not as consistent as that observed in the absence of phosphate co-catalysts. Moreover, the addition of phosphates to hafnium only gave rise to a slight increase in polycondensation rate. These results suggest that phosphates have a much stronger co-catalytic effect with titanates rather than with hafnium derivatives.

Table 1
Small scale catalyst screening results using titanium/hafnium/phosphates catalytic systems (25 min at 235 °C under dynamic vacuum)

Co-catalysts	Catalyst composition (mmol/mol$_{TPU}$)			Average DP	Standard deviation
	TBT	Hf	Phosphate		
–	–	–	–	1.7	0.3
–	1.59	–	–	10.0	1.1
Na_3PO_4	1.59	–	6.3	10.9	1.6
K_3PO_4	1.59	–	6.3	25.8	1.3
Na_2HPO_4	1.59	–	6.3	15.5	1.8
K_2HPO_4	1.59	–	6.3	24.9	3.2
NaH_2PO_4	1.59	–	6.3	31.5	1.7
KH_2PO_4	1.59	–	6.3	28.4	2.1
H_3PO_4	1.59	–	6.3	2.5	0.5
–	0.80	0.80	–	12.9	0.6
Na_3PO_4	0.80	0.80	6.3	18.3	1.1
K_3PO_4	0.80	0.80	6.3	31.4	1.7
Na_2HPO_4	0.80	0.80	6.3	22.0	1.8
K_2HPO_4	0.80	0.80	6.3	30.5	2.0
NaH_2PO_4	0.80	0.80	6.3	37.1	2.8
KH_2PO_4	0.80	0.80	6.3	34.7	1.2
–	–	1.59	–	8.0	0.5
K_3PO_4	–	1.59	6.3	8.2	0.1
KH_2PO_4	–	1.59	6.3	8.8	0.5
Na_3PO_4	–	1.59	6.3	8.9	0.1
Na_2HPO_4	–	1.59	6.3	9.0	1.2
NaH_2PO_4	–	1.59	6.3	8.4	1.5
LiH_2PO_4	–	1.59	6.3	8.7	1.2

DP (degree of polymerisation) have been measured by ^{1}H NMR.

Another set of experiments was conducted in order to investigate the optimal catalyst/co-catalyst ratio. The results obtained using NaH_2PO_4 as co-catalyst (reported in Fig. 1) show that, for co-catalyst/catalysts molar ratios over 4 there is only a slight increase in trans-esterification rate in both catalytic systems. On the contrary, for lower ratios, a consistently higher DP was observed by increasing the amount of co-catalyst. For this reason the following experiments and the scale up have been performed with a co-catalyst/catalyst molar ratio of 4. These results are in agreement with those reported by You et al. [13,14].

A further screening was conducted in order to assess the optimal titanium/hafnium ratio in the presence of phosphates. The results obtained are reported in Table 2. Ti/Hf molar ratios ranging from 0.33 to 2 were tested, keeping the overall concentration of titanium plus hafnium constant at 1.59 mmol/mol$_{TPU}$.

The data in Table 2 show that the highest DP was

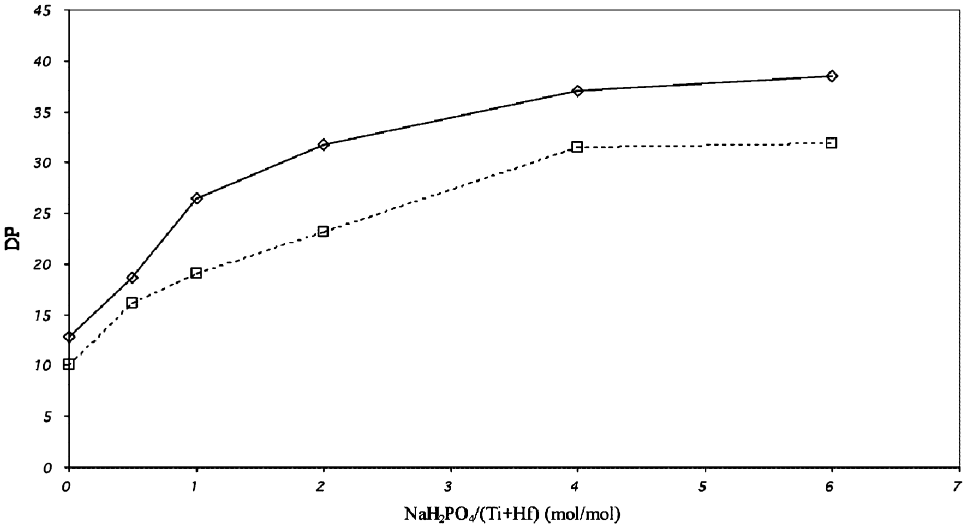

Fig. 1. Effect of NaH_2PO_4 on titanium and mixed titanium/hafnium (1:1 molar ratio) catalytic systems in small scale tests (□ titanium; ◇ titanium/hafnium).

obtained using a Ti/Hf molar ratio ranging from 1 to 2; these results are not in good agreement with those we have reported using the Ti/Hf system [15] for which the best Ti/Hf molar ratio was 0.33. One reason for this discrepancy can be the much higher co-catalytic effect of phosphate towards titanium with respect to hafnium. Therefore, the substitution of Ti with Hf reduces the co-catalytic effect thus counterbalancing the synergistic effect of titanium with hafnium that has a maximum at a molar ratio of 0.33. Nevertheless, it is very important to stress that, by the addition of hafnium, it is possible to reduce the titanium level down to one third while keeping the reaction rate almost constant. Therefore, another set of experiments has been conducted in order to verify the possibility to lower the titanium content, in order to reduce the degradation effects which accompany its use, without affecting the reaction rate. Five different titanium concentrations were used in the presence or absence of NaH_2PO_4 as co-catalysts.

The results in Fig. 2 show a clear co-catalytic effect of NaH_2PO_4 for titanium levels higher than 0.16 $mmol/mol_{TPU}$ while in the absence of the co-catalyst there is no significant DP increase for titanium concentration higher than 0.16 $mmol/mol_{TPU}$. On the contrary, a very low co-catalytic effect has been observed for titanium level lower than 0.16 $mmol/mol_{TPU}$. It is well known that TBT is able to form aggregates when its concentration increases in the reaction medium [2]. This aggregation reduces the catalytically active sites with respect to monomeric TBT, so the increase in the catalytic activity observed in the presence of phosphates can be explained assuming that the phosphate could be able to reduce the aggregation of TBT.

Table 2
Small scale screening for Ti/Hf catalytic systems in the presence of NaH_2PO_4 (phosphate/(Ti + Hf) molar ratio = 4)

Ti/Hf (mol/mol)	Average DP	Standard deviation
0.33	30.2	2.1
0.50	31.3	1.1
1.00	36.1	2.8
2.00	37.1	2.3
Only Ti	31.5	1.7

As a consequence, by adding NaH_2PO_4 it is possible to consistently reduce the titanium loading (0.16 versus 1.59 $mmol/mol_{TPU}$) without affecting the polycondensation rate.

3.2. Micro-pilot plant polymerisation

The scale up was conducted with the aim to verify if the very promising effect of decreasing titanium content and increasing the reaction rate would also be present in the overall polymerisation process. The full polymerisation reactions with the Ti/Hf/phosphate catalytic system have been performed in a 1.8 l micro-pilot plant and the main results are reported in Table 3.

The best overall results were obtained with the Ti(0.20)–Hf(0.61)–NaH_2PO_4(3.24) catalyst mixture that showed a 55% decrease in EI time and a 32% decrease in TE time as compared to the titanium control.

Comparing the Ti(0.81)–NaH_2PO_4(3.24) with the Ti(0.20)–Hf(0.61)–NaH_2PO_4(3.24) catalytic systems it is possible to notice that the presence of hafnium led to a small increase in both EI and TE stages. In all cases the synergistic effect of the NaH_2PO_4 co-catalyst affected mainly the EI time and was stronger for higher titanium contents. This is consistent with the small-scale BHBT tests where the synergistic effect of phosphates was much stronger with titanium than with hafnium. The addition of phosphate and substitution of 9:10 of Ti with Hf did not affect the EI stage, which was still faster than the Ti control. Nevertheless, with this catalyst it was not possible to prepare high molecular weight PBTs. A Hf–NaH_2PO_4 catalyst was also tested, but again in this case no increase in the torque gauge signal was

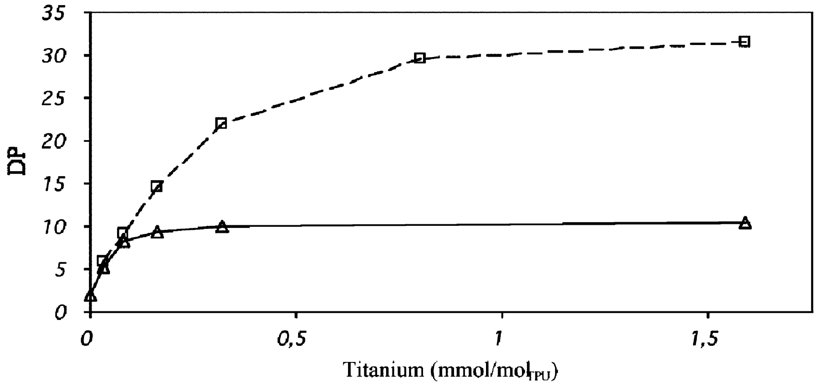

Fig. 2. Effect of phosphate addition on the polymerisation rate for different titanium levels in small scale tests (□ NaH_2PO_4; △ no phosphate).

observed, meaning that no molecular weight build-up was taking place.

Even if the trend in polymerisation rate is very similar to that observed in small scale experiments, in full polymerisation the co-catalytic effect of phosphate is of smaller extent, in particular with respect to the rate of molecular weight increase. The reason is that the results on small scale polymerisations do not take account of catalyst deactivation or of side reactions, such as chain scission occurring during polymerisation, that take place during the entire polymerisation process and that the diffusion of reaction product can be the rate limiting factor at the high melt viscosities observed in the final part of the TE stage. Therefore, as we observed in our previous works, it is not possible to assume that a three-fold increase in reaction rate in BHBT experiments corresponds to the same increase in overall polymerisation rate.

It is indeed very important to underline that the addition of NaH_2PO_4 slightly decreases the amount of THF formed by side reactions. This 10% decrease in THF for run Ti(0.20)–Hf(0.61)–NaH_2PO_4(3.24) can be ascribed to the reduction of the contribution of side reactions and/or to the shorter reaction times needed to obtain the high molecular weight polymer.

The EI conversion versus time curves of Ti(0.20)–Hf(0.61)–NaH_2PO_4(3.24), Ti(0.20)–Hf(0.61) and the Ti control are presented in Fig. 3. The conversion was evaluated by measuring the amount of methanol collected in the condenser during the EI stage.

The Ti(0.20)–Hf(0.61)–NaH_2PO_4(3.24) catalysed reaction started at almost the same rate but became faster after 70% of conversion compared to the Ti control reaction. It has to be stressed that the EI stage has not been conducted in isothermal condition since the melting point of the oligomers increases with the conversion. It is very important to notice that the addition of the phosphate counterbalances the slower reaction rate at low temperatures of the Ti–Hf mixture compared to the titanium catalyst. This difference was already ascribed [16] to the higher activation energy and higher pre-exponential factor in Arrhenius equation for the mixed catalytic system. On the basis of the distillation curves in Fig. 3 it is possible to assume that the addition of phosphates decreases the activation energy of the EI process thus having a positive effect on the low temperature part of the EI stage whereas, do not affect the higher pre-exponential factor for the Ti–Hf system and therefore, do not decrease the reaction rate at high temperature.

Table 3

Overall results of polymerisation using titanium–hafnium–phosphate catalytic systems in 1.8 l micro-pilot plant

Catalyst composition (mmol/mol$_{TPU}$)			EI stage time (min)	TE stage time (min)	$M_{w,GPC}$	IV (dl/g)	BD transformed in THF (mol%)[a]
Ti	Hf	NaH_2PO_4					
0.81	–	–	100	110	92,300	1.01	11.3
0.81	–	3.24	55	85	106,700	1.13	11.0
0.41	0.41	3.24	45	80	100,500	1.03	10.3
0.20	0.61	–	75	60	89,900	0.86	10.0
0.20	0.61	3.24	45	75	97,800	1.03	10.2
0.16	0.65	3.24	70	85	92,000	0.94	11.4
0.08	0.72	3.24	80	140	57,200	0.49	12.9
0.04	0.77	3.24	140	[b]			
–	0.81	3.24	190	[b]			

[a] Respect to the feed.

[b] Only PBT oligomers were obtained using these catalyst compositions.

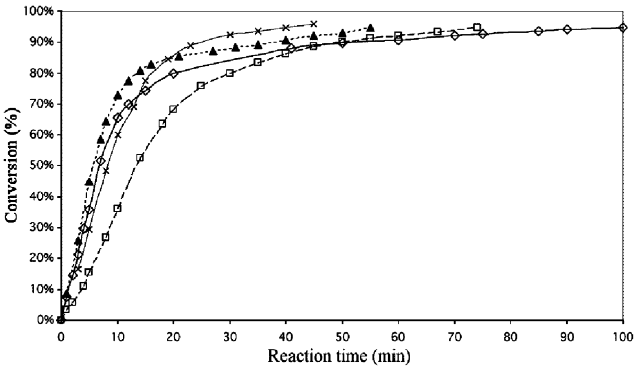

Fig. 3. Conversion curves obtained with titanium–hafnium–phosphate catalysts in the first stage of micro-pilot plant polymerisations (◇ Ti(0.81); □ Ti(0.20)–Hf(0.61); ▲ Ti(0.20)–NaH_2PO_4(3.24); × Ti(0.20)–Hf(0.61)–NaH_2PO_4(3.24)).

3.3. Thermal properties

The melting temperature and a comparison of the crystallization rates for the PBT samples prepared in the micro-pilot plant with different catalytic systems have been evaluated by DSC analysis (Table 4).

Similar melting temperatures were observed for all of the PBTs, while consistent differences were observed for the crystallization time at 200 °C. It is indeed very difficult to compare the crystallization times for polymers obtained with different catalytic systems since several parameters cooperate in affecting the crystallization kinetics (e.g. the molecular weight, the presence of nucleating agents, the presence and the nature of the catalyst). Nevertheless, it is possible to note that higher titanium levels give rise to a slower crystallization. We also observed this effect in our previous work on Ti–Hf catalytic systems [15] and again in this case the slower crystallization can be attributed to the lower mobility of the PBT chains in the melt phase when the titanium content is higher reflecting the apparent increase in molecular weight (and therefore of melt viscosity) due to the interactions of titanium with terminal groups and/or ester groups of PBT. Indeed, in our previous work [15] we have found that the polymers with higher titanium levels presented a higher melt viscosity with respect to polymers of equivalent molecular weight and lower titanium content. Comparing the sample Ti(0.81) with Ti(0.81)–NaH_2PO_4(3.24) and the sample Ti(0.20)–Hf(0.61) with Ti(0.20)–Hf(O.61)–NaH_2PO_4(3.24) it is possible to observe that the addition of NaH_2PO_4 decreases the crystallization rate. However, the reason for this slower crystallization could also be ascribable to the higher molecular weight of the polymer obtained in the presence of NaH_2PO_4.

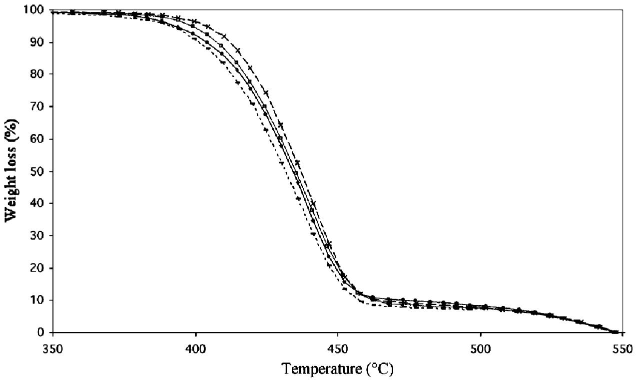

Fig. 4. Thermogravimetric curves in air (heating rate 10 °C min^{-1}) (– Ti(0.81); • Ti(0.81)–NaH_2PO_4(3.24); □ Ti(0.20)–Hf(0.61)–NaH_2PO_4(3.24); × Ti(0.08)–Hf(0.72)–NaH_2PO_4(3.24)).

The thermal stability of the polymers evaluated by thermogravimetric analysis is presented in Fig. 4.

Comparing the TGA curves for Ti(0.81) and Ti(0.81)–NaH_2PO_4(3.24) it is noteworthy that the addition of phosphate have a beneficial effect on PBT thermal stability. The thermal stability can be further increased by substituting titanium with hafnium (compare Ti(0.81)–NaH_2PO_4(3.24), Ti(0.20)–Hf(0.61)–NaH_2PO_4(3.24) and Ti(0.08)–Hf(0.72)–NaH_2PO_4(3.24) TGA curves).

4. Conclusions

Small scale polymerisation and subsequent scale up in higher capacity reactors showed the strong co-catalytic

Table 4
DSC analysis results on polymers obtained in micro-pilot plant polymerisations

Catalyst composition (mmol/mol$_{TPU}$)			M_w	T_m (°C)[a]	ΔH_m (J/g)[a]	Cryst. time[b] at 200 °C (min)	$\Delta H_{cryst.}$ at 200 °C (J/g)
Ti	Hf	NaH_2PO_4					
0.81	–	–	92,300	225	48.0	12.6	−44.2
0.81	–	3.24	106,700	220	39.4	16.5	−38.6
0.41	0.41	3.24	100,500	222	45.0	12.4	−42.8
0.20	0.61	–	89,900	223	47.7	5.6	−44.1
0.20	0.61	3.24	97,800	224	48.9	10.7	−45.8
0.16	0.65	3.24	92,000	224	47.8	8.9	−47.2
0.08	0.72	3.24	57,200	223	54.4	2.9	−47.5

[a] Scanning rate 20 °C min^{-1} on second heating scan.
[b] Measured as peak time.

effect of phosphates on PBT synthesis. In particular, NaH_2PO_4 proved to be the most active co-catalyst with an optimal co-catalyst/catalyst molar ratio of 4. Decreases in polymerisation time and side reactions (THF formation) were observed, which in turn can improve the productivity of the whole process. The co-catalysts have a stronger effect on titanium with respect to hafnium; however, it is possible to obtain a higher reaction rate, substituting the titanium with hafnium and adding the phosphate. Moreover, the use of phosphate and the substitution of titanium with hafnium both improve the thermal stability of the final polymers.

A detailed study of the catalytic mechanism will be presented in a following paper.

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