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New catalysts for poly(butylene terephthalate) synthesis 1. Titanium–lanthanides and titanium–hafnium systems

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Abstract

A complete study of the catalytic activity of lanthanide- and hafnium acetylacetonate catalysts in PBT 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 tetrabutoxide (TBT) catalyst. Small scale polymerization and subsequent scale up in higher capacity reactors showed that TBT-Hf(acac)$_4$ and TBT-La(acac)$_3$ mixed catalysts were more active with respect to TBT as single catalyst. Decreases in polymerization time and THF formation were also observed, which in turn can improve the productivity of the whole process. Furthermore, for similar values of molecular weight, a lower melt viscosity (and thus better processability and crystallizability) was obtained by using mixed catalysts, presumably due to weaker interactions of the polymer terminal groups to lanthanum and hafnium metals with respect to titanium. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(butylene terephthalate); Catalysts; Hafnium; Lanthanides

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, catalyzed by an organotitanate (e.g. titanium tetrabutoxide) [1,2]. While this is a well-known and widely practiced reaction system, it presents a few limitations. In particular, the rate of the transesterification reaction catalyzed by titanates during polycondensation, while sufficient, is relatively slow; thus, during industrial scale production, long residence times are required to prepare high molecular weight polymers. Additionally, degradation reactions can occur at the high temperatures used, producing carboxylic acid end-groups, which in turn affect the thermal stability of the final product, and waste 1,4-butanediol through conversion to unrecoverable side products (e.g. tetrahydrofuran, THF) [3–8].

Previous works have shown that lanthanide-based catalysts (LBC) are interesting for polyester synthesis and reactive blending [9–12]. In particular, studies on poly(ethylene terephthalate) (PET) synthesis have shown that LBC are much more efficient in the first stage of the process (transesterification in the presence of ethylene glycol) and less active in the second stage (polycondensation reaction) with respect to industrially used PET catalysts. Furthermore, PET synthesized with LBC was found to possess enhanced thermal and hydrolytic stability and less discoloration as compared to PET synthesized with titanium-based catalysts and to commercial PET.

The work on PET/PC reactive blending [13,14] has also shown that LBC possess a selective activity (from a kinetic point of view) toward exchange reactions in polyester/polycarbonate blends. This selective activity provides an opportunity to produce in-situ compatibilized polymer blends and block copolymers with desired structures.

For all the reasons presented above, an investigation of the catalytic activity of lanthanide- and hafnium-based catalysts in PBT synthesis was conducted in order to evaluate if the different catalytic behavior of these catalysts could lead to an improvement in the industrial process and in the final properties of the polymer. Part of the results of this study have been already published in a recent patent [15]. In this

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paper we report a complete study of these new catalytic systems together with the characterization of the PBT obtained.

2. Experimental

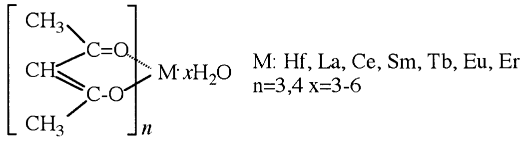
2.1. Materials

Dimethyl terephthalate (DMT) (purchased from Aussapol, Italy), 1,4-butanediol (BD), hafnium chloride, samarium chloride, erbium chloride, terbium chloride, europium chloride and lanthanum chloride (purchased from Aldrich) were high purity products and were used as received without any further purification.

Titanium tetrabutoxide (TBT) (purchased from Aldrich) was distilled under reduced pressure twice and stored in closed bottles under nitrogen at 0°C.

2.2. Catalyst preparation

Lanthanide- and hafnium-based catalysts were used as acetylacetonate complexes because they showed a better solubility compared with the respective alkoxides, as reported in the literature for PC/PET blends [10–12]. All of the catalysts were characterized by elemental analysis, FT-IR and ^{1}H-NMR spectroscopy.



2.2.1. Preparation of hafnium acetylacetonate, Hf(acac)$_4$

A solution of hafnium chloride (3.00 g; 9.37 mmol) in 50 ml of water was added dropwise to a solution of acetylacetone (5.63 g; 56.2 mmol) in 50 ml of water under stirring at room temperature. The pH was then increased to 7 by addition of 2N KOH solution. The reaction mixture, with precipitated Hf(acac)$_4$, was stirred for 6–8 h. Hf(acac)$_4$ was filtered and dried at 60°C under vacuum overnight (yield 65%).

^{1}H-NMR (solvent CDCl$_3$): δ (ppm downfield from TMS) 5.5 (1H, s); 2.1 (6H, s).

2.2.2. Preparation of lanthanide acetylacetonates

All of the other lanthanide acetylacetonates employed throughout this work were synthesized following the same procedure used for Hf(acac)$_4$, starting from the chloride of the corresponding metal.

2.3. Preparation of PBT oligomers

The PBT oligomers (PBTO) having an average degree of polymerization (DP) of 2.5 (used in the small scale polymerization) were prepared by using the 1.8 l batch reactor according to the procedure described below and stopping the reaction at the end of the first stage. TBT was used as catalyst at a concentration of 0.45 mmol/mol$_{\mathrm{TPU}}$, in which TPU stands for terephthalic units present in the reactant mixture.

2.4. Small scale polymerization procedure

A preliminary screening on the catalytic activity related to the second stage of the full polycondensation (i.e. transesterification) was carried out on small quantities of a mixture of PBTO. A typical polymerization procedure is as follow: 2.00 g of PBTO was placed in a glass tube (15 cm long, 2 cm internal diameter) provided with a stopcock. Then the catalysts (TBT and LBC or Hf(acac)$_4$) dissolved in anhydrous toluene were added and the solvent was slowly removed under vacuum. The total amount of catalyst (included TBT already present in PBTO at a concentration of 0.45 mmol/mol$_{\mathrm{TPU}}$) was kept equal to 1.35 mmol/mol$_{\mathrm{TPU}}$. The glass tubes were placed for 25 min in a thermostatic bath at 235°C under dynamic vacuum (about 1 mbar) and the transesterification reaction rate was determined by measuring the degree of polymerization (DP) by ^{1}H-NMR spectroscopy. The samples were dissolved in a CDCl$_3$/CF$_3$COOD mixture immediately before recording the spectra in order to avoid the esterification reaction between hydroxy terminal groups of PBT and CF$_3$COOD.

The ratio between the area of the triplet at 3.92 ppm (related to the methylene groups adjacent to hydroxy terminal groups) and the area of the signal at 4.52 ppm (related to the methylene groups adjacent to ester moieties) was used to determine the DP value (Fig. 1) that is here defined as the number of repeating units per polymer molecule. The two small peaks at 4.28 and 4.76 ppm are attributable to ^{13}C satellites of the 4.52 ppm peak.

2.5. Micro-pilot plant polymerization procedure

Micro-pilot plant polymerization was carried out by using the usual two-stage process in a 1.8 l stainless steel batch

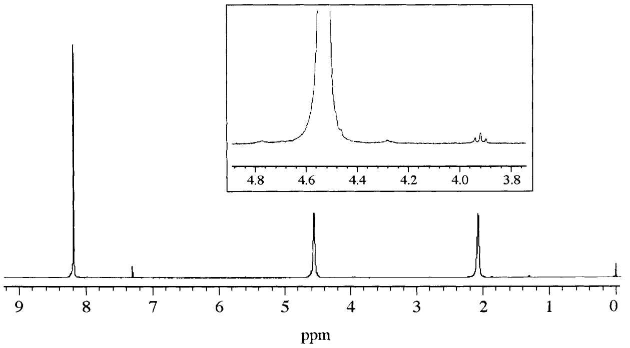


Fig. 1. ^{1}H-NMR spectrum of PBT and expanded region used to determine the DP value (related to methylene groups adjacent to hydroxy terminal groups, 3.92 ppm, and to ester moieties, 4.52 ppm, of PBT).

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 molecular weight of PBT) during the polymerization. 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 polymerization 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 up to 150°C. At this temperature, the catalyst (0.81 mmol/mol$_{TPU}$) was introduced into the reactor. Volatile products (MeOH 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 profile of the reaction melt was set to increase from 150 to 215°C at a heating rate of 3°C min^{-1}. The temperature was then kept at 215°C until 95% (corresponding to 275 ml) of the theoretical amount of MeOH was distilled off. The distilled volume was recorded versus time as an indicator of the catalytic activity during the first stage and distillated samples were analyzed by GC in order to measure the MeOH/THF ratio and thus the rate of THF formation.

Second stage: the internal pressure was slowly reduced from atmospheric pressure down to 0.5–1 mbar in about 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 run. The starting time for the second stage was taken when full vacuum was applied to the reactor. 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.

2.6. Pilot plant reactor polymerization procedure

Pilot plant reactor polymerizations were carried out by using the usual two-stage process in a 10 kg conical batch reactor equipped with twin helical agitators. A typical polymerization procedure is described below.

First stage: DMT (5.00 kg; 26.2 mol), BD (3.30 kg; 36.1 mol) and catalyst (0.81 mmol/mol$_{TPU}$) were loaded (BD/DMT ratio 1.4:1) into the reactor and then heated up to 150°C at atmospheric pressure under stirring at 60 rpm. The temperature profile was set to go from 150 to 215°C with a heating rate of 2.0°C min^{-1}. Volatile products were distilled off from the reactor.

Second stage: the internal pressure was reduced from atmospheric down to 0.5–1 mbar at a vacuum rate of 20 mbar min^{-1}. At the same time the temperature of the reaction melt was increased to 245°C. The helicon reactor was programmed with a 'three-build' profile which works as follows. The polymer is stirred at a constant and high speed (60 rpm) during the second stage. As the viscosity builds, the power required to maintain the agitator speed increases until a 'first build' amps setpoint is reached. When this 'first build' amps setpoint is reached, a step-change to a lower agitator speed, 30 rpm, is made. The melt viscosity continues to increase, resulting in an increase in power requirement until a 'second build' amps setpoint is reached. Another step-change is made to lower the agitator speed to its minimum operating value (18 rpm), and the viscosity build continues until a final 'third build' amps setpoint is reached, which sets the end of the run sequence.

2.7. Instrumental

^{1}H-NMR analysis was performed on a Varian Gemini System 300 MHz instrument by using a $CDCl_3/CF_3COOD$ mixture (80/20 by volume) 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 by volume) mixture as eluent (elution rate of 0.8 ml min^{-1}) on a HP 1100 Series apparatus equipped with a PL gel 5 μ Mixed-C column and a UV detector. Calibration was performed with polystyrene standards.

THF and MeOH quantification was performed by GC analysis on a HP 6890 Series employing a 30 m (ID 0.53 mm, film thickness 1.0 μ) Zebron ZB-Wax column and n-butanol as 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 instrument was calibrated with high purity standards. Dry nitrogen was used as purge gas. Non-isothermal crystallization experiments were carried out by cooling at 20°C/min samples pre-melted at 250°C. The crystallization time was taken as the time at which the maximum of the crystallization peak appeared for each sample.

The melt viscosity (MV) measurements were run on a Göttfert instrument at 250°C with a 21.6 kg weight. The orifice used had dimensions of 1.562 cm length and 0.107 cm diameter. The sample size was 5 g, and the sample was dried at 150°C for 1 h.

3. Results and discussion

A preliminary set of experiments using either LBCs or Hf(acac)$_4$ as single catalyst were carried out both on small scale and on pilot plant scale. All catalysts tested showed a very poor catalytic activity compared to TBT; thus the research was directed towards mixed catalytic systems taking into account that mixtures of different catalysts are widely used in the patent literature.

Table 1
Small scale polymerization: DP values for different catalytic composition

	TBT/co-catalyst molar ratio				
Catalytic mixture	1:2	1:1	2:1	3:1	4:1
TBT-La(acac)$_3$	11.3	16.2	18.7	17.5	17.6
TBT-Ce(acac)$_3$	13.4	15.5	12.9	–	–
TBT-Hf(acac)$_4$	19.1	14.6	14.3	–	–
TBT-Er(acac)$_3$	10.4	13.4	13.0	14.4	13.3
TBT-Tb(acac)$_3$	8.6	12.3	9.2	–	–
TBT-Eu(acac)$_3$	9.4	10.7	12.8	12.6	12.0
TBT-Sm(acac)$_3$	9.6	9.6	11.0	–	–
TBT control	10.2				

The previous results on PET synthesis and reactive blending combined with the above results on PBT have shown that LBCs and titanium-based catalysts have a completely different catalytic behavior. It was also reported [9] that titanium catalyzes degradation reactions, decreasing the thermal stability of PET more than lanthanides do. For these reasons PBT was synthesized using a lower amount of titanium. Decreased amounts of titanium leads to a slower reaction rate and, thus, in this work part of the titanium was substituted with lanthanides.

3.1. Small scale polymerization results

A first set of experiments was performed in order to verify if the catalyst mixtures were able to produce high molecular weight PBT. For this reason TBT-LCB and TBT-Hf(acac)$_4$ mixtures at several compositions were tested in small scale polymerizations. The results are shown in Table 1 and were surprisingly good, exhibiting a marked synergistic effect for several catalytic mixtures which showed DP values higher than those observed with only TBT as a single catalyst.

The results pointed out that TBT-La(acac)$_3$ and TBT-Hf(acac)$_4$ systems were the most promising polycondensation catalyst mixtures. In particular, the best catalytic system was the TBT-Hf(acac)$_4$ 1:2 mol/mol mixture that showed an almost doubled DP compared to the TBT control. For TBT-La(acac)$_3$ mixed catalysts the best composition was a 2:1 molar ratio.

3.2. Micro-pilot plant polymerization results

After the encouraging results from small scale screening, the polymerization process catalyzed by the titanium–hafnium system was scaled-up in the 1.8 l pilot plant for a full polymerization. The results of these tests are shown in Table 2. From the first two runs with equimolar catalyst composition, it is worth noting that no significant differences were observed if the Hf(acac)$_4$ was added either at the beginning of the first stage of the polymerization or at the beginning of the second stage. The most important result of these first two polymerization tests was that the TBT-Hf(acac)$_4$ system showed a 45% decrease in second stage time to reach a similar molecular weight (as measured by IV) as compared to TBT control run. The only minor difference observed was in the IV value of the final polymers: PBT obtained by adding Hf(acac)$_4$ at the beginning of second stage showed a 0.1 dl/g increase in intrinsic viscosity compared to the test where that catalyst was added along with TBT at the beginning of first stage. As the first and second stage duration were exactly the same for both tests, the fresh catalyst added at the beginning of the second stage, being more active, yields polymer samples with a higher molecular weight. Furthermore, it is important to note that THF formation during the second stage using the mixed catalyst was consistently lower as compared to the TBT control run, probably because of the shorter reaction time.

Taking into account that no significant difference was observed in the reaction time or the THF formation during the first stage with mixed catalyst, in all the other tests Hf(acac)$_4$ was always added at the beginning of the run.

Along with the TBT-Hf(acac)$_4$ 1:1 mol/mol system, other catalytic compositions with lower amounts of TBT were tested in the pilot plant, taking into account that in the small scale screening all the catalyst mixtures tested were more active in the second stage compared to the control. The TBT-Hf(acac)$_4$ 1:3 mol/mol system also showed a shorter first stage duration (75 min compared to 100 min for TBT

Table 2
Micro-pilot plant polymerization: TBT-Hf(acac)$_4$ mixed catalyst results

TBT-Hf(acac)$_4$ molar ratio	1st stage duration (min)	1st stage THF (% mol)[a]	2nd stage duration (min)	IV (dl g^{-1})	BD wasted (%mol)[b]
1:1[c]	100	2.1	60	0.96	8.9
1:1	100	1.8	60	0.86	9.5
1:2	90	1.9	50	0.66	8.8
1:3	75	2.0	60	0.86	10.0
1:3[d]	80	1.8	65	0.86	9.8
TBT control	100	1.8	110	1.01	11.3

[a] In condensed volatile products.
[b] Transformed in THF, respect to the feed.
[c] Hf(acac)$_4$ added at the beginning of the 2nd stage.
[d] Repeated run.

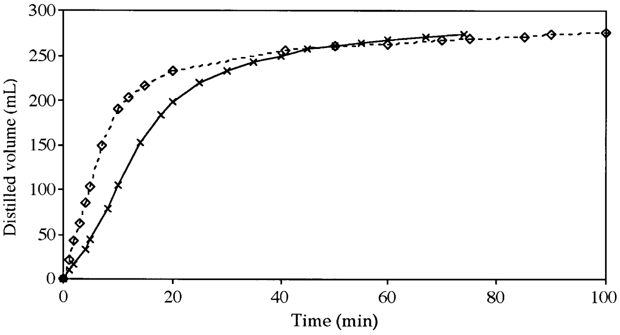


Fig. 2. Pilot plant first stage results with TBT-Hf(acac)$_4$ 1:3 mol/mol (×) and TBT control (◇).

control). This catalyst mixture was tested twice in order to evaluate the reproducibility of the method. The results of the two runs were not significantly different in all of the variables measured.

The total distillate volume curve of the first stage using the TBT-Hf(acac)$_4$ 1:3 mol/mol catalyst mixture is shown in Fig. 2. Similarly to what was observed in the preliminary tests for reactions with LBC or Hf(acac)$_4$ as single catalyst, the mixed catalysts proved to be less active at the beginning of the reaction, when the temperature was lower than 200°C. However, after about 75% of conversion the mixed catalyst was more active than TBT as single catalyst and a cross-over of the two distillation curves occurred after 50 min (about 90% conversion). The same trend was observed for the other TBT-Hf(acac)$_4$ compositions. Similarly to the lanthanide-catalyzed reactions, this suggests that the mixed catalyst reactions, as compared to the TBT-catalyzed reaction, present a higher activation energy in the Arrhenius equation and/or secondary reactions which lead to less titanium catalyst deactivation. The values of Arrhenius equation parameters have been measured using model compounds and will be reported in the Part 2 of this work [16] together with an extended investigation on the catalyzed reaction mechanism.

3.3. Pilot plant reactor polymerization results

A further scale up of TBT-Hf(acac)$_4$ and TBT-La(acac)$_3$ mixed catalysts was carried out in helicone reactors with the results reported in Table 3. For all three compositions investigated, mixed catalysts led to a significant reduction (19–26% lower) in both the '1st build' and in total polycondensation time with respect to TBT as single catalyst. Furthermore, the molecular weight (both from IV and GPC measurements) of the polymers prepared with TBT-Hf(acac)$_4$ and TBT-La(acac)$_3$ catalysts was slightly higher than that obtained with TBT alone.

It is very interesting to note an evident disagreement between MV and IV or Mw_{GPC} values; in fact the higher the TBT content the higher is the MV value, notwithstanding comparable values of IV and Mw_{GPC}. This fact can be explained by taking into account the stronger tendency of titanium (with respect to hafnium and lanthanum) to interact with terminal groups of PBT chains. This leads to an apparent increase of the molecular weight in the molten state and, thus, higher MV values with respect to other PBT samples with lower TBT contents. On the contrary, in solution measurements (IV and GPC) the solvent is able to destroy these interactions between titanium and PBT chains and the resulting molecular weight value is independent of the catalyst composition.

This interpretation is also supported by the DSC results reported in Table 4. In all cases, PBT prepared with mixed catalysts showed higher crystallization enthalpy and lower crystallization time and higher melting enthalpy with respect to PBT synthesized with only TBT. For example, in the case of TBT-Hf(acac)$_4$ crystallization time at 200°C decreases linearly (from 4.92 to 3.47 min) with the TBT content. Also, the absolute values of the crystallization and melting enthalpies (from 35.5 to 44.6 J g^{-1} and from 42.7 to 49.4 J g^{-1}, respectively) increase in the same manner. All these thermal data 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 of molecular weight due to the interactions between titanium and terminal groups of PBT; similar behavior has been already reported for titanium-containing PET [17].

4. Conclusions

New catalytic compositions for PBT polymerization, consistently more active respect to standard titanium based catalysts, have been discovered. Small scale polymerization and subsequent scale up in higher capacity reactors have shown that TBT-Hf(acac)$_4$ and TBT-La(acac)$_3$ were the most active systems. In particular, the TBT-Hf(acac)$_4$ 1:3 mol/mol catalyst permitted a 25% reduction in first

Table 3
Pilot plant reactor polymerization: TBT-Hf(acac)$_4$ and TBT-La(acac)$_3$ mixed catalyst results

Catalytic mixture	Molar ratio	1st build time (min)	Polycondensation time (min)	MV (poise)	IV (dl g^{-1})	Mw_{GPC}
TBT-Hf(acac)$_4$	1:3	34	52	4282	1.25	106800
TBT-Hf(acac)$_4$	1:1	32	49	6793	1.18	105000
TBT-La(acac)$_3$	3:1	31	45	7420	1.21	104200
TBT control	–	42	58	7468	1.16	104100

Table 4
DSC analysis on samples prepared in helicon reactors

Catalytic mixture	Molar ratio	ΔH_{melt}[a] (J g^{-1})	Cryst. time[b] at 200°C (min)	Cryst. time[b] at 205°C (min)	$\Delta H_{cryst.}$ at 205°C (J g^{-1})
TBT-Hf(acac)$_4$	1:3	49.4	3.47	9.67	−44.6
TBT-Hf(acac)$_4$	1:1	44.8	4.25	13.73	−41.2
TBT-La(acac)$_3$	3:1	46.5	4.16	12.23	−38.3
TBT control	–	42.7	4.92	15.97	−35.5

[a] Non-isothermal condition (scanning rate 20°C min^{-1}).

[b] Measured as peak time.

stage reaction time, to reach the same conversion, and a 45% reduction in second stage time, to reach similar molecular weight, respect to TBT as single catalyst. Another important feature of this catalytic system is represented by the consistent (12%) reduction in THF formation, that is the main unrecoverable by-product of the polymerization process. Furthermore, for similar values of molecular weight, a lower melt viscosity (and thus better processability and crystallizability) was obtained by using mixed catalysts, presumably due to weaker interactions of the polymer terminal groups to lanthanum and hafnium metals with respect to titanium.

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