

New Catalyst for the Synthesis of Poly(butylene terephthalate) with High Thermo-oxidative Stability

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ABSTRACT: In this paper we report the employment of $\text{Ti}(\text{acac})_2(\text{O-}i\text{Pr})_2$ (titanium bisacetylacetonate diisopropylate) as a novel catalyst for the synthesis of poly(butylene terephthalate) (PBT). Large scale synthesis of several polymers with the new catalytic system and with the standard catalyst $\text{Ti}(\text{O-}n\text{Bu})_4$ (titanium tetra-*n*-butylate) have been performed in a 20 L pilot plant. In the optimized reaction conditions, $\text{Ti}(\text{acac})_2(\text{O-}i\text{Pr})_2$ has shown significantly higher activity than standard catalyst, $\text{Ti}(\text{O-}n\text{Bu})_4$. Furthermore, a stabilized PBT has been synthesized in the presence of

$\text{Ti}(\text{O-}n\text{Bu})_4$ as catalyst with the addition of the stabilizer U626. Then, the stability of the synthesized polymers toward thermo-oxidation has been tested in a forced circulating air oven. The polymers obtained in the presence of $\text{Ti}(\text{acac})_2(\text{O-}i\text{Pr})_2$ system showed higher stability towards thermo-oxidation than stabilized and not stabilized PBT, synthesized in the presence of $\text{Ti}(\text{O-}n\text{Bu})_4$. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3071–3076, 2007

Key words: PBT; titanium; stabilization

INTRODUCTION

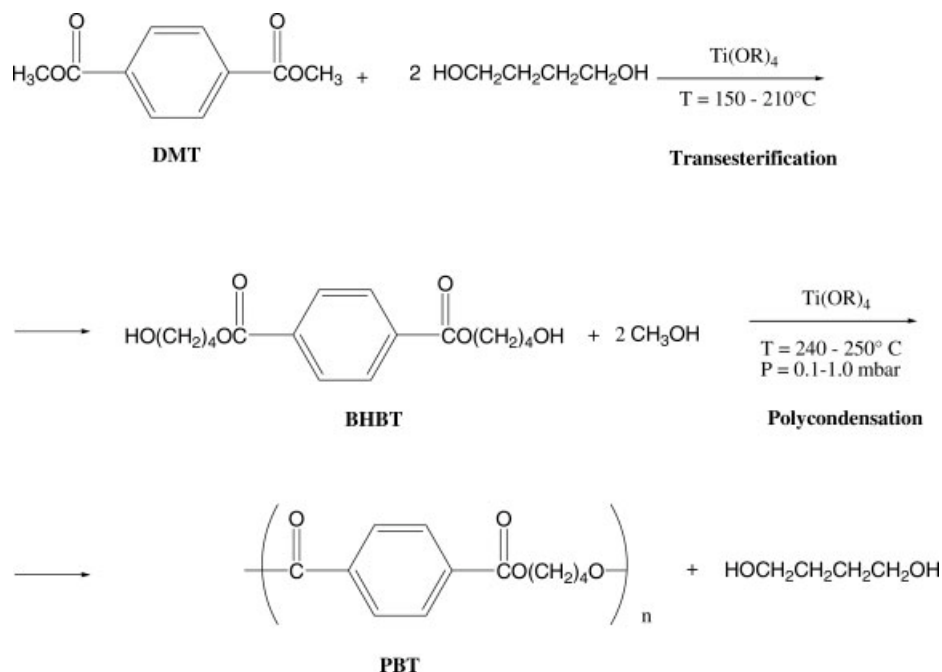
Poly(butylene terephthalate) (PBT) is one of the most important thermoplastic polyesters and is largely used to produce fibers as well as in motor and electric industry.^{1–3} PBT is synthesized in a two stages process, which consists of reaction of dimethyl terephthalate (DMT) or terephthalic acid with 1,4-butanediol, and subsequent polycondensation of the resulting oligomers (Scheme 1). Both the steps are catalyzed by Ti(IV) alcolates for both industrial and laboratory scale. Side reactions can occur at the used high reaction temperatures, causing discoloration of polymer⁴ and formation of carboxylic acid end-groups (C.E.G.),⁵ which affect the properties and the thermal stability of the polymer. The problem of stability is well-known for poly(ethylene terephthalate) (PET); in this case several phosphorous-based compounds (phosphate salts, alkyl phosphates, alkyl phosphonates) are added to both transesterification and polycondensation catalyst to suppress undesired side reactions.^{6–11}

Recently, several studies exploited the possibility to employ different catalytic systems with improved

activity.^{12–18} Two main approaches have been developed: the use of different metal complexes or the use of a cocatalyst in addition to the effective catalyst. Interesting results have been recently reported by Yamamoto and coworkers with the introduction of Hf(IV) based compounds as high active catalysts in polyesters synthesis.^{12–15} Another interesting work is related to the use of phosphorous compounds as cocatalysts in addition to Ti(IV) alcolates. This system is reported to increase the polymerization rate for PBT.^{16–18} Moreover, the use of this type of cocatalyst improves the thermal stability of the obtained polymers.¹⁶

The possibility to modify the catalyst activity and the properties of polymers with the modification of the catalyst structure attracted our attention. For these reasons we have tested in past years a series of additives, complexing agents and new titanium(IV) compounds in both the production of PET and PBT. We tested phosphorous based compounds (i.e. triethylphosphoneacetate, triethylphosphoneformiate, trimethylphosphate), well-known bidentate (i.e. acetylacetonate) and polydentate (i.e. Na_2EDTA) ligands in addition to titanium(IV) alcolates. In this paper we have reported the obtained data on the employment of titanium(IV)-acetylacetonate system as catalyst in the synthesis of PBT. We have used a 20 L pilot plant for the synthesis of PBTs in the presence of both commercially available $\text{Ti}(\text{acac})_2(\text{O-}i\text{Pr})_2$ (titanium bisacetylacetonate diisopropylate) whose

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Scheme 1 Synthesis of PBT.

structure is reported in Figure 1, and titanium(IV)-acetylacetonate system, prepared according to the reported procedure. To the best of our knowledge this system has never been used as catalyst in polyester production. Additional advantages of the chosen catalyst are the low cost, the easy of the synthesis, and its known stability toward hydrolysis.

We have also compared the characteristics of the obtained polymers with stabilized (Ultranox 626 was used as radical scavenger) and not stabilized PBT synthesized with the standard catalyst, $\text{Ti(O-}n\text{Bu)}_4$, (titanium tetra-*n*-butylate).^{19,20} Special attention has been given to the evaluation of thermal and thermo-oxidative stability of the synthesized polymers. We tested the stability toward thermo-oxidation through the ageing of large quantity of pellets in forced circulating air oven. This is considered the most acceptable method of accelerated thermo-oxidative testing.²¹ Then, the treated samples were analyzed in

terms of color, intrinsic viscosity (I.V.) and carboxyl end groups (C.E.G.), to compare the degradation level of the representative polymers.

EXPERIMENTAL

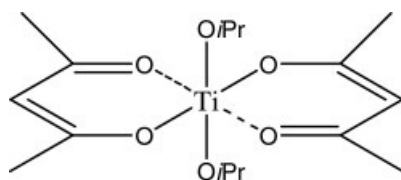
Materials

Dimethyl terephthalate (DMT) was supplied and used without further purification from Montefibre S.p.A.; 1,4-butanediol (1,4-BD) from BP; $\text{Ti(O-}n\text{Bu)}_4$, $\text{Ti(acac)}_2(\text{O-}i\text{Pr)}_2$, and acetylacetonone were purchased from Aldrich; the stabilizer U626 was purchased from General Electric.

Instrumental and analysis

Large scale polymerization was performed in a 20 L steel reactor heated with electric resistance and equipped with mechanical stirrer (driven at variable rpm), a strain-gauge sensor mounted on the stirrer shaft to monitor the melt viscosity (and indirectly the increase of molecular weight) during the polymerization, a distillation column with a water condenser, a vacuum oil pump (mod. Edwards E2M-12) with a liquid nitrogen trap. The reaction temperature was increased at a fixed heating rate according to standard procedures. All of the processing parameters were monitored by electronic recorders.

Thermal measurements were performed by a DSC-7 Perkin-Elmer calorimeter under nitrogen



$\text{Ti(acac)}_2(\text{O-}i\text{Pr)}_2$

Figure 1 Catalyst structure.

flow, at 10°C/min rate for both heating and cooling. The symbols T_m , ΔH_m , T_{mc} , ΔH_{mc} reported in Table II, respectively, refer to melting temperature, melting enthalpy, temperature of crystallization from melt, enthalpy of crystallization from melt.

Thermogravimetric analysis was performed with a METTLER TGA/SDTA 851 apparatus, in air flow, at 20°C/min rate.

The intrinsic viscosity (I.V.) was determined measuring the dropping time at 30°C in an auto viscosimeter Shotte-Gerate of solution of 0.600 g of PBT in 50.0 mL of *o*-chlorophenol. The I.V.s were determined with an accuracy of ± 0.002 dL/g, according to well-established procedures.

Color L and color b, according to Cielab scale, were determined on the pellets using a colorimeter BYK Gardner.

Carboxyl end groups (C.E.G.) were determined using an automatic titrator Metrohm 716 DMS Titrino, equipped with Photometer 662 Metrohm and a 1 mL burette. *Procedure*: a quantity of 2.000 g of PBT pellets was dissolved in 50 mL of distilled *o*-cresol at 90°C, under mechanical stirring for about 30 min. Then, at room temperature, 1 mL of a solution of blue-bromophenol was added (the indicator solution was prepared dissolving 0.040 g of blue-bromophenol in 210 mL of a mixture chloroform : ethanol = 200 : 10 mL) and the resulting mixture was titrated with a standard solution of KOH in methanol. The equivalent point was determined with the photometer at 607 nm. The accuracy of the method, according to well-established protocols, is ± 0.002 equiv/10⁶ g.

Accelerating thermo-oxidation tests were performed in a forced circulating air oven model WTC BINDER FD53 at 160°C. In the oven five identical samples of 100 g of pellets (pellet dimensions: 3 × 3 × 2 mm³) of PBT were put in bakers of perfectly identical shape. Every sample was taken out of the

oven at different times (see Tables III–VI), and color, I.V. and C.E.G. were measured.

Typical experimental procedure for Ti(IV)-acetylacetonate complex synthesis

In an oven-dried two-neck round-bottomed flask, a solution of Ti(*o*-*n*Bu)₄ (20.2 mmol), in dry 1,4-butanediol (50 mL) was heated under nitrogen at 130°C for 3 h. Then, acetylacetonate (40.4 mmol) was added and the solution was stirred at 80°C for 1 h. The obtained solution was used in the synthesis of PBT without any other treatment.

Pilot plant polymer synthesis

In a typical synthesis 8000 g (43.50 mol) of DMT and 4825 g (53.61 mol) of 1,4-BD were introduced into the reactor. The mixture was heated at 145°C under stirring at atmospheric pressure and, at this temperature, 20.2 mmol of the titanium compound were added to the melt. Then the temperature was raised to 230°C. During this period, transesterification proceeded till the complete distillation of methanol. Then the pressure was reduced in the range 0.5–1.0 mbar and the temperature increased at 255°C. These are the conditions for the polycondensation stage, in which the molecular weight increases and 1,4-BD distills off. The synthesis was monitored with an electronic torque-meter and the reaction was stopped at an I.V. in the range of 0.83–0.89 dL/g. Then, the reactor was pressurized at 1.1 bar with nitrogen and the polymer was extruded and granulated.

In the synthesis of stabilized PBT 5 (see below, Table I), the stabilizer U626 was added to the reaction mixture at the end of the transesterification stage as a suspension of 8 g in 80 g of 1,4-BD.

TABLE I
Characteristics of Different PBT

Sample	Catalyst	EI stage time (min)	PC stage time (min)	I.V. (dL/g) ^a	Color L ^b	Color b ^b	C.E.G. equiv/10 ⁶ g ^c
1	Ti(<i>o</i> - <i>n</i> Bu) ₄	86	87	0.851	89.9	2.77	20
2	Ti(acac) ₂ (<i>o</i> - <i>i</i> Pr) ₂ ^d	72	78	0.889	80.4	3.75	25
3	Ti(acac) ₂ (<i>o</i> - <i>i</i> Pr) ₂ ^{d,e}	76	92	0.898	79.0	2.90	23
4	Ti(<i>o</i> - <i>n</i> Bu) ₄ + acetylacetonate ^f	67	83	0.851	79.5	3.20	27
5 ^g	Ti(<i>o</i> - <i>n</i> Bu) ₄ + U626	85	85	0.829	90.6	5.51	22

^aI.V.s were measured on a solution of PBT in *o*-chlorophenol employing an auto viscosimeter Shotte-Gerate. The accuracy of the method is ± 0.002 dL/g.

^bAccording to Cielab scale, colors were determined employing a colorimeter BYK Gardner.

^cC.E.G. is the acronym of carboxylic end groups. They were determined according to the procedure reported in the experimental section. The accuracy of the method is ± 0.002 equiv/10⁶ g.

^dThe complex was supplied from Aldrich.

^eThe catalyst loading was reduced of 10%.

^fThe catalytic system was prepared according to the procedure reported in the experimental section.

^gThe stabilizer U626 was added in the course of the synthesis.

RESULTS AND DISCUSSION

Synthesis and characterization of PBT polymers

The first efforts were devoted to large scale synthesis of representative PBTs in 20 L pilot plant in the same reaction conditions. The characteristics of the synthesized polymers are summarized in Table I. Comparing the obtained results, the acetylacetonate complexes showed a significant higher activity than $\text{Ti}(\text{O}-n\text{Bu})_4$ for both transesterification (EI) and polycondensation (PC) stages (entries 2–4). In fact $\text{Ti}(\text{acac})_2(\text{O}-i\text{Pr})_2$ (entry 2) led to a PBT in a shorter reaction time and, according to the determined intrinsic viscosities, with a higher molecular weight.

Furthermore, it is noteworthy that the higher activity of the new catalyst gave us the possibility to reduce the catalyst loading of 10% without appreciable loss of activity (entry 3).

The use of acetylacetonate-titanium(IV) based system, prepared according to the procedure reported in the experimental section, led to results comparable to those obtained with the commercially available complex (entry 4).

The employment of a more active catalyst or the possibility to reduce the catalyst loading is an important goal to achieve, whose aim is to reduce the manufacturing costs of production. To confirm these results, the synthesis of the representative polymers (entries 1–4) were repeated in the conditions reported in the experimental section. Also in these cases, in the presence of $\text{Ti}(\text{O}-n\text{Bu})_4$, we obtained again longer reaction time for both EI and PC stages with respect to $\text{Ti}(\text{IV})$ -acetylacetonate complexes and all the parameters (I.V., color L and b, CEG) were comparable to those reported in Table I.

In addition to the reported examples, we have synthesized a stabilized polymer in the presence of commercial available stabilizer U626 and $\text{Ti}(\text{O}-n\text{Bu})_4$ as catalyst (entry 5). The stabilization of polyesters with radical scavengers is a common practice,^{19,20} and this example was useful in the analysis and comparison of thermo-oxidative stability of the samples.

It is well-known that the color and the appearance of PBT has a great importance from economical and practice point of view. The color of polymers can be numerically measured in terms of *L*-value and *b*-value directly on the pellets, according to Cielab scale (Table I). *L*-Value is related to the degree of whiteness with a greater numerical value showing a higher (desirable) whiteness. The whiteness and consequently color L is usually related to the level of crystallinity of polyesters. The *b*-value is related to the degree of yellowness, and a higher numerical value shows a higher (undesirable) degree of yellowness. A particular importance is attributed to the significance of color b: this parameter is usually related to the level of degradation of macromolecules. In

fact many studies demonstrate that degradation processes usually led to conjugated or oxidized moieties that absorbs in near UV.⁴

In our work, all the samples are very similar in terms of color b (the degree of yellowness), but surprisingly color L (the level of whiteness) is significantly lower for the polymers synthesized in the presence of titanium(IV)-acetylacetonate catalytic systems. This can be explained by a lower level of crystallinity due probably to the formation of a small amount of di(butanediol) as comonomer.

Carboxyl end groups (C.E.G.) were also determined to obtain additional information on the stability of the polymers. In fact, the influence of C.E.G. on thermal and hydrolytic degradation of polyesters is well known and it is considered an important parameter to predict the stability of PBT, during the processing and the life of the material.⁵ The determined C.E.G. can be considered comparable for all the PBTs. We have found very low numerical values pointing out again the good quality of the synthesized polymers.

Thermal properties and thermo-oxidative stability of the synthesized PBT

We have focused our efforts on the evaluation of thermal properties and thermo-oxidative stability of the three representative polymers (entries 1, 2, and 5, Table I). PBTs 3 and 4, synthesized respectively in the presence of a reduced amount of the catalyst and with the alternative sources of titanium-acetylacetonate system (entries 3 and 4, Table I), have shown similar behavior in comparison with the polymer reported in entry 2 and for this reason are not described in details.

Thermal and thermogravimetric analysis

Melting and crystallization temperatures for PBT samples have been evaluated by DSC analysis (Table II).

The comparison of the reported data shows that T_m is significantly lower for the polymer synthesized in the presence of $\text{Ti}(\text{acac})_2(\text{O}-i\text{Pr})_2$. A lower T_m can be related to a lower degree of crystallinity and also

TABLE II
Calorimetric Data of the Synthesized PBT

Sample	Catalyst	T_m^a	ΔH_m^b (J/g)	T_{mc}^c	ΔH_{mc}^d (J/g)
1	$\text{Ti}(\text{O}-n\text{Bu})_4$	222	47	177	-49
2	$\text{Ti}(\text{acac})_2(\text{O}-i\text{Pr})_2$	219	47	175	-42
5	$\text{Ti}(\text{O}-n\text{Bu})_4$ + U626	220	47	176	-46

^a The symbol T_m refers to melting temperature.

^b ΔH_m is the determined melting enthalpy.

^c T_{mc} refers to the temperature of crystallization from melt.

^d ΔH_{mc} is the enthalpy of crystallization from melt.

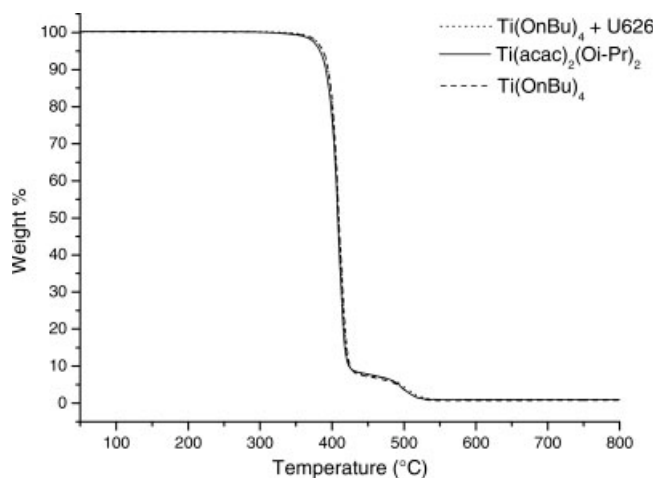


Figure 2 TGA curves of the synthesized PBT.

a lower value of T_{mc} and ΔH_{mc} is an indication of a pourer tendency to crystallize. As previously reported for the behavior of color L (see Table I), also in this case such an effect can be attributed to the formation and incorporation of a small amount of an additional comonomer as di(butanediol).

The thermal stability of the polymers evaluated by thermogravimetric analysis is presented in Figure 2.

The thermogravimetric analysis in air flow shows for all the polymers a very similar degradation pattern, which occurs in a two-step process, consistent with literature descriptions for other PBTs (see Fig. 2).^{22,23} It is worth noting that the three polymers show almost undistinguishable degradation curves, confirming that TGA is not an effective ageing test to highlight thermal and thermo-oxidative degradation.²⁴ In fact, it is well-known that TGA is frequently used only whereas strong differences are evident as between flame retardant modified versions and the standard one, while thermo-oxidation processes require longer reaction times and not as harsh conditions as in TGA analysis.^{22,23}

Thermo-oxidative stability

The evaluation of thermo-oxidative stability was performed by the ageing of large quantity of pellets in

TABLE III
Color-L^a of the PBT Polymers after the Oven Ageing at Different Time

Time (h)	1: Ti(O- <i>n</i> Bu) ₄	2: Ti(acac) ₂ (O- <i>i</i> Pr) ₂	5: Ti(O- <i>n</i> Bu) ₄ + U626
0	89.9	80.4	90.6
7	88.4	86.7	89.4
23	85.2	86.3	86.7
31	85.4	86.0	86.2
47	83.6	87.0	84.9

^a See footnote *b* of Table I.

TABLE IV
Color-b^a of the PBT Polymers after the Oven Ageing at Different Time

Time (h)	1: Ti(O- <i>n</i> Bu) ₄	2: Ti(acac) ₂ (O- <i>i</i> Pr) ₂	5: Ti(O- <i>n</i> Bu) ₄ + U626
0	2.77	3.75	5.51
7	11.32	5.05	8.80
23	16.69	6.05	12.78
31	16.40	6.89	13.41
47	19.07	7.66	14.63

^a See footnote *b* in Table I.

forced circulating air oven. We put a series of five identical samples for each polymer in the oven at 160°C and we measured, at different times, color-L (Table III), color-b (Table IV), intrinsic viscosity (I.V.; Table V) and carboxyl end groups (C.E.G.; Table VI) for the treated samples.

A comparison of the reported data shows that PBT 2, synthesized with Ti(acac)₂(O-*i*Pr)₂, is the most stable towards thermo-oxidation. After prolonged ageing time, all the measured parameters show that 2 keeps its properties practically intact. In fact PBT 2 suffers a very slight discoloring with a constant degree of whiteness (Color-L, Table III), and a very reduced increase of yellowness (color-b, Table IV); a constant value of C.E.G. (carboxyl end groups, Table VI) and a slight increase of I.V. (see Table V).

The trend of I.V. in PBT 2, since it cannot be related to the accuracy of the method (0.002 dL/g, see experimental section), can seem surprising, but both the increase and the decrease are actually very small. If on one hand the slight decrease from 7 to 47 h can be easily attributed to a slight degradation, the increase after the first 7 h can be related to a very small increase of molecular weight. Usually, SSP (solid state polycondensation) requires different reaction conditions but the possibility of milder conditions for SSP is very intriguing and other studies are in progress to evaluate the effect of variation of temperature. SSP is a well-known process used to increase sensitively molecular weight of polyesters after the extrusion on solid polymer, heating at a temperature below its T_m , but above its glass transition temperature (usually in the range is from 170 to 210°C) and reaction time between 5 and 10 h in vacuum or in N₂ flow.^{25–28}

TABLE V
Intrinsic Viscosity (dL/g)^a of the PBT Polymers after the Oven Ageing at Different Time

Time (h)	1: Ti(O- <i>n</i> Bu) ₄	2: Ti(acac) ₂ (O- <i>i</i> Pr) ₂	5: Ti(O- <i>n</i> Bu) ₄ + U626
0	0.851	0.889	0.829
7	0.829	0.904	0.806
47	0.773	0.894	0.790

^a See footnote *b* in Table I.

TABLE VI
Carboxylic End Group (C.E.G., equiv/10⁶ g) of the PBT
Polymers After the Oven Ageing at Different Time^a

Time (h)	1: Ti(O- <i>n</i> Bu) ₄	2: Ti(acac) ₂ (O- <i>i</i> Pr) ₂	5: Ti(O- <i>n</i> Bu) ₄ + U626
0	20	25	22
23	26	29	24
47	35	28	30

^a See footnote *b* in Table I.

The behavior of Color L in PBT **2** is very peculiar and has to be noted (Table III). In fact, the significant improvement of color L (and of the related level of whiteness), after the first 7 h of heating, can be related to the annealing that crystallizes the otherwise crystallinity-retarded polymer. This confirms our previous hypothesis about the formation and incorporation of an additional comonomer as di (butanediol).

On the contrary PBT **1**, synthesized with Ti (O-*n*Bu)₄ and without stabilizer, is the less stable. It shows an increase of C.E.G. and a very marked discoloring according to the strong variation of both Color-L and color-b. Also the decrease of intrinsic viscosity and of the related molecular weight is very pronounced. This is a very deleterious phenomenon, because the decreasing of molecular weight causes the loss of mechanical proprieties of materials.²¹

PBT **5**, with U626, raises an intermediate degradation level between the other two: it is more stable than **1** and less stable than **2**. In this case, the use of the stabilizer has a positive influence on the stability of the polymer obtained in the presence of Ti (O-*n*Bu)₄ as catalyst. In fact both the discoloring, the decrease of the intrinsic viscosity (I.V.) and the increase of C.E.G. are not as pronounced as in **1**.

Regarding the mechanism of degradation processes, it clearly seems that the catalyst has a strong influence on the stability of PBT, on the degradation reactions in solid polymer. Degradation reactions are very complex processes that usually bring to the discoloration and to the cleavage of macromolecules with consequent decreasing of molecular weight and increasing of C.E.G.^{4,5,29} This is in contrast with the reported data of PBT **2**, which have shown a slight increase of I.V., a slight discoloration and an almost constant level of C.E.G., even after prolonged heating time. Otherwise, in the cases of polymers **5** and especially with polymer **1**, catalyst residue seems to favor degradation processes with subsequent worsening of polymer properties.

Even if at the present stage it is difficult to formulate reasonable hypothesis on the degradation mechanism and the actual structure of the catalyst residue, these experimental data open new questions

and new possibilities about the influence of catalyst structure on polyesters properties.

CONCLUSIONS

In this paper we have described the employment of Ti(acac)₂(O-*i*Pr)₂ as new catalyst for the synthesis of PBT. The use of Ti(acac)₂(O-*i*Pr)₂ led to a polymer in shorter reaction time and with higher stability toward thermo-oxidation with respect to PBTs obtained with the standard titanium alcolate catalyst. The presence of the stabilizer U626 had a positive effect on the stability of the polymer synthesized in the presence of Ti(O-*n*Bu)₄, but it is not necessary when Ti(acac)₂(O-*i*Pr)₂ is used.

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