

# PET Synthesis in the Presence of Lanthanide Catalysts

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## SYNOPSIS

Syntheses of poly(ethylene terephthalate), PET, by transesterification of dimethyl terephthalate with ethylene glycol in the presence of well-known catalysts and various lanthanide compounds were performed. Lanthanide catalysts appeared to be much more efficient in the first stage of the process (transesterification in the presence of an excess of ethylene glycol), and less active in polycondensation. PET produced with lanthanides was found to possess enhanced thermal and hydrolytic stability as compared to PET synthesized with well-known catalysts and commercial PET. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

In our previous article,<sup>1</sup> we have reported some results on reactive blending of bisphenol A polycarbonate (PC) and PET synthesized with lanthanide catalysts. These catalysts appeared to possess a selective activity (from kinetic point of view) toward exchange reactions in PC/PET systems, providing an opportunity to produce *in situ* compatible polymer blends and block copolymers with desired structure. That unusual behavior of lanthanide catalysts needs to be studied in more detail from the beginning. As was established, the difference in catalytic behavior of lanthanides and such well known catalysts as titanium tetrabutoxide and calcium acetate/antimony oxide appeared not only in exchange reactions but in polycondensation itself and in degradation processes of PET. This will be the subject of our considerations in the present report.

## EXPERIMENTAL

### Materials and Reagents

Ethylene glycol and dimethyl terephthalate (polymerization grade), used without further purification,

and commercial PET were supplied by EniChem (Italy).

Ti(OBu)<sub>4</sub>, Sb<sub>2</sub>O<sub>3</sub>, Ca(CH<sub>3</sub>COO)<sub>2</sub>, La(CH<sub>3</sub>COO)<sub>3</sub>·xH<sub>2</sub>O (x = 4–6), Sm(CH<sub>3</sub>COO)<sub>3</sub>·xH<sub>2</sub>O (x = 4–6), La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, SmCl<sub>3</sub>·6H<sub>2</sub>O, EuCl<sub>3</sub>·6H<sub>2</sub>O, Er(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and TbCl<sub>3</sub>·6H<sub>2</sub>O were purchased from Aldrich and Fluka and used without further purification.

Some of the catalysts, known in the literature<sup>2</sup> (Table I), were synthesized by standard methods.

### Synthesis of Acetyl Acetonates of Lanthanides

A solution of a lanthanide chloride in H<sub>2</sub>O at the concentration of 5–7% was added to the solution of acetyl acetone in H<sub>2</sub>O in the molar ratio 1 : 6 at room temperature. Then pH was increased to 7 by adding 2N solution of KOH, and reaction mixture with precipitated acetyl acetonate of lanthanide was stirred for 6–8 h to form a neutral acetyl acetonate salt which then was filtered and dried at 60°C under reduced pressure overnight. All products were characterized by elemental analysis and IR spectroscopy.

### Synthesis of Lanthanide Acetyl Acetonate Complexes with 2,2'-Dipyridyl

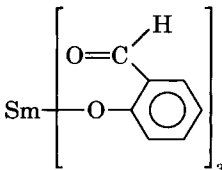
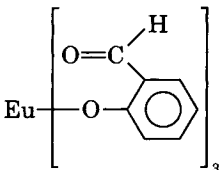
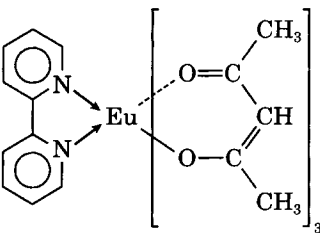
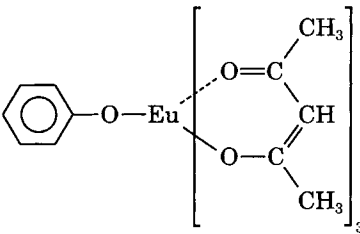
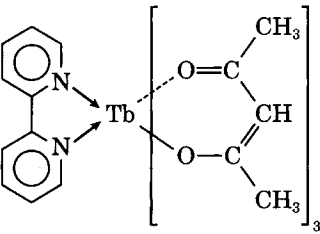
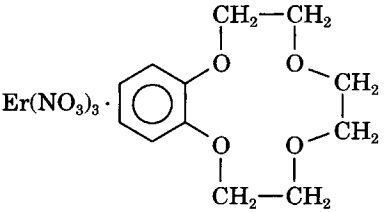
A solution of 2,2'-dipyridyl in ethanol or isopropanol was added to a solution of acetyl acetonate of lanthanide (5–6%) in the same solvent at the molar ratio of 1.5 : 1 at room temperature. After stirring

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**Table I** Data of Intrinsic Viscosity and Calculated Number-Average Molecular Weight<sup>3</sup> of PET Obtained with Various Catalysts in the Pilot Lab. Reactor (1.8 L)

Catalyst	Code	$[\eta]$ (dL/g)	$M_n^a$	Color <sup>b</sup> (Yellowness Index) <sup>c</sup>
Ti(OC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub>	Ti(OBu) <sub>4</sub>	0.90	26,800	Light yellow (9.7)
Ca(OOCCH <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O + Sb <sub>2</sub> O <sub>3</sub>	Ca/Sb	0.85	25,200	Colorless (6.1)
	Sm(L) <sub>3</sub>	0.82	24,100	Light yellow (21.4)
	Eu(L) <sub>3</sub>	0.76	21,950	Light yellow (20.8)
	Eu(acac) <sub>3</sub> · diPy	0.74	21,250	Light yellow (17.1)
	Eu(acac) <sub>3</sub> Ph	0.71	20,150	Brown (89.3)
Ce(CH <sub>3</sub> COO) <sub>3</sub> · xH <sub>2</sub> O x = 4–6 mol	Ce(ac) <sub>3</sub>	0.61	16,250	Colorless (8.9)
	Tb(acac) <sub>3</sub> · diPy	0.74	21,250	Brown (25.2)
	Er(NO <sub>3</sub> ) <sub>3</sub> B <sub>4</sub> C <sub>12</sub>	0.81	23,750	Colorless (9.9)

<sup>a</sup>  $[\eta] = 2.1 \times 10^{-4} M_n^{0.82}$ .<sup>b</sup> Visual evaluation on powders.<sup>c</sup> Measured as described in Experimental section.

for 1 h, the complex of lanthanide acetyl acetonate with 2,2'-dipyridyl precipitated from the reaction solution was filtered and dried at 40°C under reduced pressure overnight. All products were characterized by elemental analysis and IR spectroscopy.

### Synthesis of Lanthanide *o*-Formyl Phenolates

A solution of lanthanide chloride in H<sub>2</sub>O at the concentration of 5–6% was added to the emulsion of salicylic aldehyde (2-hydroxybenzoic aldehyde) in H<sub>2</sub>O in the molar ratio 1 : 6 at room temperature. Then pH was increased to 7 by adding 2*N* solution of KOH and the reaction mixture with precipitated lanthanide *o*-formyl phenolate was stirred for 3 h. The precipitate was filtered and dried at 60°C under reduced pressure overnight. All products were characterized by elemental analysis and IR spectroscopy.

### Synthesis of Lanthanide Nitrate Complexes with Crown Ether Benzo-12-crown-4

The solution of crown ether benzo-12-crown-4 in dried acetonitrile was added to the solution of lanthanide nitrate hexahydrate in the same solvent at the concentration of 5–6% in the molar ratio 1.5 : 1 at room temperature. After 10 h of stirring the product precipitated from the reaction solution was filtered, washed with acetonitrile and methylene chlo-

ride, and then dried at 40°C under reduced pressure overnight. All products were characterized by elemental analysis and IR spectroscopy.

### PET Synthesis

Polycondensation of dimethyl terephthalate (DMT) and ethylene glycol (EG) was performed by the usual two stage process in the presence of 0.1–0.2 wt % of catalyst (so that the molar concentration was the same for all catalysts employed, 0.063 mol % with respect to DMT).

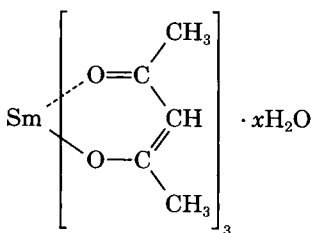
### Equipment

A 1.8-L stainless-steel batch reactor equipped with a paddle agitator (30 rpm) with a strain-gauge bridge mounted on the driving shaft to measure the torque, which gives an indication of the viscosity of the reaction melt, was used. For pilot scale syntheses a 20-L stainless-steel batch reactor equipped with a system for temperature and vacuum control was used.

### First Stage

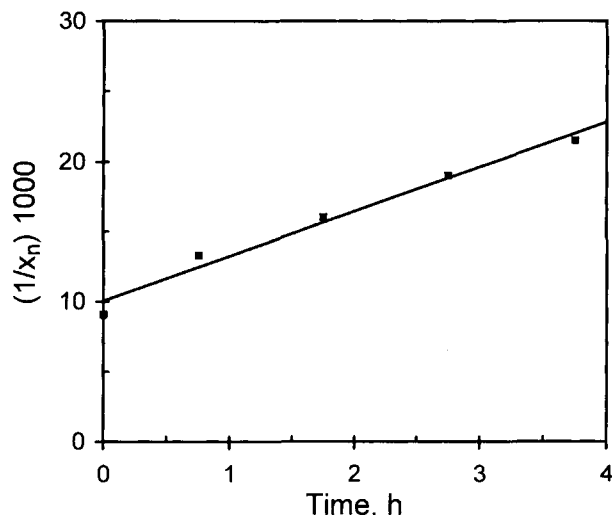
The reaction mixture of 970 g of DMT (5 mol) and 703 g of EG (11.34 mol) with dissolved 1.37 g (3.15 × 10<sup>-3</sup> mol) of samarium acetate hydrate was stirred in the reactor at atmospheric pressure, while the

**Table II** Data of Intrinsic Viscosity and Calculated Number-Average Molecular Weight<sup>3</sup> of PET Obtained with Various Catalysts in the Pilot Plant Reactor (20 L)

Catalyst	Code	$[\eta]$ (dL/g)	$M_n^a$	$x_n$	Color
Mn(CH <sub>3</sub> COO) <sub>2</sub> + Sb <sub>2</sub> O <sub>3</sub>	Mn/Sb	0.57	15,400	80	Colorless (n.d.) <sup>b</sup>
Sm(CH <sub>3</sub> COO) <sub>3</sub> · xH <sub>2</sub> O x = 4–6 mol	Sm(ac) <sub>3</sub>	0.65	18,100	94	Light yellow (3.8)
	Sm(acac) <sub>3</sub>	0.65	18,100	94	Light yellow (4.6)
x = 3–6 mol					
La(CH <sub>3</sub> COO) <sub>3</sub> · xH <sub>2</sub> O x = 4–6 mol	La(ac) <sub>3</sub>	0.65	18,100	94	Light yellow (4.4)

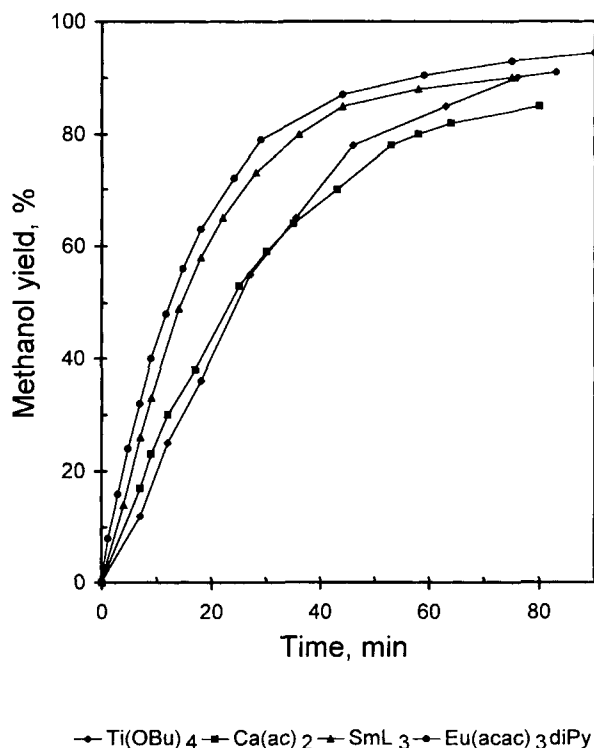
<sup>a</sup>  $[\eta] = 2.1 \times 10^{-4} M_n^{0.82}$ .

<sup>b</sup> n.d., not determined.

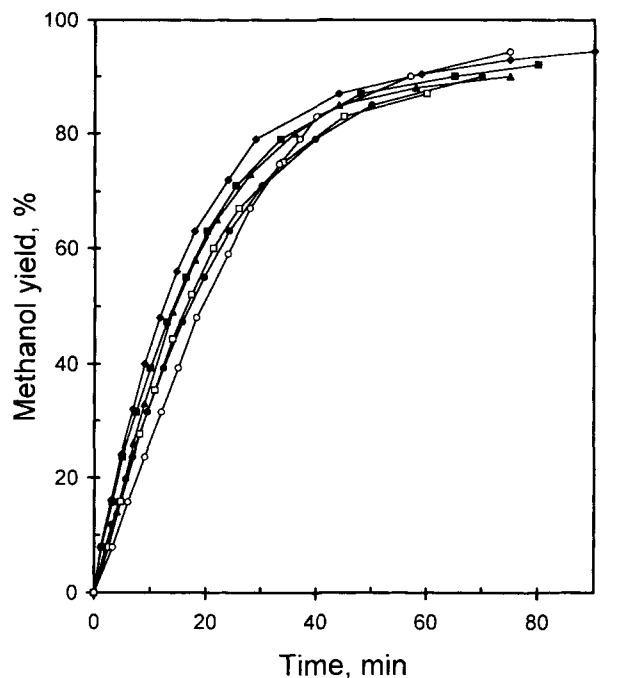


**Figure 1** Degradation of PET synthesized with  $\text{Eu}(\text{acac})_3 \text{ diPy}$  (ampoule method,  $270^\circ\text{C}$ ).

reaction temperature was raised to  $195^\circ\text{C}$  and maintained at this value until more than 95% of the theoretical amount of methanol was distilled off. Evaluation of the reaction rate in the first stage was made by measuring the amount of methanol distilling off.



**Figure 2** Methanol yields in the first stage of PET synthesis in the presence of various catalysts.



**Figure 3** Catalytic activity of lanthanides in the first stage of PET synthesis.

### Second Stage

During the second stage the pressure was gradually reduced to 0.3 mbar, while the temperature was raised to  $268\text{--}270^\circ\text{C}$  and maintained until the end of the synthesis (1.5–2.0 h). PET produced was unloaded into cold water with a pressure of nitrogen, ground after cooling with liquid nitrogen, and dried overnight in a vacuum oven at  $100^\circ\text{C}$  and reduced pressure. Intrinsic viscosity of PET samples dissolved in tetrachloroethane/phenol (60/40 w/w) was measured using Ubbelohde viscometers at  $25^\circ\text{C}$  in the concentration range of 0.3 to 1.0 g/dL. Data of intrinsic viscosity and estimated number-average molecular weight<sup>3</sup> are presented in Tables I and II.

### PET Degradation in the Molten State

Two different techniques were used:

1. The sealed ampoule method was used for kinetic study of PET degradation. The ampoules (Pyrex) with 0.3 g of PET, sealed after repeated nitrogen blowing, were placed into a metallic thermoblock heated at  $270^\circ\text{C}$ . Ampoules taken at different times from the heated block were cooled in cold water.

**Table III Data of PET Degradation in the Melt for 1 Hour (ampoule method, 270°C)**

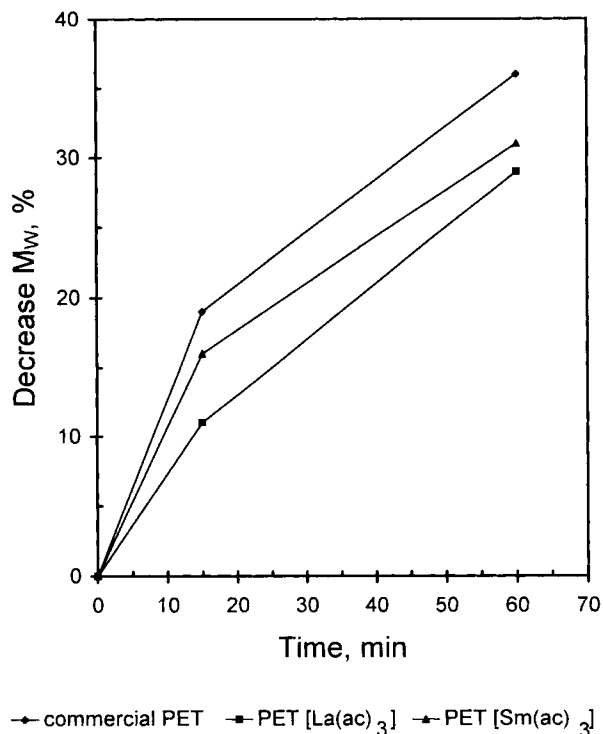
No.	Catalyst	Initial Viscosity [ $\eta$ ] <sub>0</sub> (dL/g)	Final Viscosity after Degradation [ $\eta$ ] <sub>i</sub> (dL/g)	$M_n^i/M_n^0$ (%)	Ratio of Degradation Rate Constants $k_i/k_{Eu}^a$
1	Eu(acac) <sub>3</sub> · diPy	0.74	0.58	74	1.00
2	SmL <sub>3</sub>	0.82	0.62	71	1.04
3	Sm(ac) <sub>3</sub>	0.65	0.49	70	1.20
4	Ti(OBu) <sub>4</sub>	0.90	0.30	26	6.43
5	Ca/Sb	0.85	0.25	22	8.42

<sup>a</sup>  $k_{Eu}$ , degradation rate constant of PET sample synthesized with Eu(acac)<sub>3</sub> · diPy.

Reaction rate constants,  $k$ , were estimated by the following equation,<sup>4</sup> valid for the initial stage of degradation:

$$kt = 1/x_n^i - 1/x_n^o \quad (1)$$

where  $t$  is the time of degradation test,  $x_n^o$  and  $x_n^i$ , estimated on the basis of intrinsic viscosity data, are the number-average degrees of polymerization of the PET samples before and after degradation, respectively. The values of reaction rate constants were calculated by the slopes of the linear dependence of  $1/x_n$  versus time (Fig. 1).

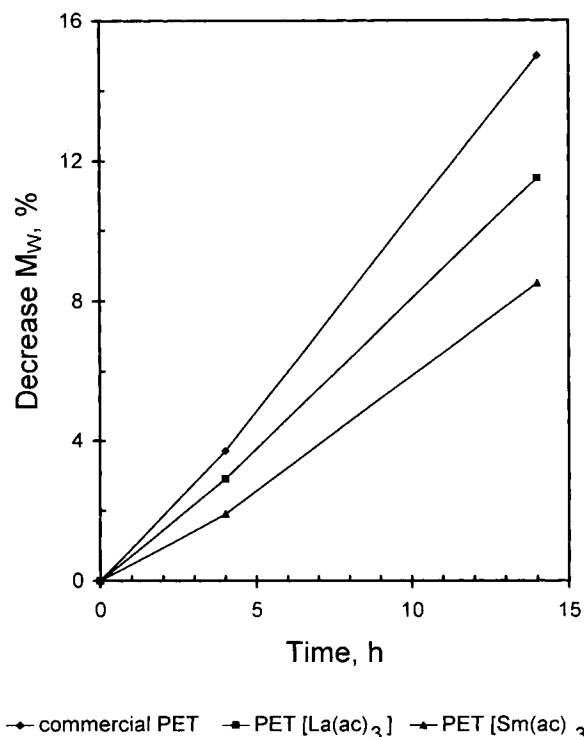


**Figure 4** PET degradation in the melt under polymer processing conditions (Brabender Plasticorder apparatus, 275°C in air).

2. A Brabender Plasticorder 2000 apparatus was used for degradation tests under polymer processing conditions at 275°C, 48 rpm, in air. Intrinsic viscosity was measured in tetrachloroethane/phenol (60/40 w/w) at 25°C in the concentration range of 0.3 to 1.0 g/dL. The decrease in molecular weight was calculated on the basis of intrinsic viscosity data.<sup>3</sup>

**Hydrolytic Stability.** Tests were performed on finely ground samples immersed in boiling water at atmospheric pressure for 14 h.

**Thermal Stability.** Aging tests were carried out on PET granules (3–5 mm) at 200°C in air for 72 h.



**Figure 5** Hydrolytic stability of PET in boiling water.

**Molecular-Weight Distribution.** Molecular-weight distribution of PET was investigated by size exclusion chromatography (SEC) performed on samples dissolved in hexafluoro-*iso*-propanol (HFIP)/methylene chloride (10/90 v/v) and eluted with a solvent mixture of HFIP/methylene chloride/chloroform (5/20/75, v/v) at 0.6 mL/min using a set of PL-gel columns 500,  $10^3$ ,  $10^4$  Å, and a UV detector at 25°C.

**Color Measurements.** Color measurements on PET samples in the form of film (with thickness in the range 0.38–0.42 mm) were carried out with a Gardner TCS spectrophotometer. Tristimulus values were calculated according to CIE specification in the following conditions: transmittance mode, measurement area diameter 25 mm, illuminant C,  $10^\circ$  standard observer, spectral range 380–780 nm with a 10 nm sampling interval. The yellowness index values, calculated according to ASTM D1925, were an average of 10 measurements.

## RESULTS AND DISCUSSION

PET with various catalysts were produced from DMT and EG by the usual two stage process in a pilot lab. reactor (1.8 L) and at a pilot plant scale (20 L). As can be seen from the results presented in Tables I and II, values of the molecular weight of PET synthesized with lanthanides are similar or even higher than those of samples obtained with well known catalysts, especially in the case of industrial pilot plant syntheses (Table II). Discoloration of polymers observed in some cases, see yellowness index values in Tables I and II, can be easily avoided by using phosphorus additives<sup>5</sup> as color inhibitors. Molecular-weight distribution of PET samples synthesized with lanthanide catalysts were found to be very close to those of the samples obtained with Ti(OBu)<sub>4</sub> and Ca(ac)<sub>2</sub>/Sb<sub>2</sub>O<sub>3</sub>, with an  $M_w/M_n$  ratio close to 2.

Measurements of the distillation rate of methanol at the first stage of the reaction make it possible to evaluate the catalytic activity of the catalysts employed, even though the nonisothermal character of the process (the temperature was gradually raised from 150 to 195°C during the distillation of methanol) does not allow calculation of reaction rate constants. Nevertheless, data of the reaction conversion versus reaction time presented in Figure 2 allow us to compare the activities of the catalysts employed. Lanthanide catalysts appeared to be much more efficient as compared with well-known catalysts as Ti(OBu)<sub>4</sub> and Ca(ac)<sub>2</sub>. It should be

noted that Ca(ac)<sub>2</sub>, one of the industrial catalysts for the first stage of PET synthesis, proved to be less efficient as compared with lanthanides; in the latter case the conversion of 50% was reached in half the time needed in the case of Ca(ac)<sub>2</sub> catalyst (Fig. 2).

Data presented in Figure 3 show that there is no significant difference between the efficiency of the different lanthanides tested. In addition, the curves obtained from reactions performed in the presence of europium compounds with different ligands were found to be quite similar. These data allowed us to conclude that, among the catalysts tested in the present study, the nature of lanthanide metal and structure of ligand had a negligible effect on the catalytic activity in the first stage of PET synthesis.

Another feature of lanthanide catalysts was observed by measuring the torque during the polycondensation step. Torque values for PET synthesized with Ti or Sb catalysts were found to be much higher than those obtained with lanthanides for the samples with quite similar molecular weights. This phenomenon could be caused by the coordinative ability of Ti and Sb to create some kind of coordinative network in the polymer melt<sup>6</sup> that results in enhanced values of melt viscosity; lanthanides are unable to form such network and, as a consequence, lead to lower values of torque, which can be considered a further advantage in their application.

As was established, the duration of the second stage of the reaction in the presence of lanthanides is usually twice as long as compared with the time needed to reach the same viscosity of PET synthesized in the presence of Ti(OBu)<sub>4</sub> and Sb<sub>2</sub>O<sub>3</sub>. During the second stage the composition of the reaction medium changes from a large excess of ethylene glycol to a large excess of ester. This change in the chemical nature of the reaction system probably results in the reduced activity of lanthanides.

According to Otton et al.,<sup>7</sup> the most efficient catalysts for the first stage of the reaction such as Zn, Mn, Co, Ca compounds are almost not active in the second stage. On the contrary, Sb compounds, not being active in the first stage, proved to be active enough in the second one. Moreover, when the percentage of ester in the reaction medium increases, the catalytic activity of Sb catalysts increases as well; this was a reason for industrial application of two different types of catalysts for the PET synthesis. Titanium is less sensitive to the nature of the reaction medium and its catalytic activity decreases only at the end of the second stage.<sup>7</sup> Thus, lanthanide catalysts, being very active in the first stage of the PET synthesis, were found to be less active in the second stage than Ti and Sb catalysts, but ef-

ficient enough to reach high-molecular-weight PET. Unlike Zn, Mn, Ca, and Sb compounds, lanthanide derivatives work during the whole reaction process.

As was found, one of the important features of lanthanide catalysts is their reduced activity in thermal and hydrolytic degradation of PET as compared with that of Ti, Sb, Ca, and Mn. It should be noted that the latter two catalysts, not being active in polycondensation (second stage), nevertheless, lead to a severe degradation of PET in the melt.<sup>8</sup> This was confirmed by degradation tests of PET samples performed in ampoules sealed under nitrogen (Table III). These data revealed that the observed rate constant of PET degradation in the presence of residues of Ti or Ca/Sb catalysts appeared to be 6–8 times higher than that of PET synthesized with lanthanides.

Degradation tests performed in a Brabender Plasticorder apparatus at 275°C allowed us to evaluate PET thermal stability under the conditions of polymer processing. PET samples synthesized with lanthanides in the industrial pilot plant reactor were found to possess higher thermal stability than commercial PET, produced with Ca or Mn acetates and Sb<sub>2</sub>O<sub>3</sub>, stabilized with *o*-phosphoric acid after the first stage of the process (Fig. 4).

Data of hydrolytic stability of PET presented in Figure 5 reveal one more advantage of lanthanide catalysts; the decrease in the molecular weight of commercial PET after 14 h in boiling water was twice that of PET obtained with Sm(ac)<sub>3</sub>.

Results of aging tests at 200°C in air for 72 h (Fig. 6) show again that the polymer obtained with lanthanides is more stable than commercial PET.

All the results described above allowed us to conclude that lanthanide compounds appeared to be perspective catalysts with a selective activity toward transesterification, polycondensation, and degradation processes. Application of lanthanide catalysts provides an opportunity to produce PET with enhanced thermal and hydrolytic stability. As we reported before,<sup>1</sup> the selective activity of lanthanides was also observed in exchange reactions between PET and bisphenol A polycarbonate; this provides an opportunity to produce *in situ* compatible polymer blends and block copolymers with controlled structure without adding further catalysts. The mechanism of selective catalytic activity of lanthanides needs to be studied in more detail.

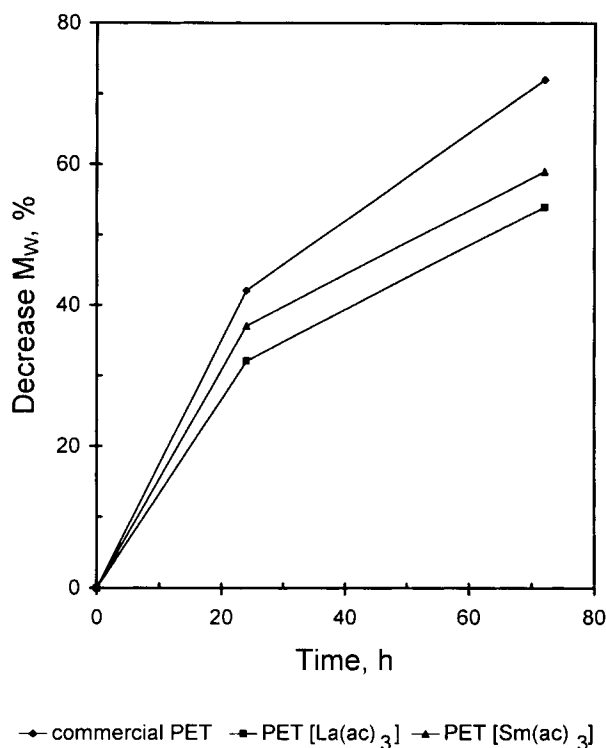


Figure 6 Aging tests of PET in air at 200°C.

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