

# New Catalysts for Poly(ethylene terephthalate)-Bisphenol A Polycarbonate Reactive Blending

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## SYNOPSIS

The effects of various catalysts on the reactive blending of poly(ethylene terephthalate) (PET) and bisphenol A polycarbonate (PC) was investigated. The various catalysts employed for PET syntheses,  $\text{Ti}(\text{OBU})_4$ ,  $\text{SmL}_3$ ,  $\text{EuL}_3$ ,  $\text{Ca} + \text{Sb}$ ,  $\text{CeAc}_3$ ,  $\text{Er}(\text{NO}_3)_3 \cdot \text{B}_{12}\text{C}_4$ , and  $\text{Tb}(\text{acac})_3 \cdot \text{diPy}$  (where L is *o*-formylphenolate;  $\text{B}_{12}\text{C}_4$  is a crown ether, benzo-12-crown-4; acac is acetylacetonate; and diPy is 2,2'-dipyridyl) have shown a different catalytic activity toward exchange reactions. Solubility tests, in solvents able to separate unreacted PET and PC, and selective degradation of the PC segments, combined with <sup>1</sup>H NMR spectroscopy and size exclusion chromatography, made it possible to order the catalysts according to their catalytic activity:  $\text{Ti}(\text{OBU})_4 \gg \text{SmL}_3 > \text{EuL}_3 > \text{Ca} + \text{Sb} > \text{CeAc}_3 \approx \text{Er}(\text{NO}_3)_3 \cdot \text{B}_{12}\text{C}_4 > \text{Tb}(\text{Acac})_3 \cdot \text{diPy} \approx 0$ . © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The reactive blending of poly(ethylene terephthalate) (PET) and bisphenol A polycarbonate (PC) have proved to be a successful and inexpensive route for producing new polymeric materials with enhanced and/or modified properties.<sup>1-8</sup> It is presently being used for the production of engineering alloys from both virgin and recycled PET and PC.<sup>9</sup> In principle, it is possible to prepare many different polymeric materials by this process simply by changing the weight fraction of PET and PC or the reaction conditions. For instance, we used it to obtain block copolymers, useful as compatibilizers in PET-PC blends,<sup>10</sup> and poly(ether-ester) random copolymers with properties enhanced or intermediate to those of PET and PC.<sup>3</sup>

The chemical structure, and therefore the properties of the resulting polymeric materials, is controlled by the relative rate and extent of several reactions that may occur during the melt mixing and

that were described previously.<sup>2,3</sup> The catalyst, present as a residual from PET polymerization or purposely added, may play a primary role in controlling the chemical structure of the final product. For this reason we decided to carry out reactive blending of PC with PETs obtained by polymerizations in the presence of various catalysts in order to investigate their effect on exchange reactions during reactive blending.

## EXPERIMENTAL

### Materials

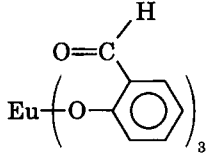
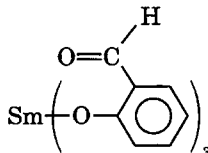
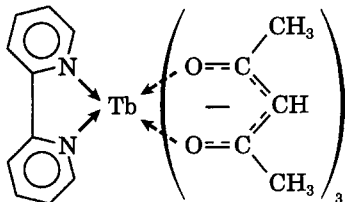
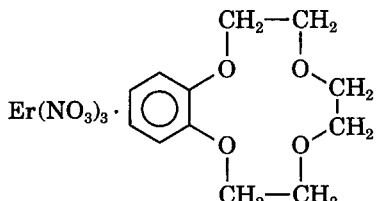
PC (intrinsic viscosity 0.65 dL/g in chloroform at 30°C) was kindly supplied by ENICHEM.

Various PETs were prepared in our laboratory by reacting dimethyl terephthalate (DMT) and ethylene glycol in the presence of different catalysts (0.063 mol % based on the metal and with respect to DMT); intrinsic viscosity was measured in phenol/1,1,2,2-tetrachloroethane (40/60 by wt) at 25°C. The catalysts employed were in part prepared at and supplied from the Institute of Organo-Element Compounds of the Russian Academy of Sciences (Moscow), and in part were commercial products purchased from Aldrich [ $\text{Ti}(\text{OBU})_4$ , Ca acetate,

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**Table I Catalysts Used for PET Synthesis**

Formula	Code
$\text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$	$\text{Ti}(\text{OBu})_4$
$\text{Ca}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O} + \text{Sb}_2\text{O}_3$	Ca + Sb
$\text{Ce}(\text{OOCCH}_3)_3 \cdot x\text{H}_2\text{O}$	CeAc
	$\text{EuL}_3$
	$\text{SmL}_3$
	$\text{Tb}(\text{acac})_3 \cdot \text{diPy}$
	$\text{Er}(\text{NO}_3)_3 \cdot \text{B}_{12}\text{C}_4$

In any case a concentration of 0.063 mol % of the metal catalyst (based on DMT) was used; for Ca + Sb the concentration is 0.063 mol % for each element.

$\text{Sb}_2\text{O}_3$ , Ce acetate). The formulas and codes of the catalysts employed are listed in Table I. The PET synthesis with various lanthanide compounds will be described in a future study.<sup>11</sup>

Di-*n*-octadecyl phosphite (DNOP) was purchased from Aldrich and used as supplied.

### Melt Mixing

A Brabender mixer (Plasti-Corder PL 2000) equipped with two counter-rotating, double-winged rotors was used for the melt mixing. The bowl capacity of the mixer was 50 mL and the total volume of the polymers charged about 45 mL based on the temperature of 270°C. PET, synthesized with various catalysts, and PC, previously dried at 140°C under vacuum overnight, were loaded into the pre-

heated mixer; no further catalyst was added during this step. The rotor speed was kept at 30 rpm throughout the overall reaction time. During the blending, the mixing room was fluxed with a moderate stream of dry nitrogen to avoid the hydrolytic degradation of the polymers.

### Selective Solubility

The procedure for the selective solubility tests was as follows: to a sample of 1 g (exactly weighed) taken from each blend, 25 mL of dichloromethane and 1 mL of trifluoroacetic acid (TFA) were added and magnetic stirring was started. As soon as complete dissolution was achieved, precipitation was started by adding, dropwise, 75 mL of tetrahydrofuran (THF). When the precipitation was completed, the insoluble fraction was separated by filtration, washed with a mixture of dichloromethane-THF (25/75, v/v), and finally with THF. The soluble fraction was recovered by evaporation under reduced pressure. Soluble and insoluble fractions were finally dried at 100°C under vacuum and weighed. Usually, the difference between the initial and recovered weights was  $\pm 5\%$ .

This method was tested on simple blends of PET and PC obtained by mixing these polymers in the Brabender apparatus in the presence of DNOP (0.5 wt %), an inhibitor of catalysts of ester exchange reactions.<sup>12</sup>

As discussed below, from these results we can conclude that the selective solubility method employed is able to quantitatively separate PET and PC homopolymers, even when they are thoroughly dispersed.

### Selective Degradation of PC Sequences

The procedure for the selective degradation of PC blocks was as follows (similar to one previously proposed<sup>1</sup>): to a sample of 1 g (exactly weighed) taken from each blend, 25 mL of dichloromethane and 1 mL of piperidine were added and magnetic stirring was started. The reaction of carbonate groups with the aliphatic amine leads to the formation of urethane groups and was monitored by following the disappearance of the PC band in the IR spectra of samples taken from the solution at various times. After 1 h the carbonate band had already disappeared for all samples.

Once the degradation had been completed, 100 mL of methanol were added dropwise to ensure the complete recovery of even the shortest PET blocks. The PET residue was then filtered off, washed with

methanol, dried under vacuum at 100°C overnight, and weighed. The effectiveness of the degradation procedure was tested on the samples obtained by melt mixing PET and PC in the presence of DNOP. The weight fraction recovered, the  $^1\text{H}$  NMR spectrum, and the intrinsic viscosity of the residue confirmed that piperidine attacks PC selectively. In fact, the amount of the residue was identical to the initial amount of PET; there was virtually no bisphenol-A left in the polymer residues; and only a slight decrease of the intrinsic viscosity of PET was observed (for instance the intrinsic viscosity of PET decreased from 0.82 to 0.78 dL/g).

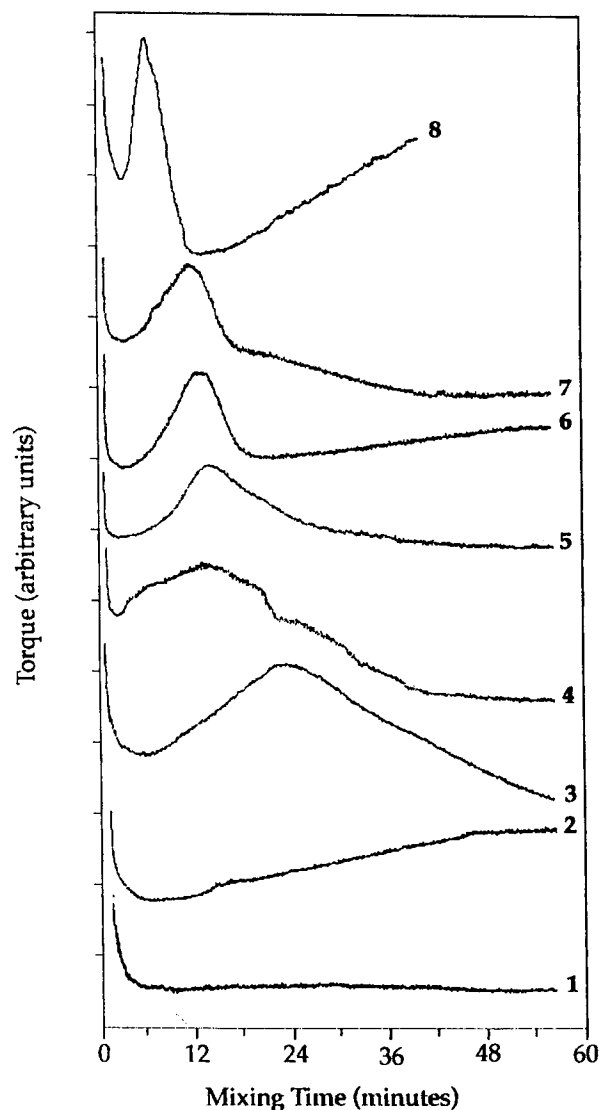
### Measurements

IR spectra were recorded on an IFS 48 Bruker Fourier transform infrared (FTIR) instrument.  $^1\text{H}$  NMR spectra were recorded on a 200 MHz Varian instrument. Intrinsic viscosity was calculated on the basis of viscosity measurements of diluted solutions (at least four for each sample) by Ubbelohde viscometers. Molecular weight distribution was investigated by size exclusion chromatography (SEC) carried out on samples dissolved in hexafluoroisopropanol (HFIP)/methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) (10/90 v/v), and eluted with a solvent mixture HFIP/ $\text{CH}_2\text{Cl}_2$ / $\text{CHCl}_3$  (5/20/75 by wt) at 0.6 mL/min and 25°C using a set of PLgel columns 500,  $10^3$ ,  $10^4$  Å, and a UV detector.

## RESULTS AND DISCUSSION

The first evidence of different behavior by the various catalysts tested was observed by comparing the signals of the torque recorded during melt mixing in the Brabender under the same conditions; these traces are shown in Figure 1. For most catalysts, the torque increases in the first period of reaction, goes through a maximum, then decreases until a constant or almost constant level is reached. On the contrary, in the presence of DNOP, added as catalyst inhibitor, there was no significant change of the torque (curve 1 in Fig. 1). It is clear that the torque profiles and the different positions of the maxima reflect different chemical histories and indicate that the reaction path strongly depends on the type of catalyst used.

The main reactions that may occur during melt mixing of PET and PC have already been described.<sup>2</sup> They are: exchange reactions with the formation of PET-PC block copolymers; intramolecular exchange reactions with the formation of cyclic ethylene car-



**Figure 1** Traces of the torque measured in the Brabender during melt mixing of PET-PC blends (50/50 wt/wt) at 270°C and 30 rpm. The residual catalyst in PET is: 1) Ca + Sb in the presence of DNOP; 2)  $\text{Tb}(\text{acac})_3 \cdot \text{diPy}$ ; 3)  $\text{Er}(\text{NO}_3)_3 \cdot \text{B}_{12}\text{C}_4$ ; 4) Ca + Sb; 5)  $\text{CeAc}_3$ ; 6)  $\text{EuL}_3$ ; 7)  $\text{SmL}_3$ ; 8)  $\text{Ti}(\text{OBu})_4$ .

bonate; splitting of carbon dioxide from an aromatic-aliphatic carbonate group; and finally, PET chain splitting as a consequence of thermal-degradation reactions. Obviously, the torque profiles reflect a different catalytic activity toward one or more of these reactions.

$^1\text{H}$  NMR spectroscopy of the crude samples obtained from melt mixing and of samples derived from these by selective-solubility and selective-degradation tests was used to achieve more information about the effects of the various catalysts.

The method used for the selective-solubility ex-

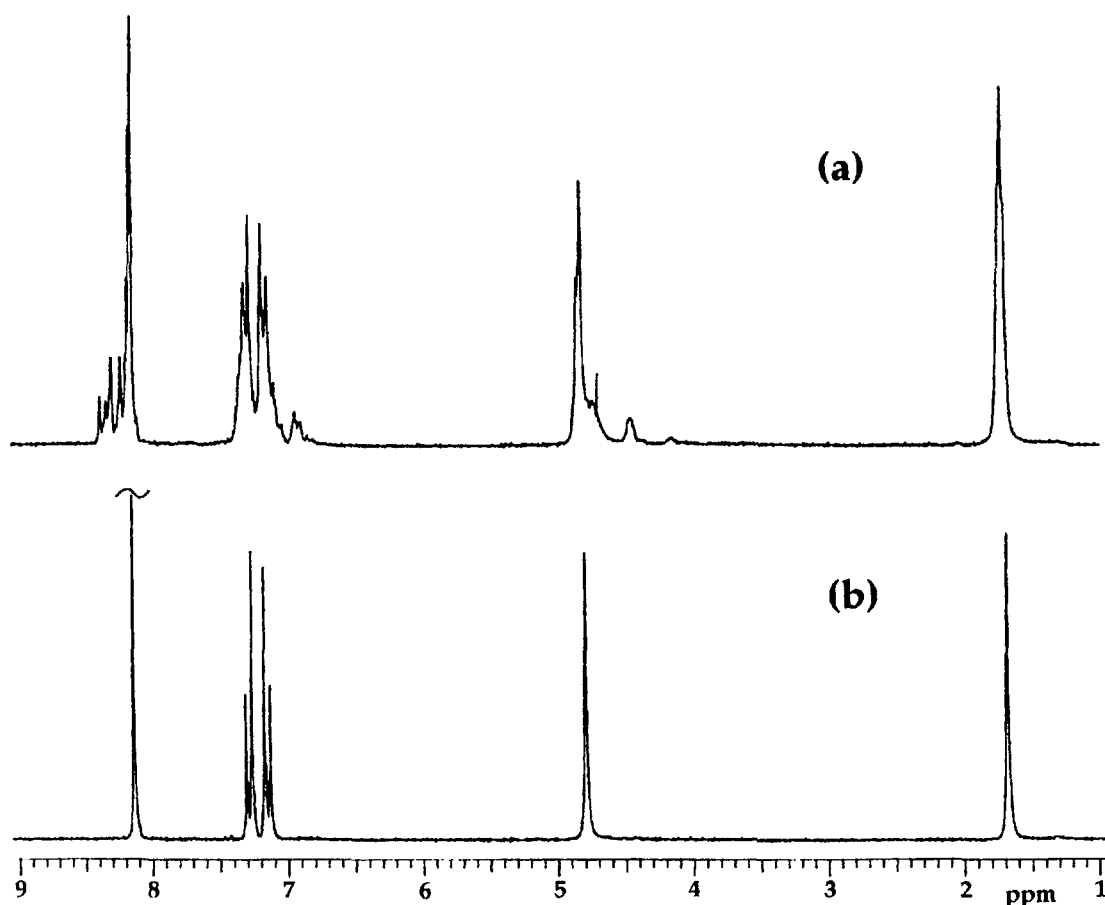
periments was previously tested on samples obtained by melt mixing PET and PC at 270°C for various times over 60 min in the presence of DNOP, a catalyst inhibitor previously used for melt mixing of PC-poly(butylene terephthalate).<sup>12</sup> Our results confirmed that DNOP is also a good inhibitor for PET-PC blends and that the selective-solubility method is able to quantitatively separate unreacted PET and PC. In fact, from FTIR and <sup>1</sup>H NMR analyses, the soluble and insoluble fractions were almost pure PC and PET, respectively.

On the same products, resulting from melt mixing in the presence of DNOP, we also tested the selective-degradation method that is able to completely destroy PC segments while leaving the molecular weight of PET almost unchanged.

For samples obtained in the presence of various catalysts, we first examined the <sup>1</sup>H NMR spectra of the crude products taken from the Brabender after 20 min of mixing at 270°C; some typical spectra are

shown in Figure 2. The effect of Ti(OBu)<sub>4</sub> catalyst was previously described<sup>2</sup>; it was found to be an efficient catalyst for ester-carbonate exchange reactions. Those results were confirmed by the present study as it appears from the <sup>1</sup>H NMR spectrum [Fig. 2(a)] where strong signals of aromatic-aliphatic, aromatic-aromatic ester groups, of aromatic-aliphatic ether moieties and of cyclic ethylene carbonate are present.<sup>2</sup> For all of the other catalysts tested, the <sup>1</sup>H NMR spectra were similar to that obtained from a simple mixture of unreacted PET and PC [Fig. 2(b)] and therefore are consistent with both a simple blend of PET and PC homopolymers and with PET-PC block copolymers with a limited number of block junctions.

In order to verify whether block copolymers were formed we investigated the samples using some other techniques. The selective-solubility method followed by the <sup>1</sup>H NMR analysis of soluble and insoluble fractions can give evidence of the formation of PET-



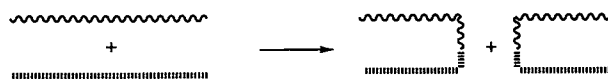
**Figure 2** <sup>1</sup>H NMR spectra after 20 min of mixing at 270°C in the presence of (a) Ti(OBu)<sub>4</sub> and (b) unreacted PET and PC. All other catalysts, except Ti(OBu)<sub>4</sub>, gave spectra almost identical with spectrum (b).

PC block copolymers. In fact, the presence of PET in the soluble fraction and of PC in the insoluble one proves the formation of block copolymers. If no reactions had occurred between PC and PET they would have been found completely in the soluble and insoluble fractions, respectively.

It seems reasonable to assume that the content of PET in the soluble fraction and of PC in the insoluble one is higher when the extent of exchange reactions increases, as the initial unreacted blend of PET and PC is progressively transformed into block copolymers (with shorter and shorter segments of PET and PC). Therefore, for the same time of reaction the amount of PET in the soluble fraction and of PC in the insoluble one is higher when the catalytic activity is higher.

Based on these arguments we can derive some information about the catalytic activity by comparing the composition data of soluble and insoluble fractions after 20 min of melt mixing at 270°C. These data (see Table II) indicate that the various catalysts lead to different products and allowed us to order the catalytic activity of the various catalysts as follows:  $\text{Ti}(\text{OBu})_4 \gg \text{SmL}_3 > \text{EuL}_3 > \text{Ca} + \text{Sb} > \text{CeAc}_3 \approx \text{Er}(\text{NO}_3)_3 \cdot \text{B}_{12}\text{C}_4 > \text{Tb}(\text{acac})_3 \cdot \text{diPy} \approx 0$ . It was also found that the high catalytic activity of  $\text{Ti}(\text{OBu})_4$  determined the chemical structure of the products obtained from melt mixing when it was present in the PET-PC mixture along with some of the catalysts listed in Table I.

A further contribution confirming the different behavior of the catalysts tested was derived from



Scheme 1

the results of selective degradation of the PC segments; this method leaves the PET blocks unchanged and made it possible to get information on the average length of the PET segments after melt mixing. These data can be used to derive more information about the exchange rate and the reaction mechanism. In fact, every time an exchange reaction takes place between an ester group of PET and a carbonate group of PC there is a decrease in the average length of the PC and PET segments (Scheme 1).

The intrinsic viscosity data of Table II indicate that the decrease in the PET block length occurs in the following order:  $\text{Ti}(\text{OBu})_4 > \text{Ca} + \text{Sb} > \text{SmL}_3 > \text{EuL}_3 > \text{CeAc} \approx \text{Er}(\text{NO}_3)_3 \cdot \text{B}_{12}\text{C}_4 > \text{Tb}(\text{acac})_3 \cdot \text{diPy} \approx 0$ . This order is the same as for the catalytic activity previously derived from solubility data, except for the Ca + Sb catalytic system. The reason for this last anomalous behavior may be tentatively ascribed to a relatively stronger effect by this catalytic system on the degradation reaction of PET,<sup>13,14</sup> which can contribute to shorten the average length of the PET segments.

Our data also rule out the formation of block copolymers predominantly by the reaction of the terminal groups of PET with carbonate groups of

**Table II** Characterization Data of Samples Obtained by Melt Mixing of PET and PC (50/50 w/w) for 20 min at 270°C in a Brabender Apparatus

Catalyst Code	Soluble Fraction <sup>a</sup> (wt %)	PET in Soluble Fraction <sup>b</sup> (wt %)	PC in Insoluble Fraction <sup>b</sup> (wt %)	Wt % of PET in Soluble Fraction <sup>c</sup>	Wt % of PC in Insoluble Fraction <sup>d</sup>	Intrinsic Viscosity of PET <sup>e</sup> (dL/g)	Intrinsic Viscosity of PET Segments <sup>f</sup> (dL/g)
Ca + Sb	35.5	5.8	37.3	4.8	41.6	0.82	0.13
CeAc <sub>3</sub>	29.0	7.3	31.7	3.6	17.5	—	0.47
Er(NO <sub>3</sub> ) <sub>3</sub> · B <sub>12</sub> C <sub>4</sub>	43.4	4.1	15.6	3.6	17.5	0.79	0.42
EuL <sub>3</sub>	28.3	11.0	33.7	6.2	48.9	0.74	0.30
SmL <sub>3</sub>	19.9	26.7	44.1	10.6	70.7	0.80	0.22
Tb(Acac) <sub>3</sub> diPy	50.7	—	—	—	—	0.69	0.63
Ti(OBu) <sub>4</sub>	100	50	—	100	—	0.91	0.09

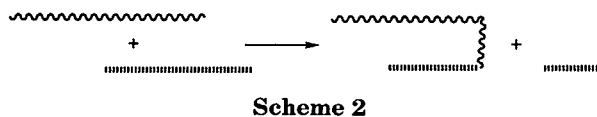
<sup>a</sup> In THF/CH<sub>2</sub>Cl<sub>2</sub>/TFA (75/25/1, by vol.).

<sup>b</sup> From <sup>1</sup>H NMR spectra.

<sup>c</sup> With respect to the overall PET.

<sup>d</sup> With respect to the overall PC.

<sup>e,f</sup> In phenol/TCE (40/60) at 25°C, <sup>e</sup>before reactive blending, <sup>f</sup>after selective degradation.

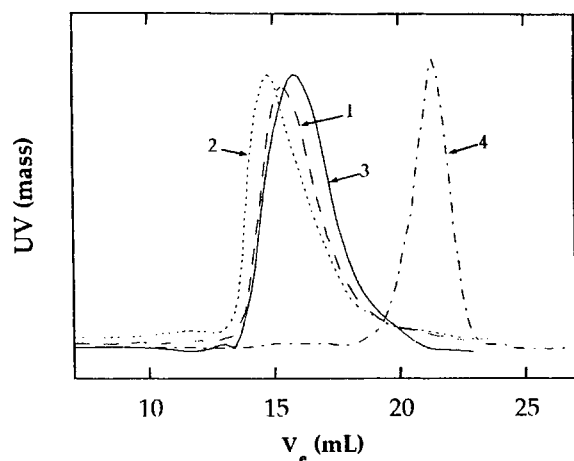


PC. In fact, in this case, there would not be a decrease in the average length of the PET segments (Scheme 2).

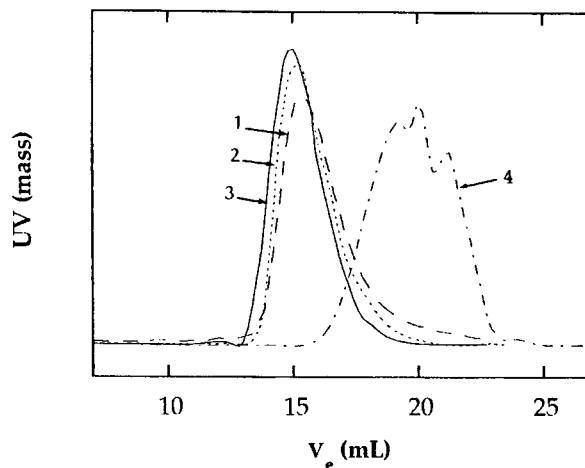
This scheme, based on our assumption about selective activity of lanthanides toward exchange reactions and the polycondensation process, is confirmed by the high catalytic activity of lanthanides in the first stage of PET synthesis (transesterification of DMT with ethylene glycol when there is some excess of ethylene glycol) and a lower activity in the second stage of polycondensation. Moreover PET synthesized using lanthanide compounds was found to possess higher thermal and hydrolytic stability with respect to PET prepared with the traditional catalysts.<sup>11</sup> Of course the mechanism of this phenomenon needs to be explored in more detail. It will be the subject of a further investigation.

The effect of the different catalysts is also reflected on the molecular weight distribution (MWD) of both the crude products withdrawn from the Brabender and the residual PET after selective degradation of PC. Some typical SEC curves are shown in Figures 3–5 for samples obtained from melt mixing in the presence of  $\text{Ti}(\text{OBU})_4$ ,  $\text{Ca} + \text{Sb}$ , and  $\text{EuL}_3$ , respectively.

In all cases the SEC curve of crude products after 20 min of mixing is similar to that expected from

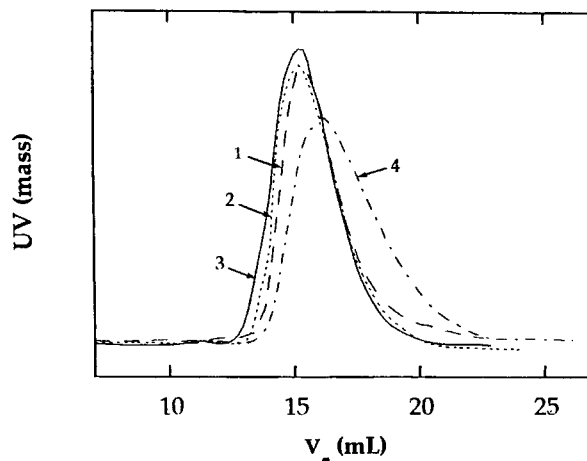


**Figure 3** SEC curves of the samples obtained by melt mixing PET and PC for 20 min at 270°C in the presence of  $\text{Ti}(\text{OBU})_4$ ; (3) crude sample after mixing; (4) residual PET after selective degradation. Dashed and dotted lines are for starting (1) PC and (2) PET.



**Figure 4** SEC curves of the samples obtained by melt mixing PET and PC for 20 min at 270°C in the presence of  $\text{Ca} + \text{Sb}$ : (3) crude sample after mixing; (4) residual PET after selective degradation. Dashed and dotted lines are for starting (1) PC and (2) PET.

the combination of the starting PET and PC; the peak shape is similar and there is no evidence of broadening either at high or low elution volumes ( $V_e$ ). On the contrary, after selective degradation, we had to expect that the SEC peaks of PET were shifted to higher  $V_e$  (lower molecular weights) with respect to initial PET if ester-carbonate exchange reactions took place. As expected, the  $V_e$ s and the peak shape are quite different from those of the initial PET (Figs. 3–5). In particular, we observed that the shifting to higher  $V_e$ s is larger for  $\text{Ti}(\text{OBU})_4$  (Fig.



**Figure 5** SEC curves of the samples obtained by melt mixing PET and PC for 20 min at 270°C in the presence of  $\text{EuL}_3$ ; (3) crude sample after mixing; (4) residual PET after selective degradation. Dashed and dotted lines are for starting (1) PC and (2) PET.

3) and much smaller for  $\text{EuL}_3$  (Fig. 5). While for both Ti and Eu catalysts the SEC peaks after selective degradation are unimodal with a shape similar to that of the starting PET, for the sample derived from Ca + Sb catalyst the peak is broader and trimodal (Fig. 4).

These data confirm once more that Ti derivatives are much more efficient than the other catalysts and that the reaction mechanism is more complex in the presence of Ca + Sb.

In conclusion, all the above results confirm that the chemical structure of the products resulting from melt mixing of PET and PC is strongly affected by the catalytic activity of the metal derivatives present as residues in PET, and therefore that the choice of the catalyst is of primary importance to obtain the desired product. In particular, lanthanide catalysts behave quite differently from Ti and Ca + Sb catalysts and seem to provide an opportunity for the control of the chemical structure during reactive blending of PET and PC.

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Received June 2, 1994

Accepted August 7, 1994