

# Catalytic Aspect of Chemical Modifications of Polymers by Transesterification: NMR Study with Model Compounds

I. PESNEAU, M. GRÉGOIRE, A. MICHEL

Laboratoire d'Etudes des Matériaux Polymères et Biomatériaux, UMR CNRS 5627, Institut des Sciences et Techniques de l'Ingénieur de Lyon, Université Claude Bernard, Lyon I, 43 Boulevard du 11 Novembre 1918, 69 622 Illeurbanne Cedex, France

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**ABSTRACT:** The catalytic activity of different compounds (dibutyl tin oxide, titanium tetrabutoxide, zirconium tetraethoxide, and *para*-toluenesulfonic acid) for transesterification reactions between polymers was studied. This study was carried out on three different reactions: between two model compounds (methyl benzoate and octyl acetate), between a polymer and a model compound (ethylene-vinyl acetate copolymer and methyl benzoate), and for crosslinking of ethylene-vinyl acetate copolymer with dimethyl terephthalate. For these three reactions dibutyl tin oxide presented the higher catalytic activity. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1556–1562, 2001

**Key words:** transesterification; dibutyl tin oxide; titanium butoxide; model reaction

## INTRODUCTION

Previous works with aliphatic and aromatic model esters and polymers bearing either pendant ester groups or ester groups in the backbone showed that dibutyl tin oxide (DBTO) was not a catalyst in the common sense but was instead the precursor of dimeric difunctional tetraorganodistannoxanes  $[\text{Bu}_4\text{Sn}_2\text{XYO}]_2$  (with  $\text{X} = \text{O}-\text{CO}-\text{R}$  and  $\text{Y} = -\text{OR}'$ ), which are the true catalysts in an ester-ester interchange reaction. Furthermore, an exchange reaction at the tin sites between alkoxy and acyloxy ligands of these distannoxanes and the ester groups was apparent above 100°C.<sup>1–3</sup>

Uncatalyzed transesterification reactions are not easy and occur between 250 and 300°C. In the presence of DBTO the interchange temperature is lowered from 100°C (according to Cassagrau et al.<sup>4</sup>) and the kinetic of these reactions becomes

compatible with the residence time of a continuous process such as extrusion.

The ester-ester interchange reaction in the presence of DBTO was used to co-crosslink ethylene-*co*-vinyl acetate (EVA) and ethylene-*co*-methylacrylate (EMA) in the molten state either in bulk in a rotomolding process or in a dispersed phase in a polypropylene matrix during an extrusion operation.<sup>5,6</sup> These transesterification reactions were also used to promote the compatibility of immiscible polymer blends of polyethylene/polyethylene or poly(butylene terephthalate) (PBT) through the *in situ* synthesis of the grafted polyester and EVA copolymer<sup>7–9</sup> during the processing operations in the conditions of a reactive extrusion.

The catalytic efficiency assessment of DBTO as the precursor of either difunctional distannoxanes or monofunctional distannoxanes has always been in good agreement with the studies with model esters and the polymers bearing ester groups.

The purpose of this article is to compare the catalytic efficiency of DBTO as a precursor of distannoxanes with other transesterification cat-

Correspondence to: A. Michel.

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alysts such as titanium tetrabutoxide, zirconium tetraethoxide, and *para*-toluenesulfonic acid through either the ester-ester interchange reactions of model esters or the grafting and crosslinking of polymers bearing pendant ester groups.

## EXPERIMENTAL

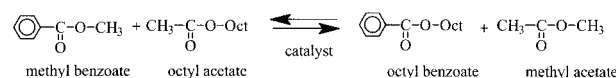
### Materials

Methyl benzoate, octyl acetate, methyl acetate, dimethyl terephthalate (DMT), DBTO, titanium butoxide [Ti(OBu)<sub>4</sub>], zirconium tetraethoxide [Zr(OEt)<sub>4</sub>], and *para*-toluenesulfonic acid monohydrate (*p*-TsOH, H<sub>2</sub>O) were all commercial products (Aldrich). The EVA copolymer was supplied by Atochem (EVATANE 2803). It contained about 28 wt % of VA units.

### Reactions

#### Reaction between Methyl Benzoate and Octyl Acetate

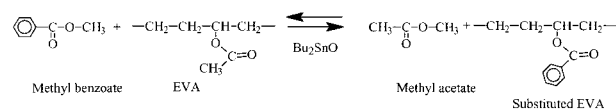
Methyl benzoate (0.09 mol), 0.09 mol of octyl acetate, and  $1.7 \times 10^{-3}$  mol of catalyst (about 2 mol %) were heated in a flask at 180°C (see Scheme 1). Samples were withdrawn and analyzed by NMR to determine the extent of the reaction.



**Scheme 1** The exchange reaction between methyl benzoate and octyl acetate in the synthesis of methyl acetate and octyl benzoate.

#### Reaction between EVA Copolymer and Methyl Benzoate

Methyl benzoate (19.2 g) and 40 g of EVA copolymer were mixed with 0.014 mol of the catalyst (about 10 mol %) in an internal mixer (Rheomix 600 of a Haake plasticorder, see Scheme 2). The temperature of the mixer was set at 180°C, and

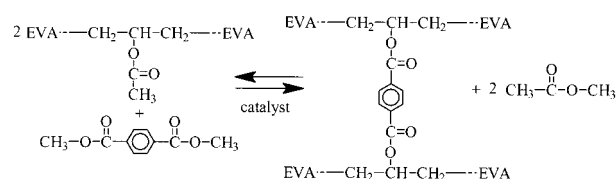


**Scheme 2** The exchange reaction between EVA copolymer and methyl benzoate in the synthesis of EVA partially substituted with benzoate groups.

the rotation speed was 50 rpm. The blend was mixed for 10 min; then it was solubilized in tetrachloroethylene (TCE), filtered off, and precipitated with methanol. This treatment was repeated twice to eliminate unreacted methyl benzoate.

#### Reaction between EVA Copolymer and DMT

Forty grams of EVA copolymer (0.14 mol ester groups), 13.6 g of DMT (0.14 mol ester groups), and  $2.1 \times 10^{-3}$  mol of catalyst (about 2 mol %) were mixed and rapidly poured into the internal mixer (see Scheme 3). The temperature of the mixer chamber was set at 180°C, and the rotation speed was 50 rpm. The blend was mixed for 10 min as the torque and temperature were recorded.



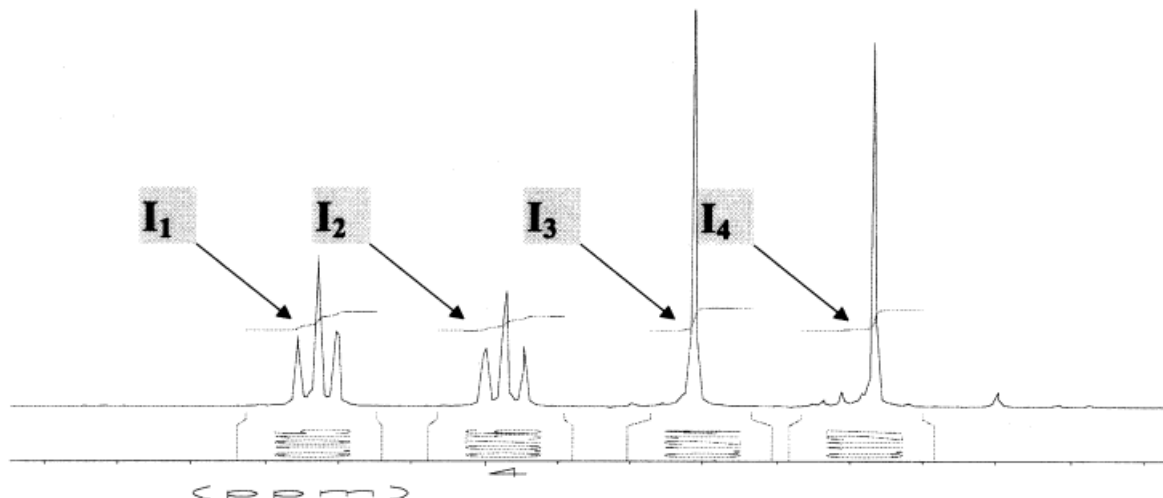
**Scheme 3** The exchange reaction between EVA copolymer and dimethyl terephthalate in the crosslinking of EVA through terephthalate groups.

### NMR Analysis

Liquid <sup>1</sup>H-NMR spectroscopy was carried out with a Bruker AC250 apparatus at 250 MHz. The spectra were carried out in a TCE/deuterated benzene (C<sub>6</sub>D<sub>6</sub>) mixture (2/1 v/v) at room temperature. The chemical shift values ( $\delta$ ) found were in reference to internal tetramethylsilane. The evolution of the reaction between the ester groups was determined from these spectra and eq. (1).

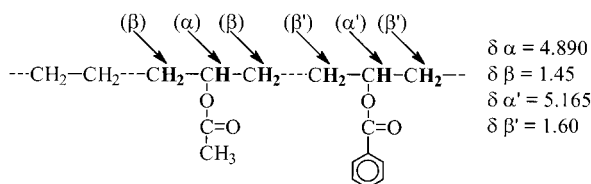
$$\xi = \frac{r}{1+r} 100 \quad (1)$$

In the reaction between methyl benzoate and octyl acetate,  $\xi$  is the percentage of octyl benzoate formed and  $r$  is the ratio of the integrals  $I_1$  and  $I_2$  (see Fig. 1). They are assigned respectively to the protons in the  $\alpha$  position of the oxygen atoms of octyl benzoate and octyl acetate. In the reaction between EVA copolymer and methyl benzoate,  $\xi$  is the percentage of benzoate groups grafted on



**Figure 1** The methyl benzoate–octyl acetate reaction: the  $^1\text{H}$ -NMR spectrum in  $\text{TCE}/\text{C}_6\text{D}_6$  of the reactive medium in the range of 3–5 ppm.

EVA and  $r$  is the ratio of the integrals assigned to the protons in the  $\alpha'$  and  $\alpha$  positions of the benzoate and acetate groups (see Scheme 4).



**Scheme 4** The EVA partially substituted by benzoate groups; chemical shifts in  $\text{TCE}/\text{C}_6\text{D}_6$ .

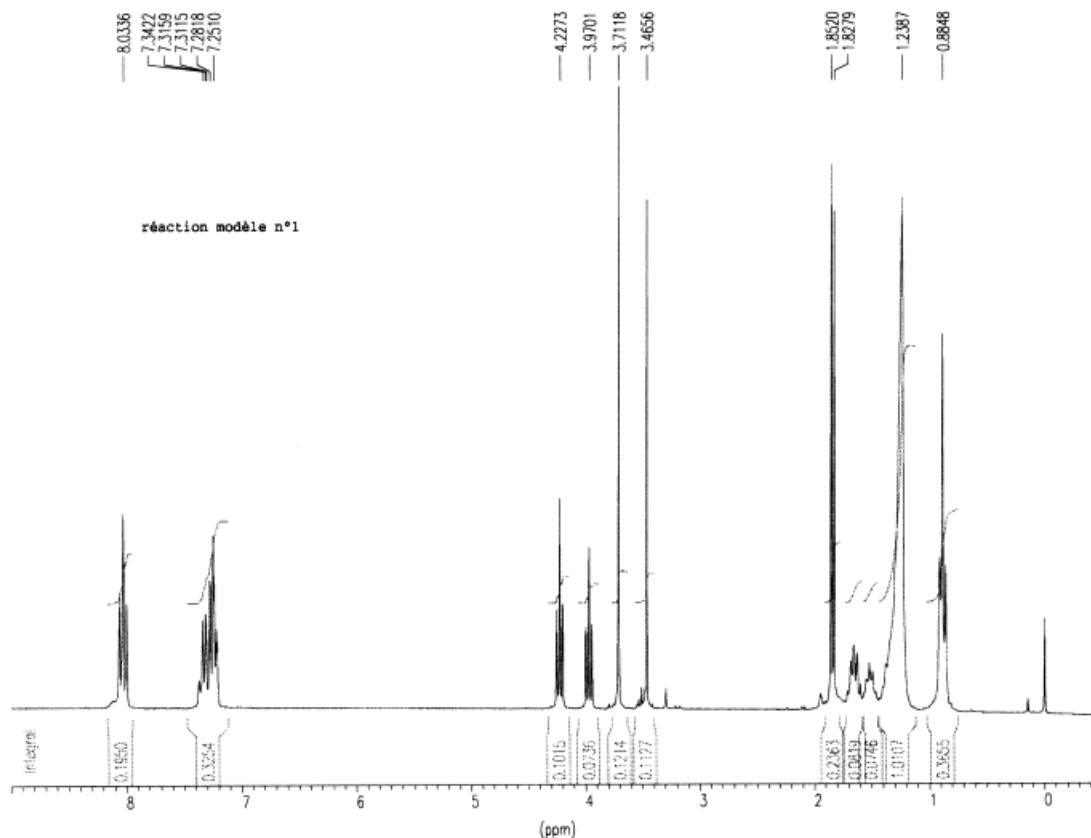
## RESULTS AND DISCUSSION

### Reaction between Methyl Benzoate and Octyl Acetate

Octyl acetate was selected to model the EVA copolymer and methyl benzoate was selected to model PBT. Butyl benzoate was not chosen in order to simplify the NMR spectra in the resonance range of 0.8–2 ppm. Indeed a previous study<sup>9</sup> showed that it was possible to differentiate the protons in the  $\beta$  and  $\beta'$  positions (Scheme 4) of the benzoate groups of EVA that are partially substituted in this range of resonances. Furthermore, methyl benzoate appeared to be a good model for PBT.<sup>9</sup> The reaction was carried out in a flask. Because the aim was to carry out the reaction during processing of a blend, we mainly studied the first steps of the reaction.

When the reaction proceeded, two other esters were formed: octyl benzoate and methyl acetate (see Scheme 1). The extent of the reaction was determined from the NMR spectra. Figure 2 presents an example of the spectra obtained. Four resonances were present in the 3–5 ppm range. They were assigned to protons in the  $\alpha$  position of the oxygen atoms of the ester groups (Table I). Because four resonances corresponding to four types of protons were present in the NMR spectrum, four esters were present in the medium. These resonances were compared to those of commercial products (methyl benzoate, octyl acetate, and methyl acetate) and were assigned to these different esters (see Table I). The extent of the reaction after different reaction times and with different catalysts are summed up in Table II. The transesterification reaction does not occur without a catalyst. Even after 1 h at 180°C, synthesis of octyl benzoate and methyl acetate was not clearly shown.

Table II shows that DBTO,  $\text{Ti}(\text{OBu})_4$ ,  $\text{Zr}(\text{OEt})_4$ , and  $p$ -TsOH had catalytic activity for the transesterification reaction. The *para*-toluenesulfonic acid had the lowest one. The amounts of octyl benzoate formed after 4 and 10 min of reaction were too small to be determined by NMR, and after 1 h only 11% were formed. The  $p$ -TsOH is an acid catalyst whereas the three others are either metallic or organometallic compounds. Zirconium and titanium compounds present intermediate activity. The difference between  $\text{Zr}(\text{OEt})_4$  and  $\text{Ti}(\text{OBu})_4$  was more pronounced at the first steps.



**Figure 2** The methyl benzoate–octyl acetate reaction: the  $^1\text{H-NMR}$  spectrum in  $\text{TCE}/\text{C}_6\text{D}_6$  of the reactive medium with the DBTO.

After 4 min of reaction there was 5 times as much octyl benzoate formed with  $\text{Ti}(\text{OEt})_4$  than with  $\text{Zr}(\text{OEt})_4$  whereas after 1 h only 1.1 times as much was formed with  $\text{Ti}(\text{OEt})_4$ . DBTO presented the best activity with 20% octyl benzoate formed after only 4 min of reaction [6.8 times as much as with  $\text{Zr}(\text{OEt})_4$ ]. DBTO first reacted with the ester groups to form distannoxane structures, the true catalysts of the reaction. This first reaction favored dispersion of the catalyst in the medium and can explain the high efficiency of DBTO with

respect to transesterification. Because the purpose of this study was to carry out the reaction during processing operations, the reaction rate had to be very high at a small reaction time, which was the case with DBTO.

#### Reaction between Methyl Benzoate and EVA

The previous reaction was carried out in a liquid homogeneous medium (Scheme 2). In a second step we tried to verify if the order of the catalyst

**Table I** Chemical Shift in  $\text{TCE}/\text{C}_6\text{D}_6$  of Protons in  $\alpha$  Position of Oxygen Atom with Respect to  $\text{O-CO-R}$  Groups

Compounds	Protons	$\delta$ (ppm)
Methyl benzoate	$\phi\text{-CO-O-CH}_3$	3.70
Octyl acetate	$\text{CH}_3\text{-CO-O-CH}_2\text{-(CH}_2\text{)}_6\text{-CH}_3$	3.96
Octyl benzoate	$\phi\text{-CO-O-CH}_2\text{-(CH}_2\text{)}_6\text{-CH}_3$	4.22
Methyl acetate	$\text{CH}_3\text{-CO-O-CH}_3$	3.46

**Table II** Percentage of Octyl Benzoate ( $\xi$ ) with Different Reaction Times and Catalysts

Catalyst	$\xi$		
	4 min	10 min	60 min
—	0	0	0
DBTO	20	23	33
Ti(OBu) <sub>4</sub>	15	19	25
Zr(OEt) <sub>4</sub>	2.9	8.3	22
<i>p</i> -TsOH	UD	UD	11

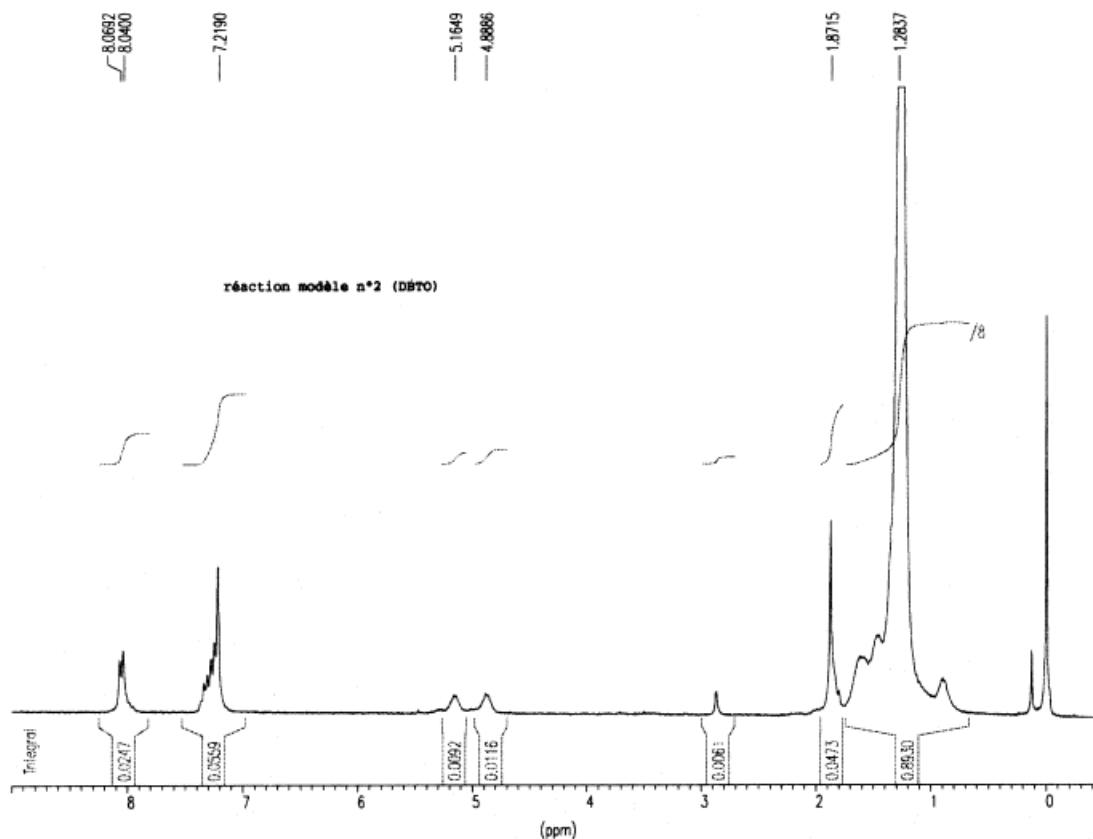
UD, undetermined.

reactivity was conserved in the presence of a polymer. So this reaction was carried out between a polymer (EVA) and a model compound (methyl benzoate) during processing in an internal mixer (Haake Rheocord). The blend was mixed for 10 min; then reacted EVA was isolated and analyzed by NMR.

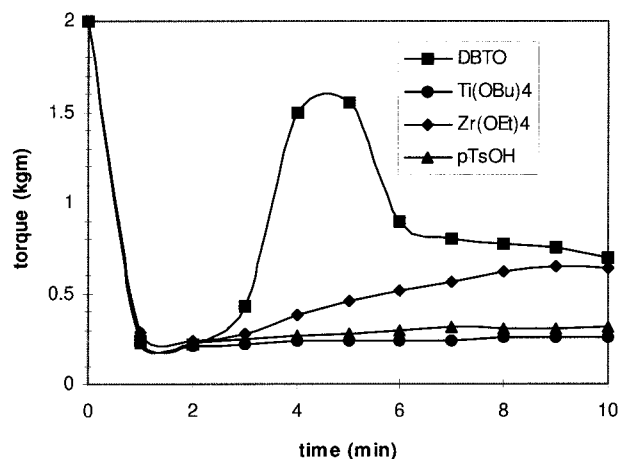
Substitution of acetate groups by benzoate groups involves chemical shift evolution of differ-

ent types of protons. A deshielding effect was observed on CH $\alpha$  and CH $_2\beta$ , but it was lower in this last case (Scheme 4) when acetate groups were substituted by benzoate groups. Moreover, typical aromatic resonances were found on NMR spectra in the range of 7–8.5 ppm after substitution (Fig. 3). In the reactional medium two compounds can present aromatic resonances: methyl benzoate and substituted EVA. However, methyl benzoate presented a resonance on the NMR spectra at 3.69 ppm due to the —O—CH $_3$  group. Lack of this resonance was proof of complete elimination of this product by solubilization in TCE.

The reaction was carried out with DBTO, Ti(OBu)<sub>4</sub>, Zr(OEt)<sub>4</sub>, and *p*-TsOH. In these conditions DBTO was always the most efficient catalyst of the redistributive transesterification reaction. After 10 min it led to the substitution of almost 44% of the acetate groups. As previously, this high efficiency can be correlated with its ability to give distannoxane structures by the reaction with ester groups. This reaction led to a molecular dispersion of DBTO in the polymeric me-



**Figure 3** The transesterification of EVA–methyl benzoate in the presence of DBTO: the  $^1\text{H-NMR}$  spectrum in TCE/ $\text{C}_6\text{D}_6$  after elimination of unreacted methyl benzoate.



**Figure 4** The torque evolution versus time for DMT/EVA blends with different catalysts.

dium. With  $\text{Ti}(\text{OBu})_4$  only 10% of acetate groups were substituted after 10 min. In relation to previous liquid conditions, in melt conditions this compound was much less efficient than DBTO whereas with  $\text{Zr}(\text{OEt})_4$  and  $p\text{-TsOH}$  the substitution was not enough to be characterized by NMR analysis.

The only compound that could replace DBTO was  $\text{Ti}(\text{OBu})_4$ , although it presented lower activity. This could be an important drawback for an *in situ* reaction during processing operations, mainly to make kinetic and residence times compatible.

#### Reaction between DMT and EVA Copolymer

The crosslinking of thermoplastics is a route to improve thermomechanical properties above either the glass-transition temperature or the melting point by preventing molecular flowing that initiates creep and shrinkage. We studied crosslinking of EVA by a transesterification reaction in the presence of DMT (Scheme 3). The evolution of the reaction was easily followed by recording the torque evolution of the medium, because these values were relevant to the evolution of medium viscosity. Figure 4 presents the evolution of torque versus time in the presence of different transesterification catalysts. For all the blends, after introduction of EVA copolymer, DMT, and catalyst in the mixing chamber, a torque decrease was observed that was due to the polymer melting; then the curve reached a plateau. After about 2 min in the presence of DBTO the torque increased strongly because of polymer

crosslinking. It reached a maximum after about 2 min more before falling again. The maximum torque value corresponded to a high crosslinking density where the polymer becomes brittle. Further mixing transformed it into a powder. The strong torque increase confirmed the high catalytic activity of DBTO for transesterification reactions. With the three other catalysts previously studied [ $\text{Ti}(\text{OBu})_4$ ,  $\text{Zr}(\text{OEt})_4$ , and  $p\text{-TsOH}$ ] there was no evidence of a crosslinking peak as with DBTO. This confirmed either poor catalytic activity or lack of catalytic activity for transesterification reactions. These results obtained with DBTO,  $\text{Ti}(\text{OBu})_4$ ,  $\text{Zr}(\text{OEt})_4$ , and  $p\text{-TsOH}$  were in good agreement with previous studies in liquid and melt conditions.

#### CONCLUSION

This study shows that classification of catalytic activity of different compounds for a redistributive or direct transesterification reaction is the same whatever the viscosity of the medium (very low as for the liquid medium or higher with the polymer). In all cases  $\text{DBTO} > \text{Ti}(\text{OBu})_4 > \text{Zr}(\text{OEt})_4 > p\text{-TsOH}$ .

However, the activity of these compounds depends on experimental conditions. With model compounds in homogeneous and liquid conditions, the catalytic activities of DBTO and  $\text{Ti}(\text{OBu})_4$  are the same. The  $\text{Zr}(\text{OEt})_4$  activity is lower and the  $p\text{-TsOH}$ , which is an acid catalyst, has very poor activity. In melt conditions our results display the high efficiency of DBTO with respect to  $\text{Ti}(\text{OBu})_4$ . This high catalytic activity can be related to the reaction of DBTO with ester groups to form distannoxane structures, the true catalyst of transesterification reactions. This chemical reaction enables the DBTO dispersion on a molecular scale. In melt conditions the catalytic activity of  $\text{Zr}(\text{OEt})_4$  is very poor.

In the EVA copolymer crosslinking through a transesterification reaction with DMT, the DBTO also shows the best catalytic activity whereas with the other catalyst the catalytic activity is very poor.

This study confirms that, because of its high efficiency for transesterification, DBTO can promote the reaction during processing operations with a kinetic time compatible with the residence time, typically on the order of 1 min for a continuous process such as extrusion.



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