

# Graft Copolymers Synthesis by Dynamic Covalent Reorganization of Polycaprolactone and Poly(ethylene-*co*-vinyl alcohol)

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**ABSTRACT:** Dynamic covalent reorganization of polycaprolactone (PCL) and poly(ethylene-*co*-vinyl alcohol) (EVOH) were realized by solvent free transesterification reactions. Organometallic and organic catalysts effect on these reactions was first evaluated from kinetic studies on small molar mass model reactants. Kinetic constants and activation energies of these second order reverse reactions were calculated. At the higher temperatures, side reactions were observed; they were identified as being principally dehydration reactions. Reactions conducted onto polymers were slower than those on model reactions. This was due to the immiscibility of the used polymers resulting in diffusion controlled reactions. Two competitive types of

reactions were detected, since at the catalyst addition, fast induced reorganization of PCL leading to low PCL molar mass decreases the mixing torque, followed by grafting reactions of PCL onto EVOH, resulted in an important increase of the mixing torque. Substitution rate of the EVOH hydroxyl groups were measured up to 14% by <sup>1</sup>H-NMR spectroscopy. Increasing substitution rate led to a decrease of the copolymer crystallinity and the more substituted copolymers were amorphous. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3145–3153, 2012

**Key words:** biopolymers; compatibility; graft copolymers; kinetics; immiscibility

## INTRODUCTION

A particular interest in Dynamic Covalent Chemistry, where covalent bonds are formed and broken under conditions of equilibrium thermodynamic control, have been related in interesting studies during the last decades.<sup>1</sup> Dynamic covalent reactions allow readjustment of the product distribution of a reaction, even once the initial products have been formed, by changing the reactions environment (concentration, temperature).<sup>2–6</sup> Unifying concepts concerning these dynamic covalent reactions were proposed in the last decades.<sup>1,2,4</sup> The concept of the dynamic covalent chemistry was clearly defined by Rowan et al in a review with numerous examples.<sup>4</sup> Covalent bonds may be reversibly formed and broken under thermodynamic control to form the most stable products.

Poly(ethylene-*co*-vinyl alcohol)-*g*-polycaprolactone properties depends on the structure of these copolymers.<sup>3</sup> Crystallinity, biodegradability, biocompatibility, and adhesion properties are function of

poly(ethylene-*co*-vinyl alcohol) (EVOH) to polycaprolactone (PCL) ratios and also of the molar mass of each constituent.

The graft copolymers prepared in this study are candidates for developing therapeutic devices such as temporary prostheses, and also as scaffolds for tissue engineering.

Alcoholysis reaction, often used in dynamic covalent chemistry and used here for poly(ethylene-*co*-vinyl alcohol)-*g*-polycaprolactone preparation, is a well-known reaction between ester functions and alcohol functions leading to new ester and alcohol by an exchange reaction. This reaction is more commonly called transesterification considering the interchange where at least one ester function is involved in the reaction. Two main applications of these reactions are found in the literature: the first one concerns fatty acids chemistry, whereas the second one is used for depolymerization by methanolysis or glycolysis generally for recycling purpose of polycondensation polymers. Primary alcohols are known as the most reactive, with some exceptions, where secondary alcohol are more reactive when specific catalysts, such as organocadmium compounds are used.<sup>7</sup>

Two categories of catalyst were found in literature: alkoxydes like Mg(CH<sub>3</sub>O)<sub>2</sub>, Ca(CH<sub>3</sub>O)<sub>2</sub>, and

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TABLE I  
Reagents Properties

Reagents	Melting point (°C)	Boiling point (°C)	$T_g$	$M_n$ (g/mol)	Origin
EVOH E105B (44% of ethylene)	165°C		54°C	20000	EVAl Europ
PCL 6250	60°C		-60°C	25000	Solvay
Tin(IV) tert-butoxide	40–44			411.16	ABCR
Tin(II) 2-ethylhexanoate	202			405.12	ABCR
Calcium ethoxyde	170			112.15	ABCR
Calcium 2-ethylhexanoate	200–220			326.49	ABCR
Titanium(II) 2-ethylhexanoate				620.69	ABCR
Titanium (IV) oxide acetylacetonate	184			262.12	ABCR
2-tert-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine		74°C (0.03mm. Hg)		274.39	Aldrich
1,5,7-Triazabicyclo[4.4.0]dec-5-ene	125–130	–		139.2	Aldrich

Ca(C<sub>8</sub>H<sub>17</sub>O)<sub>2</sub>. They are generally insoluble in organic solvents acting in heterogeneous catalysis. Barium metal reported as being the more efficient metal, is particularly toxic. Alkali metals are rarely used because high concentrations are required and Claisen condensation may occur as a side reaction.

A second class of catalysts, organometallic compounds applied to polymer, such as polyesters or polycarbonates glycolysis is used at higher temperatures.<sup>8–11</sup> Acetate group is commonly present in these catalysts, linked to lead, zinc, cobalt, and manganese. Zinc acetate is described as the more efficient one.<sup>11,12</sup> Metal oxides are also commonly used. Lead oxide is described as efficient around 250°C but its toxicity remains a problem.<sup>13</sup> Dibutyl tin oxide is also efficient at high temperature; it first reacts to form a distannoxane structure (1-acyloxy-3-alkoxydistannoxane) directly linked to the ester function. These new structures, even if they are very efficient for PET glycolysis in molten state, are now forbidden for common applications.

Otera<sup>14</sup> compared the difference between organotin compounds and titanium alkoxy to synthesize polyester by alcoholysis reactions. Ti(OBu)<sub>4</sub> was found more reactive than organotin catalysts, such as dilaurate, diphenoxy or dibutyl tin oxide. Therefore, more reactive distannoxanes may be also synthesized from tin dihalide and dialkyltin oxide. These distannoxane structures are generally present as dimers in solution or solid state.

The catalysts used in literature for transesterification reactions are very numerous and indications concerning their efficiency are often in contradiction: Kinetics concerning these reactions does not allow a reasonable choice of the catalyst structure in relation with a reaction conditions (temperature, concentration, duration...). No allusion concerning secondary reactions in relation with reaction conditions and specially temperature was found in literature. Seen the importance of these transesterification and particularly alcoholysis in dynamic covalent reactions applied to polymer modification, kinetic, and

structural studies on model reactants were first realized in this study. As recommended in literature, organometallic catalysts were chosen, for their reported efficiency and also because they are often soluble in organic media. Nonionic strong basis, as guanidines, amidines, triaminophosphoranes, and 1,5,7-Triazabicyclo[4.4.0]dec-5-ene were recently used for lactones and lactides ring opening polymerization instead of common organometallic compounds.<sup>15–18</sup> Reactions can be made at relatively low temperature generally between room temperature and 100°C. Their efficiency as alcoholysis catalysts were also examined in this study. The kinetic and structural studies on model reactants will allow a reasonable choice of catalyst in relation with reaction conditions. The results of this study will be used for exchange reactions by reactive processing.

## EXPERIMENTAL

### Materials

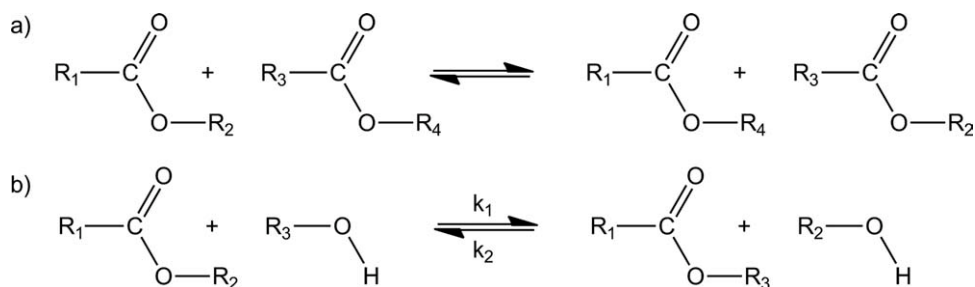
The reactants used in this study are listed in Table I.

### NMR analysis

The <sup>1</sup>H-NMR analyses were performed with a Bruker DRX250 spectrometer operating at 250 MHz, in DMSO-d<sub>6</sub> at 90°C with tetramethylsilane as internal standard.

### DSC analysis

The thermal analyses were done with a Setaram Q10. Each sample was heated, under a nitrogen flow, by two consecutive ramps at 10°C min<sup>-1</sup> from room temperature to 180°C for the first one. After, a cooling ramp at 10°C min<sup>-1</sup>, a second ramp was realized from -70 to 200°C.



**Scheme 1** General presentation of the reversible reactions of transesterification (a) and alcoholysis (b).

### SEM analysis

Scanning electron microscopy experiments were carried out in a HITACHI S3000N. Samples were prepared by cryofracturing. The fracture surfaces were coated with gold-palladium before being observed. Surface images were recorded at a voltage of 8 kV.

### Gas-chromatographic analysis

GC-MS analyses were made with a Hewlett-Packard GCD 1800 A, with an EID detector, using an Innowax silica capillary column from Agilent, 50 m × 0.20 mm ID × 0.5 μm with a helium flow at 1.0 mL min<sup>-1</sup>. The injector and detector temperatures were, respectively, set at 200 and 250°C. Thermal cycle began with an initial temperature fixed at 50°C (5 min), followed by a ramp at 20°C min<sup>-1</sup> up to 180°C. The split was fixed at 120 to work in a linear mode with injections of 1 μL.

The conversion of 2-dodecylbenzoate was calculated from a calibration curve using dibutylphthalate as internal standard. Withdrawn samples in the reaction media were dissolved in ethyl acetate before injection.

### Synthesis of 1-dodecylbenzoate

1-dodecanol (34 mL, 0.15 mol) was added in small portions to a 100-mL three-necked flask charged with (20 mL, 0.15 mol) benzoyl chloride and equipped with a magnetic stirring and a condenser. The flask was connected to a bottle containing 50 mL of 5wt % NaOH. The reaction mixture was heated at 110°C for 4 hours and cooled to room temperature and washed by a 0.5M NaHCO<sub>3</sub> and extracted three times with ethyl acetate. The organic solution was then washed with saturated NaCl solution and dried under MgSO<sub>4</sub>. The 1-dodecylbenzoate purity was confirmed by a GC-MS analysis (more than 98%). The analyzed molecule, that is liquid at room temperature, was injected at 200°C under vacuum in the GC.

### Alcoholysis on model reactants and EVOH-g-PCL synthesis in melt processing

Melt transesterification model reactions were made in a 100-mL three necked glass reactor. 1-dodecylbenzoate (0.017 mol, 5 g) and 2-dodecanol (0.017 mol, 3.2 g) were first added, the catalyst (70 mg) was added in the second time. A steel anchor stirrer operating with a RW28WIKKA motor at 80 rpm, a condenser and a connector for nitrogen flow were fixed to the cover. The reactor was heated at the desired temperature using an IKA HBR4 bath with silicon oil. An oil bath was used to adjust the temperature at the desired temperature. Reactions were conducted under a nitrogen flow, dried in a silica column.

Melt transesterification on polymers were made in the same process used for alcoholysis on model reactants. A 250 mL and 90 mm diameter glass reactor with a three necked steel cover was used in this second case. EVOH (40 g) and polycaprolactone (70 g) were mixed in the glass reactor during 30 min. The catalyst (4 g) was added after in the second time. Samples were taken each 30 min of reaction.

### Kinetic modeling

For kinetic study, a second order kinetic model was used for alcoholysis and back reactions according to the general scheme presented (Scheme 1). The law rate is given in eq. (1).<sup>19</sup>

$$\frac{dx}{dt} = k_1(a-x)^2 - k_2x^2 \quad (1)$$

where  $a$  is the initial mole fraction of 1-dodecylbenzoate,  $x$  and  $x_e$  are the fractions of 2-dodecylbenzoate formed at time  $t$  and at equilibrium.  $k_1$  and  $k_2$  are the rates of alcoholysis reaction for the direct and inverse reactions, respectively.

At the equilibrium, the corresponding  $x_e$  is defined by eq. (2).

$$k_1(a-x_e)^2 - k_2x_e^2 = 0 \quad (2)$$

The equilibrium constant  $K$  is:

$$K = \frac{k_1}{k_2} = \frac{x_e^2}{(a - x_e)^2} \quad (3)$$

From eqs. (1) and (3), the reaction rate is:

$$\frac{dx}{dt} = \frac{k_1 a (2x_e - a)}{x_e^2} (x_e - x) \left( \frac{a x_e}{2x_e - a} - x \right) \quad (4)$$

The integration gives:

$$k_1 t = \frac{x_e}{2a(a - x_e)} \left[ \ln \frac{x_e}{x_e - x} - \ln \frac{\frac{a x_e}{2x_e - a}}{\frac{a x_e}{2x_e - a} - x} \right] = X \quad (5)$$

$X$ , calculated from eq. (5), and must vary linearly with  $t$  if the second order is confirmed. The slope of the obtained line gives directly access to  $k_1$  [eq. (5)] and  $k_2$  [eq. (3)].

From the determined constants and the conversion at the equilibrium, the kinetics may be fitted from the chosen model by the following equation:

$$x = \frac{a x_e (1 - \exp y)}{2 x_e - a (1 + \exp y)} \quad (6)$$

With

$$y = \frac{2a(a - x_e)}{x_e} k_1 t \quad (7)$$

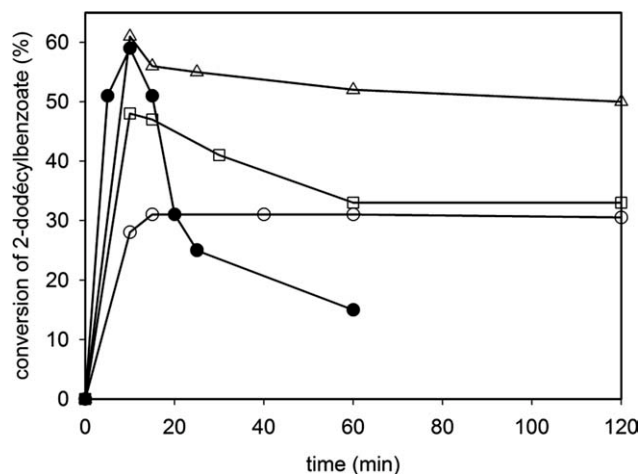
## RESULTS AND DISCUSSION

### Model reactions

Before using alcoholysis reaction in dynamic covalent reorganization of PCL and EVOH, model reactions were used to analyze reactions parameters effects particularly on kinetics and side reactions. Catalysts were chosen because it was reported in literature that they were already efficient for alcoholysis reactions with polymers bearing the reactive functions (i.e., organometallic catalysts). Organic catalysts generally used for alcoholysis of fatty acids at room temperature were also chosen (Table I).

2-Dodecanol has a structure similar to the reactive functions of EVOH. In addition, high boiling point of the chosen reagents allows their use at the relatively high temperatures requested for EVOH and PCL dynamic covalent exchange reactions (over the melting point of EVOH, 165°C).

Reactions between, 1-dodecylbenzoate with 2-dodecanol using tin(II) bis(2-ethylhexanoate) ( $\text{SnOct}_2$ ) and respective molar ratio 1/1/0.01 were conducted between 110 and 210°C not only to cover a larger



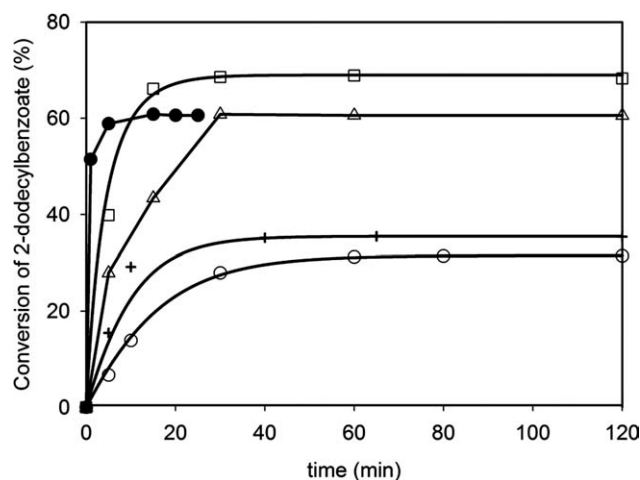
**Figure 1** Conversion evolution of 2-dodecylbenzoate with Tin(II) bis(2-ethylhexanoate). 1-dodecylbenzoate/2-dodecanol/ $\text{SnOct}_2$  = 1/1/0.01 mol/mol/mol. ○: 110°C, △: 176°C, □: 195°C, ●: 210°C.

domain than the one reported in literature but also because reactions on polymers are to be made at relatively high temperatures. Conversion evolution of 2-dodecylbenzoate are reported in (Fig. 1). High conversions are obtained after few minutes, typically 5 min. This general observation was generally followed by a rapid decrease in 2-dodecylbenzoate concentrations. This evolution is very marked at the higher temperatures and becomes less intense with temperature decrease. At 110°C the 2-dodecylbenzoate concentration slightly increased.

Completely different evolutions are observed when the catalyst changed. With 1.5.7-triazabicyclo [4.4.0]dec-5-ene catalyst, conversions progressively increased with reaction time and temperature and leveled after few minutes. The reaction at 186°C leveled at lower conversion than at 176°C (Fig. 2).

### Reactions at different temperatures

To understand these particular evolutions, mass spectra (from GC/MS analyses) of reactions products between 1-dodecylbenzoate with 2-dodecanol using  $\text{SnOct}_2$  and respective molar ratio 1/1/0.01 were realized. First, reactions were made at different temperatures and samples taken at different reaction times. An example is given in (Fig. 3). At 110°C, only the four expected reactants and products are detected. Increasing temperature to 176°C and 210°C, the mass spectra show several other side products (Fig. 3). They mainly result from alcohol dehydration and from double bonds migration (isomerization). When TDB is used instead of  $\text{Sn}(\text{Oct})_2$ , up to 176°C, only the four precedent products were observed. For higher temperatures by products were also obtained.

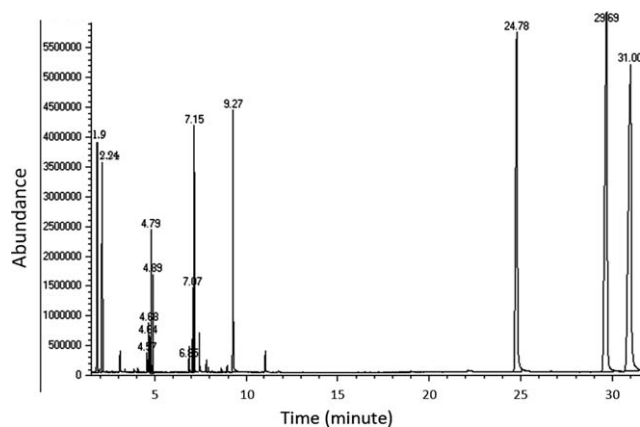


**Figure 2** Conversion evolution of 2-dodecylbenzoate with 1.5.7-triazabicyclo [4.4.0]dec-5-ene. 1-dodecylbenzoate/2-dodecanol/TBD = 1/1/0.01 mol/mol/mol. ○ 90°C, +110°C, □176°C, △186°C, ● 210°C.

Two groups of reactions are finally present, the first one leading to dynamic covalent exchange reactions and the other one becoming more important when the reaction temperature increase leading to principally dehydration and migration of the issued alkenes (Table II). This explains the apparent decrease of conversion increasing temperature.

Nevertheless, when SnOct<sub>2</sub> is the used catalyst (Fig. 1), exchange reactions are obtained in the first 5 to 10 minutes for the higher temperatures. This result shows that these reactions can be realized efficiently using a process where reaction times are low, such as reactive extrusion.<sup>20–27</sup> In this case, the exchange reactions are favored while side reactions even if they can be present are not predominant.

These results also indicate that working at low temperature is therefore necessary to study the



**Figure 3** Products formed during alcoholysis reaction and their retention times obtained by GC/MS analysis.  $T = 210^{\circ}\text{C}$  1-dodecylbenzoate/2-dodecanol/catalyst = 1/1/0.01, reaction time = 15 min.

**TABLE II**  
List of Secondary Products Obtained Alcoholysis Reaction and Their Retention Times Obtained by GC/MS.  $T = 210^{\circ}\text{C}$  1-dodecylbenzoate/2-dodecanol/catalyst = 1/1/0.01, Reaction Time = 15 min

Name	Retention time (min)
Solvent (acetone)	1.9
Solvent (ethyl acetate)	2.24
4-dodecenez	4.57
4-dodecenee	4.64
1-dodecene	4.68
2-dodecenee	4.79
2-dodecenez	6.85
2-dodecanol	9.27
2-dodecanone	7.07
Cyclododecane	7.15
2-dodecylbenzoate	24.78
Dibutylphtalate	29.69
1-dodecylbenzoate	31.00

catalytic behavior and kinetics of alcoholysis reaction without side products formation.

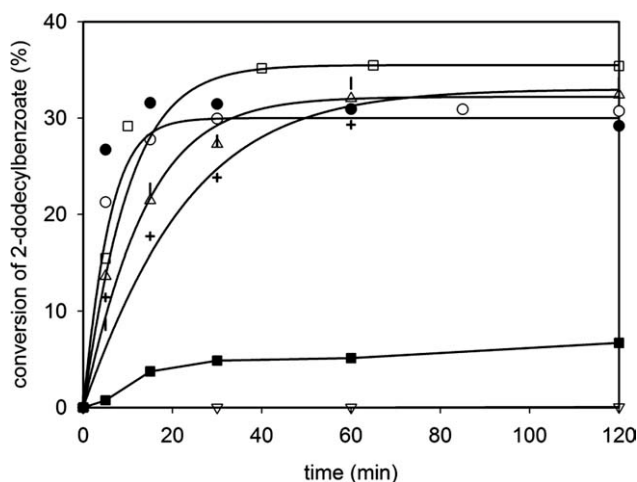
### Catalysts efficiency at 110°C

In the first experiments, the efficiencies of these catalysts were compared at 110°C with model reactants, 2-dodecanol and 1-dodecylbenzoate, leading to 1-dodecanol, and 2-dodecylbenzoate by the exchange reaction. This temperature is too low to be chosen for the alcoholysis reaction between PCL and EVOH homopolymers, but at this temperature, no secondary reactions or degradation is observed. All the experiments were made in stoichiometric conditions without solvent. Reactions were analyzed by GS/MS as described in the experimental part. The results are presented in Figure 4.

At 110°C, between 20 and 30 min are necessary to reach a maximum of conversion for the used catalysts except for both titanium 2-ethylhexanoate and titanium oxide acetylacetonate. In this case, the reactions are relatively slow and 2 hours are needed to obtain a relatively low conversion, less than 10%. The maximum of conversion are very different going from 5% for the less reactive catalyst, to more than 35% for the more reactive one, 1.5.7-triazabicyclo [4.4.0]dec-5-ene.

### Kinetic study

The kinetic model, previously presented [eqs. (1)–(7)], was applied to the different systems first to confirm the second order mechanism for both the direct and the reverse reactions, and also for the kinetic constants determination. This model is satisfying for all the catalysts excepted for the slowest reactions where the conversion rate at the equilibrium was not reached and also for the tin



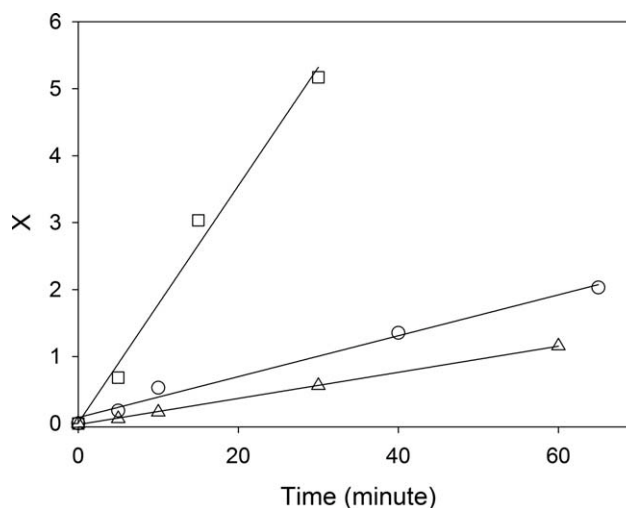
**Figure 4** Reactivity of different catalysts for alcoholysis between 2-dodecanol and 1-dodecylbenzoate at 110°C with 1 mol % of catalyst in stoichiometric conditions ● Tin 2-ethylhexanoate, ○ Tin tert-butoxide, ▽ Titanium oxide acetylacetonate, ■ Titanium 2-ethylhexanoate, □ 1.5.7-triazabicyclo [4.4.0]dec-5-ene, I: 2-tert-butylimino-2-diethylamino-1.3-dimethylperhydro-1.3.2-diazaphosphorine, △ Calcium 2-ethylhexanoate, + : Calcium ethoxide.

bis(2-ethylhexanoate), because this model does not match with the kinetic data. Table III summarizes the obtained results.

#### Temperature effect with 1.5.7-triazabicyclo [4.4.0]dec-5-ene

To complete the description of the 1.5.7-triazabicyclo [4.4.0]dec-5-ene and to calculate the activation energies of the kinetic constants by Arrhenius law, additional reactions were made at 90°C and 176°C.

The evolution of  $X$  calculated from eq. (5) with reaction time is given in Figure 5. As expected, a linear evolution was obtained. From the slopes  $k_1$  were determined (Fig. 5), then from eq. (4),  $k_2$  were calculated (Table IV). From Arrhenius law, activation energy was determined:  $E_a = 23.98 \text{ kJ mol}^{-1}$ .



**Figure 5** Representation of  $X = f(t)$  as expected from eq. (5) from kinetic data. △ 90°C, ○ 110°C, □ 176°C, for alcoholysis kinetic using 1-dodecylbenzoate/dodecan-2-ol, 1.5.7-triazabicyclo [4.4.0]dec-5-ene : 1/1/0.01 mol/mol/mol.

#### EVOH-g-PCL synthesis by alcoholysis reaction

EVOH-g-PCL copolymers were synthesized by alcoholysis reaction between pure EVOH and PCL in the melt at 176°C with, respectively, ester functions of PCL/alcohol function of EVOH/catalyst molar ratio of 1/1/0.01. For this system, two catalysts were used, 1.5.7-triazabicyclo[4.4.0]dec-5-ene and tin(II) bis(2-ethylhexanoate). Reactions evolutions were evaluated by  $^1\text{H-NMR}$  as described in a precedent study<sup>3</sup> from the EVOH methines.

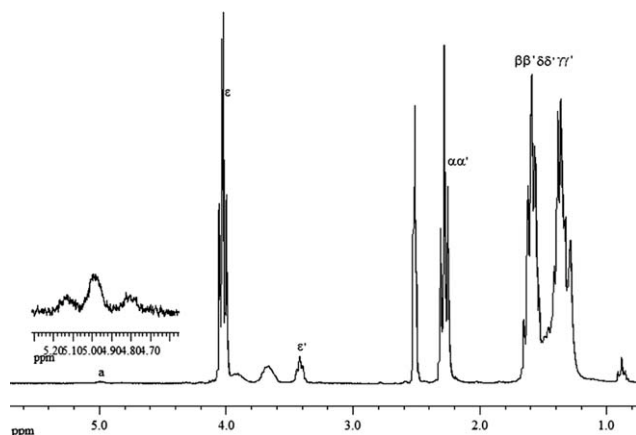
An  $^1\text{H-NMR}$  spectrum of poly (ethylene-co-vinyl-alcohol)-g-polycaprolactone is given in Figure 6 and Scheme 2. Triplets at 4.1 and 2.31 ppm, respectively, are relative to protons  $\epsilon$  and  $\alpha\alpha'$  of polycaprolactone sequences. The methylene protons of EVOH are between 1.3 ppm and 1.4 ppm. The signals corresponding to the methine protons of EVOH are also

**TABLE III**  
Conversion and Kinetic Constants Obtained for Different Catalysts from the Reaction Between 1-Dodecylbenzoate/2-dodecanol/catalyst = 1/1/0.01 (mol/mol/mol).  $T = 110^\circ\text{C}$

Catalyst	Conversion at equilibrium (%) *	$k_1(\text{mol}^{-1} \text{min}^{-1})$	$k_2(\text{mol}^{-1} \text{min}^{-1})$	$K$
Tin(IV)tert-butoxide	30	0.0461	0.251	0.184
Tin(II) 2-ethylhexanoate	31.6	—	—	—
Calcium ethoxyde	33	0.0132	0.0544	0.243
Calcium 2-ethylhexanoate	32.2	0.211	0.0935	0.226
Titanium (IV) tetrapropoxide	31.5	0.0179	0.0846	0.211
Titanium(II) 2-ethylhexanoate	35.5	—	—	—
Titanium (IV) oxide acetylacetonate	0	—	—	—
2-tert-butylimino-2-diethylamino-1.3-dimethylperhydro-1.3.2-diazaphosphorine	33.4	0.0205	0.0805	0.252
1.5.7-Triazabicyclo[4.4.0]dec-5-ene	35.5	0.323	0.1066	0.303

**TABLE IV**  
Effect of Temperature in Kinetic Constants for Alcoholysis Reactions Between 1-dodecylbenzoate and 2-dodecanol Catalyzed by 1.5.7-triazabicyclo [4.4.0]dec-5-ene : 1/1/0.01 mol/mol/mol

Temperature (°C)	$k_1$ (mol <sup>-1</sup> min <sup>-1</sup> )	$k_2$ (mol <sup>-1</sup> min <sup>-1</sup> )	K
90	0.01795	0.0849	0.211
110	0.323	0.1066	0.303
176	0.1775	0.0358	0.954



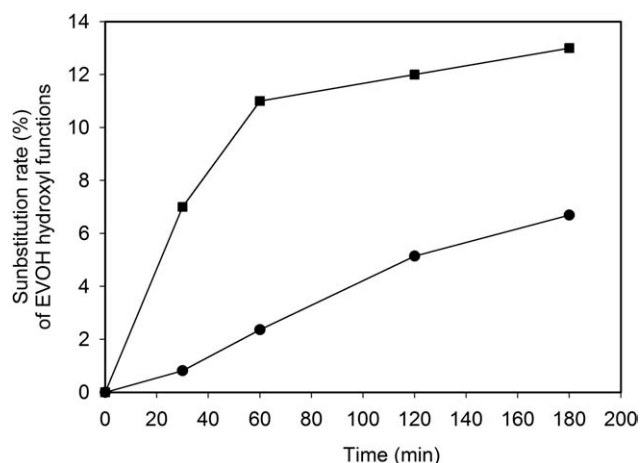
**Figure 6** <sup>1</sup>H-NMR in DMSO-d<sub>6</sub> spectrum of EVOH-g-PCL. Synthesis conditions: EVOH/PCL 1/1 mol/mol, catalyst = SnOct<sub>2</sub>, EVOH/SnOct<sub>2</sub> 1/0.01 mol/mol, temperature = 176°C, process = reactor.

present at 3.5 ppm and 4 ppm. The substitution rate is equal to:

$$SR = \frac{I_a \times 2}{I_{\alpha\alpha'} \times R}$$

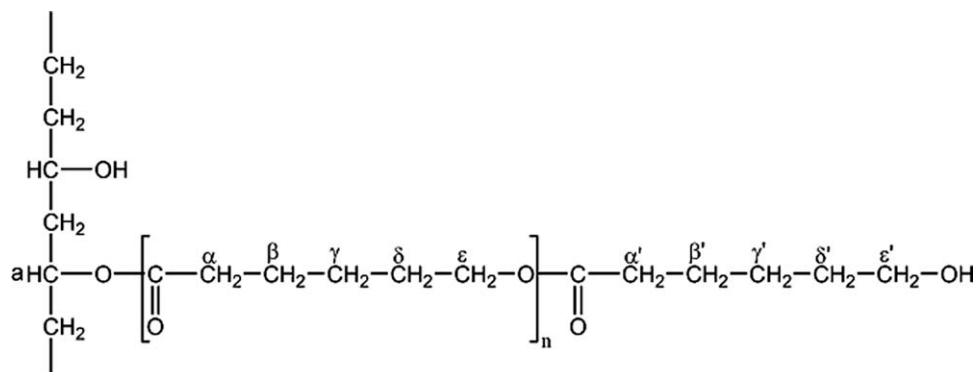
$I_a$  = integration corresponding to the methine proton of the EVOH ( $a$ ),  $I_{\alpha\alpha'}$  = integration corresponding to the methylene proton of the PCL ( $\alpha\alpha'$ ),  $R$  = the initial CL/OH ratio.

Substitution rates evolution with time are given in Figure 7 and Table V.



**Figure 7** Substitution rate (%) of alcoholysis reaction between EVOH and PCL with tin(II) bis(2-ethylhexanoate) (●) and 1.5.7-triazabicyclo [4.4.0]dec-5-ene (■) at  $t = 176^\circ\text{C}$ . [OH]/[Ester]/[catalyst] = 1/1/0.01 mol/mol/mol.

The evolution of the reactive system was observed too by DSC as shown in Table V and Figure 8. EVOH and PCL crystalline phases are present during the reaction first stages and decrease with the structure evolution leading progressively to grafts formation and comb structures. For the first 2 hours, the two crystalline phases are observed. For higher reaction times the crystalline phase of EVOH completely disappeared when around 5.5% of the EVOH methines are substituted, showing that the structural changes consecutive to grafts formation annealing chains organization in a crystalline structure. At 176°C and near 5.5% of substitution rate, the reactive system behavior totally changed, since before this fast transition, it was a viscous liquid and afterwards, became in a rubbery state, impossible to mix anymore. This rubbery state is kept above 250°C till an apparent thermal degradation. At room temperature, before this transition, the reactive system is a brittle material, very near to the pure PCL properties, and afterward the observed transition at 176°C, the rubbery state is also kept with possible crystallinity of the remaining PCL homopolymers



**Scheme 2** Chemical structure of EVOH-g-PCL.

**TABLE V**  
 $^1\text{H}$  NMR and Thermal Analysis Results for EVOH-g-PCL Copolymers Synthesized at 176°C and Different Reaction Times: 30, 60, 120, 180, 240, and 300 min

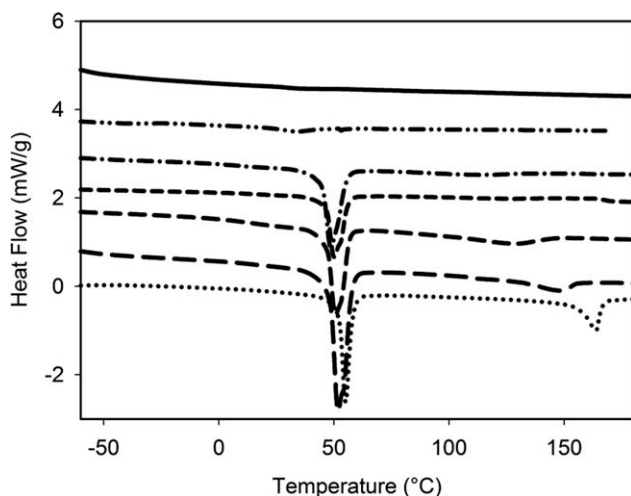
Catalyst	Reaction time (min)	EVOH substitution rate (%)	$T_m$ PCL (°C)	$\Delta H_{\text{PCL}}$ (J/g)	$T_m$ EVOH (°C)	$\Delta H_{\text{EVOH}}$ (J/g)	$T_{g1}$ (°C)
Tin (II) bis 2-ethylhexanoate	30	0.7	53	43.7	162	16.6	-52
	60	2.3	52	68.2	150	8.6	-53.4
	120	5.1	51	46.6	148	5.9	-57.3
	180	6.7	48.7	29.5	-	-	-48.6
	240	7.6	33.9	39.7	-	-	-62
	300	8	-	-	-	-	-56.1
1.5.7-triazabicyclo [4.4.0]dec-5-ene	30	6.9	53	8.05	122.5	2.4	24.5
	60	11.4	51	28.3	-	-	3.1
	120	14.7	51.2	30.3	-	-	-3.4

Ester function from PCL/OH function from EVOH/catalyst = 1/1/0.01 mol/mol/mol.

chains. This remaining PCL crystallinity disappeared later than the one of the substituted EVOH.

Reactions catalyzed by 1.5.7-triazabicyclo[4.4.0]dec-5-ene gave equivalent thermal properties compared with tin(II) bis(2-ethylhexanoate) at the same substitution rates, but since the reaction kinetic is faster when 1.5.7-triazabicyclo [4.4.0]dec-5-ene is used, the EVOH directly lose its crystallinity, because the substitution rate over passed 6% only after thirty minutes of reaction.

Even if the evolution of the reactive system was dramatic, still is that in the best cases the kinetics for polymer reactants are slower than those conducted on the small molar mass reactants. In case one supposes that the reaction is kinetically controlled, this difference of reactivity cannot only be a result of lower concentrations when polymers are used rather than small molecules. To examine the possibility of diffusion controlled reaction, SEM analysis of the reactive system were performed.

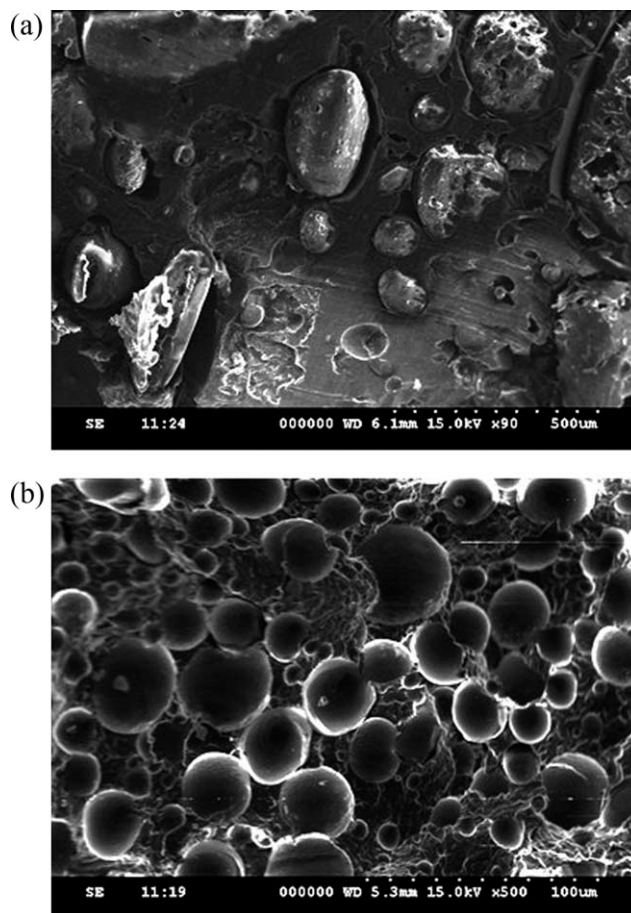


**Figure 8** EVOH-g-PCL thermograms of samples taken at different reaction time with tin(II) bis(2-ethylhexanoate) at 176°C. Second ramp at 10°C min<sup>-1</sup>.

### Morphological evolutions

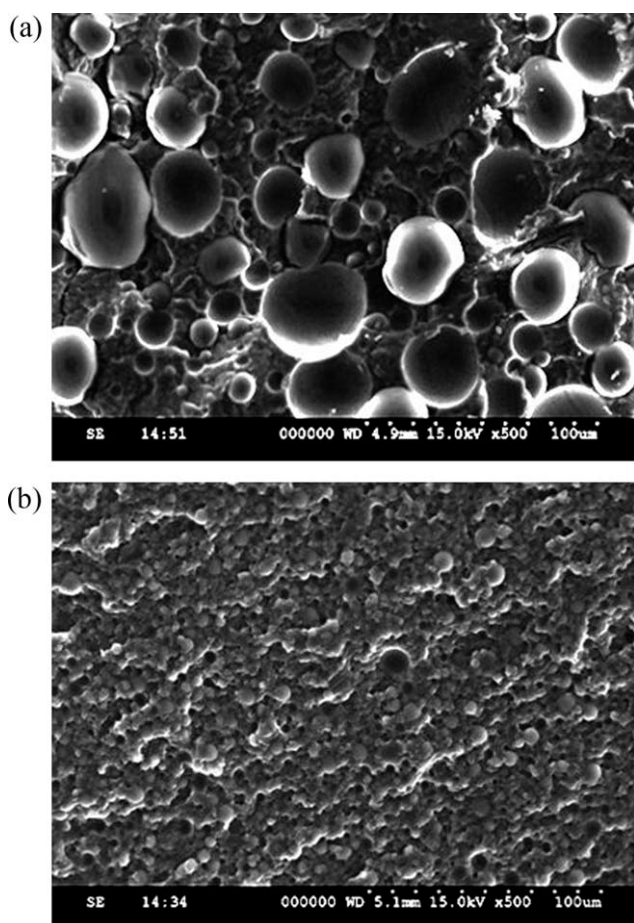
Figures 9 and 10 present the evolution of EVOH-g-PCL morphologies at different reaction times.

The size of particles decrease with increasing reaction time. When SnOct<sub>2</sub> was the catalyst, after 30 min of reaction the size of particles was 100 μm, it



**Figure 9** SEM photography of EVOH-g-PCL synthesized with tin (II) bis(2-ethylhexanoate) at different reaction time. (a) after 30 min of reaction (2.31% of substitution). (b) 120 min (5.16%).





**Figure 10** SEM photography of EVOH-g-PCL synthesized with 1.5.7-triazabicyclo [4.4.0]dec-5-ene at different reaction time. (a) after 30 min of reaction (6.9% of substitution). (b) 120 min (12.69%).

became 25  $\mu\text{m}$  after 120 min. In the case of TBD, the particle size was 20  $\mu\text{m}$  after 30 min of reaction, it became to 5  $\mu\text{m}$  obtained after 120 min.

At reaction beginning, a heterogeneous system is observed. Polymers being nonmiscible, the reaction is not kinetically controlled but diffusion controlled.<sup>22</sup> This explains the relative low molar mass model reagents. The size of the dispersed phase decreases gradually with time and these phases are not visible by SEM after 300H for  $\text{SnOct}_2$  and 180H for TBD catalyzed reaction. These morphological evolutions can be explained by the fact that the reactive system produces copolymer that acts as emulsifier leading to a decrease in the size of the dispersed<sup>28,29</sup> phase and auto acceleration of reactions.

## CONCLUSIONS

Reactions on model reagents showed that at the higher temperatures both organometallic and organic catalysts are efficient for alcoholysis exchange reactions. For longer reaction times,  $\text{SnOct}_2$  use

results in dramatic degradations. This effect was less important when TBD was used. At lower reaction temperature, all the used catalysts have equivalent effect on reaction kinetics except titanium oxide acetylacetonate and titanium 2-ethylhexanoate. Reactions on polymers were slower than those on model reagents. An emulsification effect of the formed copolymer on the reactive system morphology and kinetic was clearly established.

Next studies on these reactive systems will analyze the processing conditions effect on such heterogeneous system kinetics.

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