

## New Titanium-Based Catalysts for the Synthesis of Poly(ethylene terephthalate)

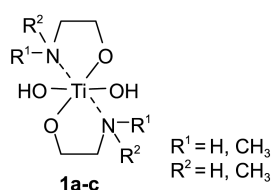
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Received June 21, 2012, Accepted July 7, 2012**Key Words** : Titanium catalyst, Antimony, Poly(ethylene terephthalate), Polycondensation, Esterification

Poly(ethylene terephthalate) (PET) is a polymer with relatively low cost and high performance, which is widely used in various applications such as bottles, textile fibers, films and engineering plastics for automobiles and electric industries.<sup>1</sup> Commercial catalysts used for synthesis of PET are in general antimony (Sb) compounds.<sup>2</sup> Antimony(III) oxide, antimony(III) acetate and antimony(III) glycolate are used as a catalyst in 95% of PET manufacturing industries worldwide.<sup>3</sup> The few organoantimony compounds that have been identified in environmental and biological samples are all in the form of methylated Sb-species.<sup>4</sup> The Sb trace element is extremely toxic to mammals, and interferes with embryonic and fetal development, also, carcinogenic to humans.<sup>5</sup> In addition to being found in drinking water, food packaging and soft-drink bottles.<sup>6</sup> According to the World Health Organization (WHO), Sb species concentration lower than 20 ppb are acceptable for drinking water.<sup>6b,7</sup> According to a recent study, in 14 brands of bottled water from Canada, Sb concentrations increased on average 19% during 6 months storage at room temperature, but 48 brands of water from 11 European countries increased on average 90% under identical conditions.<sup>8</sup> Therefore, a very important challenge for polyester catalysis is to come-up with a new Sb-free catalysts with low environmental impact.

Intensive efforts have been made to find other stable and more environmental friendly non-antimony catalysts, such as those based on titanium.<sup>9</sup> Titanium-based catalysts have been known for many years and actually are used for polybutylene terephthalate (PBT)<sup>10</sup> and polypropylene terephthalate (PPT)<sup>11</sup> production, however, polycondensation (PC) of PET manufacture is not well studied in literature.<sup>12</sup> To date, only few esterification processes have been applied for the synthesis of PET by titanium catalysts. Herein, we report an efficient synthesis characterization and polymerization of PET for a series of new nontoxic organotitanium catalyst.

Titanium metal has strong activity in polyesterification and forms stable complex with heteroatom-containing ligands

**Scheme 1.** Proposed structure of catalyst.

(Scheme 1). These properties of titanium have been used advantageously in simple methods of syntheses and production of inexpensive metal catalyst. The high activity and selectivity of titanium-containing catalysts, their good solubility, and the absence of acidic effluent, which causes corrosion, are the reasons why these catalysts are frequently used in industry.

It is expected that the oxygen and nitrogen atoms could stand as strong metal binders such as aminoethanol. To extend this chemistry, we synthesize new titanium species with ethanolamine, 2-(methylamino)ethanol and 2-(dimethylamino)ethanol as ligands. The starting materials were prepared by commercially available titanium(IV) chloride (TiCl<sub>4</sub>) and aminoethanol derivatives. These substrates were investigated under several different conditions in a 1:2 molar ratio in dichloromethane solution and the behavior of the titanium with aminoethanol complexes reactions were summarized in Table 1. Catalysts **1a-c** was synthesized from TiCl<sub>4</sub> with aminoethanol in an only one step procedure. Treatments of TiCl<sub>4</sub> with aminoethanol complexes reactions under low temperature conditions good yields produced compounds **1a** (92%), **1b** (95%) and **1c** (96%).

The titanium metal has coordinated by oxygen and nitrogen atoms such as aminoethanol molecules. The titanium complex **1a-c** was recrystallized several times, but no single

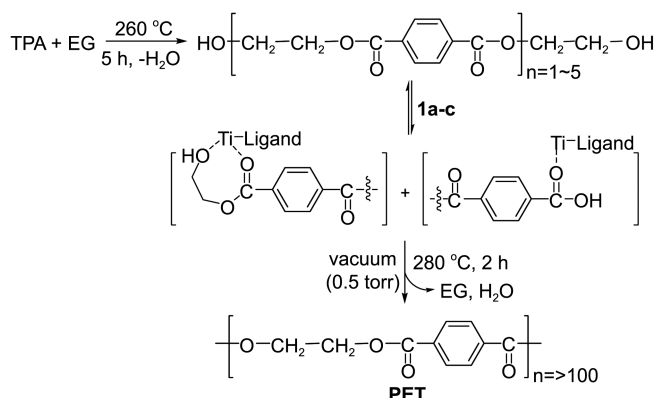
**Table 1.** Synthesis of **1a-c**<sup>a</sup>

$$\text{TiCl}_4 + \begin{array}{c} \text{R}^1 \\ | \\ \text{N} \\ | \\ \text{CH}_2\text{CH}_2\text{OH} \\ | \\ \text{R}^2 \end{array} \xrightarrow{\text{CH}_2\text{Cl}_2} \mathbf{1a-c}$$

a: R<sup>1</sup> = R<sup>2</sup> = H  
b: R<sup>1</sup> = H, R<sup>2</sup> = CH<sub>3</sub>  
c: R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>

| Entry | Catalyst  | Temp. (°C) <sup>b</sup> | Time (hr) <sup>b</sup> | Yield (%) <sup>c</sup> |
|-------|-----------|-------------------------|------------------------|------------------------|
| 1     | <b>1a</b> | 23                      | 2                      | 71                     |
| 2     | <b>1a</b> | 0                       | 1                      | 92                     |
| 3     | <b>1a</b> | -78                     | 3                      | 60                     |
| 4     | <b>1b</b> | 23                      | 2                      | 75                     |
| 5     | <b>1b</b> | 0                       | 2                      | 63                     |
| 6     | <b>1b</b> | -78                     | 1                      | 95                     |
| 7     | <b>1c</b> | 23                      | 3                      | 73                     |
| 8     | <b>1c</b> | 0                       | 1                      | 96                     |
| 9     | <b>1c</b> | -78                     | 2                      | 68                     |

<sup>a</sup>Conditions: TiCl<sub>4</sub> (1.0 equiv.); Ethanolamine (2.0 equiv.); 2-(Methylamino) ethanol (2.0 equiv.); 2-(Dimethylamino)ethanol (2.0 equiv.).  
<sup>b</sup>Reaction temperature and time. <sup>c</sup>Isolated yields by filtration, washing with CH<sub>2</sub>Cl<sub>2</sub> and hexane.

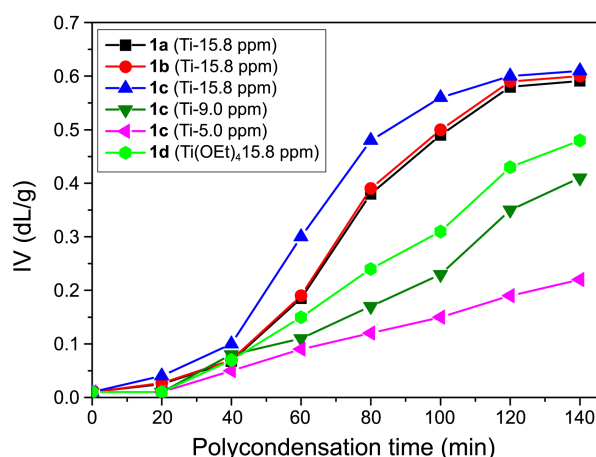


**Scheme 2.** Reactions for the preparation of PET.

crystal was obtained. However, their structural characters were established by NMR spectroscopy and elemental analyses. The NMR of **1a-c** shows the presence of only one pure compound. The stoichiometry of the reaction was ascertained from the ratio of  $^1\text{H}$  NMR. In comparison with the free aminoethanol derivatives,  $-\text{OCH}_2$  and  $-\text{NCH}_2$  proton and carbon peaks in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the complexes **1a-c** are shifted to the downfield, which is a consequence of the high Lewis acidity of titanium (see Supplementary data).  $^1\text{H}$  NMR analysis indicated that  $\text{H}_2\text{O}$ , function as strong hydrogen bonding to take care of the hydroxide ( $-\text{OH}$ ) protons.<sup>13</sup> Therefore, it can be tentatively suggested that **1a-c** exist most likely a titanium complex chelated by the two aminoethanol ligands, because the analytical calculation for the corresponding complexes and broad proton peak (10.47 ppm) in  $^1\text{H}$  NMR of **1c** presents it as a hydroxide group (see also Supplementary data).

The synthesis of PET involves two steps, the synthesis of oligomers and the polycondensation of oligomers to produce PET (Scheme 2). For the first step, a catalyst is not necessary because terephthalic acid (TPA) and ethylene glycol (EG) can undergo direct esterification under high temperature to form oligomers while water is distilled out of the reaction system. However, the PC of oligomers must be catalyzed if a technically useful polymer is to be obtained because the reaction without a catalyst is too slow and many side reactions do occur when the melt is heated at high temperatures for a long time.

Figure 1 illustrates plots of the intrinsic viscosities (I.V.) versus the PC time of PET catalyzed by the **1a-c** series samples and reaching an I.V. of about 0.6 dL/g.<sup>14</sup> The visible differences in the activities of the catalysts could be assigned to the elemental titanium contents. When the titanium amount of the fed catalyst **1c** is as low as 9.0 or 5.0 ppm, the polymerization process take a very long time, and the final products are mixtures oligomer and PET. As the amounts of catalyst **1c** increases, the rate of PC increases gradually. Especially, PC time of **1c** was shorter than those of **1a-b** and  $\text{Ti}(\text{OEt})_4$  (**1d**) under the same reaction conditions. In the case of catalysts **1a-c**, the obtained material had an I.V. around 0.6 dL/g over 120 min, therefore, a small amount **1c** catalyst was of used because of low catalytic activities as portrayed



**Figure 1.** Plots of the number-average intrinsic viscosities versus the polycondensation time of PET catalyzed by the titanium catalysts series.

**Table 2.** Synthesis and characteristics of PET resin

| Catalyst  | $T_m$<br>( $^{\circ}\text{C}$ ) <sup>a</sup> | Color <sup>b</sup> |       |      | C.E.G.<br>(mmol/kg) <sup>c</sup> | D.E.G. content<br>(wt %) <sup>d</sup> |
|-----------|--|--------------------|-------|------|----------------------------------|---------------------------------------|
|           |  | L                  | a     | b    |                                  |                                       |
| <b>1a</b> | 252  | 51.85              | -0.27 | 4.38 | 21.60                            | 3.67                                  |
| <b>1b</b> | 254  | 52.78              | -1.08 | 5.51 | 12.20                            | 4.00                                  |
| <b>1c</b> | 251  | 55.22              | -0.22 | 4.01 | 13.70                            | 3.63                                  |

<sup>a</sup> $T_m$  is the melting temperature. <sup>b</sup>According to Gielab scale, colors were determined employing a colorimeter SA-2000; the lightness of the color ( $L = 0$  yields black and  $L = 100$  indicates diffuse white, its position between red and green (a, negative values indicate green while position values indicate red), its position between yellow and blue (b, negative values indicate blue and position values indicate yellow). <sup>c</sup>C.E.G. is the acronym of carboxylic end group. They were determined according to the procedure reported in the experimental section. The accuracy of the method is  $\pm 0.002$  mmol/kg. <sup>d</sup>D.E.G. is the acronym of diethylene glycol. They were determined employing a spectrophotometer HP 6890. The accuracy of the method is  $\pm 0.001$  wt %.

in Figure 1.

The first sets of efforts were devoted to large scale synthesis of PET representatives in 20 L pilot plant. The characteristics of the synthesized polymer resin are summarized in Table 2. Comparing the obtained results, the catalyst **1c** showed a significant higher activity than **1a-b** for the PC stage. In fact, all the PET samples were very similar in terms of melting temperature, colors and diethylene glycol, but surprisingly carboxyl end group is significantly higher for the polymers synthesized in the presence of catalyst **1a**. Furthermore, it is noteworthy that the higher activity of the new catalysts **1a-c** gave the possibility to using small amounts of elemental titanium.

In summary, we have described the development of titanium catalysts series as new catalyst for the synthesis of PET. Our preliminary results showed the feasibility of the one step synthesis of titanium catalyst and high yield from commercially available titanium(IV) chloride and aminoethanol derivatives. A series of polyethylene terephthalate have been synthesized using TPA and EG in presence of titanium catalysts. The use of titanium catalyst has the major advantage to be effective in PC step. Also, new titanium

catalysts have high activity for manufacture of PET in a 20 L pilot plant running under a general reaction conditions. Furthermore, this catalyst is readily available at reasonable cost and does not contribute to environmental pollution problems.

### Experimental Section

**Typical Procedure for the Synthesis of 1c.** To a solution of 2-(dimethylamino)ethanol (1.5 mL, 14.90 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added dropwise into a titanium(IV) chloride 1.0 M solution in CH<sub>2</sub>Cl<sub>2</sub> (7.0 mL, 7.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and then was added with water (0.144 g, 8.0 mmol). After 1 h, the volume was reduced to 15 mL, and the white precipitate was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL) and hexane (2 × 10 mL) and dried under vacuum to give 1.73 g (6.70 mmol, 96%) of compound **1c** as a white solid.

**Compound 1c:** mp 89-91 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.47 (br, 2H), 3.70 (t, *J* = 5.20 Hz, 4H), 3.09 (t, *J* = 5.36 Hz, 4H), 2.73 (s, 12H); <sup>13</sup>C NMR (100.6 MHz, DMSO-*d*<sub>6</sub>) δ 58.37, 55.32, 42.43; IR (KBr, film) 3279, 3021, 2970, 2708, 1465, 1387, 1074 cm<sup>-1</sup>; Anal. Calc. for C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>Ti: C 37.22, H 8.59, N 10.85%; Found: C 37.13, H 8.51, N 10.61%.

**Typical Procedure for the Synthesis of Poly(ethylene terephthalate) in Pilot Plant.** To a solution of terephthalic acid (14.0 kg, 84.27 mol) in monoethylene glycol (6.42 kg, 105.75 mol) were introduced into the 20 L reactor. The mixture was heated at 150 °C under stirring at atmospheric pressure. Then the temperature was raised to 260 °C. During this period, esterification proceeded till the complete distillation of H<sub>2</sub>O for 4-5 h. On completion of the esterification reaction the contents of the reactor were transferred to a stirred autoclave. Catalyst **1c** (1.473 g, 5.71 mmol), cobalt acetate (1.729 g, 9.77 mmol) and triethyl phosphate (2.421 g, 13.29 mmol) were added and the mixture heated to 280 ± 2 °C under vacuum to remove ethylene glycol. Then, the reactor was pressurized at 0.5 torr for 1 h. The synthesis was monitored with an electronic torque meter and the reaction was stopped at an I.V. in the range of 0.620-0.625 dL/g and molecular weight was 16,000-22,000 g/mol. Finally, chip-type melting materials were obtained (yield: 95%). ATR-IR: 2958, 2922, 1711, 1238, 1089, 1015 cm<sup>-1</sup>.

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- The facts that the disappearance of -OH protons in <sup>1</sup>H NMR titration spectra suggest that the equilibrium between catalyst **1c** and the H<sub>2</sub>O causes -OH/H<sub>2</sub>O hydrogen bonding system.
- The intrinsic viscosity that was reached 0.6 dL/g (the corresponding molecular weight was 15,000-22,000 g/mol).