

## Supporting Information

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

Young-Keun Yang,\* Seung-Woong Yoon, Yong-Taek Hwang, and Bo-Geun Song

Catalyst Research 5<sup>th</sup> Team, Honam Petrochemical Corporation, Daejeon 305-726, Korea. \*E-mail: ykyang@lottechem.com  
Received June 21, 2012, Accepted July 7, 2012

#### Reagents, General Methods and Analysis

**General Synthetic Materials and Methods:** All the syntheses were performed under a nitrogen atmosphere by using standard Schlenk techniques. Titanium(IV) chloride 1.0 M in dichloromethane, Titanium(IV) chloride 1.0 M in toluene, TiCl<sub>4</sub>, ethanolamine, 2-(methylamino)ethanol and 2-(dimethylamino)ethanol were obtained from Aldrich and used without purification. All reagents and solvents for reactions were used as received with the following exceptions. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled over calcium hydride (CaH<sub>2</sub>) for weeks before use. All other chemicals used were purchased from Sigma-Aldrich and were used as received.

**Spectroscopic Materials and Methods:** DMSO-*d*<sub>6</sub> was obtained from Cambridge Isotope Laboratories and stored over activated molecular sieves (4 Å). Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-*d*<sub>6</sub> unless otherwise stated, with tetramethylsilane (TMS) as internal reference at ambient temperature, mainly on a Bruker Avance II-400 Fourier Transform Spectrometer operating at 400 MHz for <sup>1</sup>H and at 100.6 MHz for <sup>13</sup>C. *J* values were given in Hz. Elemental analyzer was recorded on an EA1110. Melting points were measured on a Z289078 (Sigma-Aldrich) microscope and were uncorrected. Infrared absorption spectra were recorded as solid forms on a Nicolet iN10MX spectrophotometer.

**Characterization and Analysis:** Color *L*, *a* and *b* according to Cielab scale, were determined on the pellets using a colorimeter SA-2000. The intrinsic viscosity (I.V.) of all the samples were measured at 25 ± 0.1 °C in a SKYVIS 4000 viscometer with a 50/50 w/w mixture of phenol and 1,1,2,2-tetrachloroethane as the solvent. The molecular weights of the PET samples were calculated according to the formula mentioned in the literature.<sup>1</sup> The carboxyl end group (C.E.G.) content ([COOH]) was measured by titration according to the methods reported in the literature.<sup>2</sup> In a nitrogen atmosphere, about 0.3 g of the PET material was dissolved in 10 mL of benzyl alcohol under heating and titrated with a 0.01 mol/L KOH/EG solution with phenol red as an indicator. The titrations were carried out at a temperature higher than 100 °C to avoid the precipitation of

the polymer, and blank runs were carried out for correction. The test was repeated three times to get an average value. The diethylene glycol (D.E.G.) contents of the samples were examined on an Agilent (Berkshire, UK) 6890N gas chromatograph and the chroma *L* and *b* values were obtained with a HP 6890 spectrophotometer.

#### Synthesis of Complexes as a Catalysts 1a-b

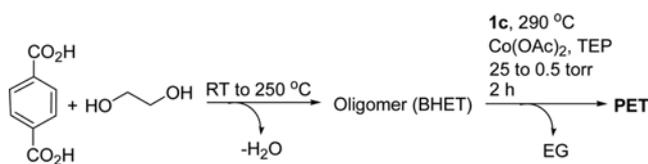
To a solution of aminoethanol (1 mL, 16.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added dropwise into a titanium(IV) chloride 1.0 M solution in CH<sub>2</sub>Cl<sub>2</sub> (8.1 mL, 8.10 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and then was added with water (0.144 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 1.51 g (7.47 mmol, 92%) of compound **1a** as a white solid.

**Compound 1a:** mp 70-72 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.10 (br, 4H), 3.57 (t, *J* = 5.32 Hz, 4H), 2.81 (t, *J* = 5.56 Hz, 4H); <sup>13</sup>C NMR (100.6 MHz, DMSO-*d*<sub>6</sub>) δ 58.15, 41.95; IR (KBr, film) 3256, 3030, 1625, 1495, 1068, 1000 cm<sup>-1</sup>; Anal. Calc. for C<sub>4</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>Ti: C 23.78, H 6.98, N 13.87%; Found: C 23.61, H 7.10, N 13.55%.

To a solution of 2-(methylamino)ethanol (2 mL, 26.64 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added dropwise into a titanium(IV) chloride 1.0 M solution in CH<sub>2</sub>Cl<sub>2</sub> (13.3 mL, 13.3 mmol) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C and then was added with water (0.144 g, 8.0 mmol). After 50 min, the reaction mixture was warmed to room temperature and stirred for 10 min. The volume was reduced to 25 mL, and the white precipitate was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 15 mL) and hexane (2 × 14 mL) and dried under vacuum to give 2.9 g (12.60 mmol, 95%) of compound **1b** as a white solid.

**Compound 1b:** mp 81-83 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.00 (br, 2H), 3.63 (t, *J* = 5.60 Hz, 4H), 2.94-2.88 (m, 4H), 2.49 (s, 6H); <sup>13</sup>C NMR (100.6 MHz, DMSO-*d*<sub>6</sub>) δ 60.29, 51.99, 34.64; IR (KBr, film) 3007, 2791, 1585, 1456, 1074, 1023 cm<sup>-1</sup>; Anal. Calc. for C<sub>6</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>Ti: C 31.32, H 7.89, N 12.18%; Found: C 31.21, H 7.68, N 12.11%.

### Synthesis of Poly(ethylene terephthalate) in Pilot Plant<sup>3</sup>



In a typical synthesis, 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 **1a** (1.154 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 0.61-0.62 dL/g and molecular weight was 15,000-21,000 g/mol. Finally, chip-type melting materials were obtained (yield: 95%).

The other polyesterifications were prepared by a similar procedure in pilot plant reaction.

### References

- Conix, A. *Makromol. Chem.* **1958**, 26, 226.
- (a) Berti, C.; Bonora, V.; Colonna, M.; Lotti, N.; Sisti, L. *Eur. Polym. J.* **2003**, 39, 1595. (b) Pilati, F.; Toselli, M.; Messori, M.; Manzoni, C.; Turturo, A.; Gattiglia, E. G. *Polymer* **1997**, 38, 4469.
- Ridland, J.; Hepplewhite, I. W.; Jolly, B. S. *Esterification Process*; EP 0,812,818, 1997.

### Synthesis of Bis(2-hydroxyethyl) terephthalate (BHET) with Catalyst **1c**



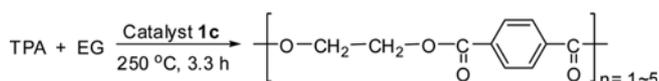
**Catalyst 1a**  
Elemental titanium contents (15.8 ppm)  
Intrinsic viscosity (IV): 0.621  
Color L: 51.85  
Color a: -0.27  
Color b: 4.38



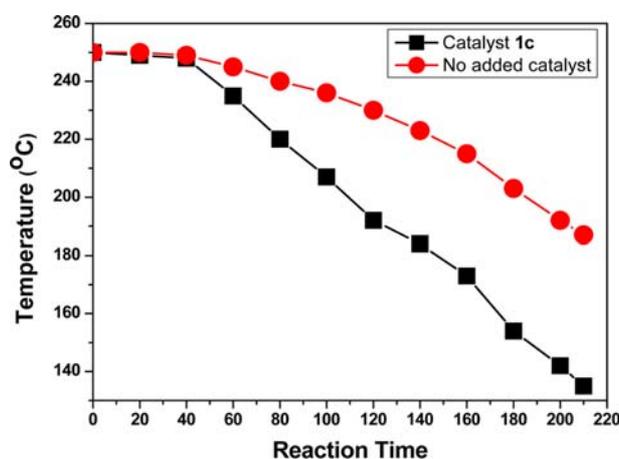
**Catalyst 1b**  
Elemental titanium contents (15.8 ppm)  
Intrinsic viscosity (IV): 0.621  
Color L: 52.78  
Color a: -1.08  
Color b: 5.51



**Catalyst 1c**  
Elemental titanium contents (15.8 ppm)  
Intrinsic viscosity (IV): 0.622  
Color L: 55.22  
Color a: -0.22  
Color b: 4.01

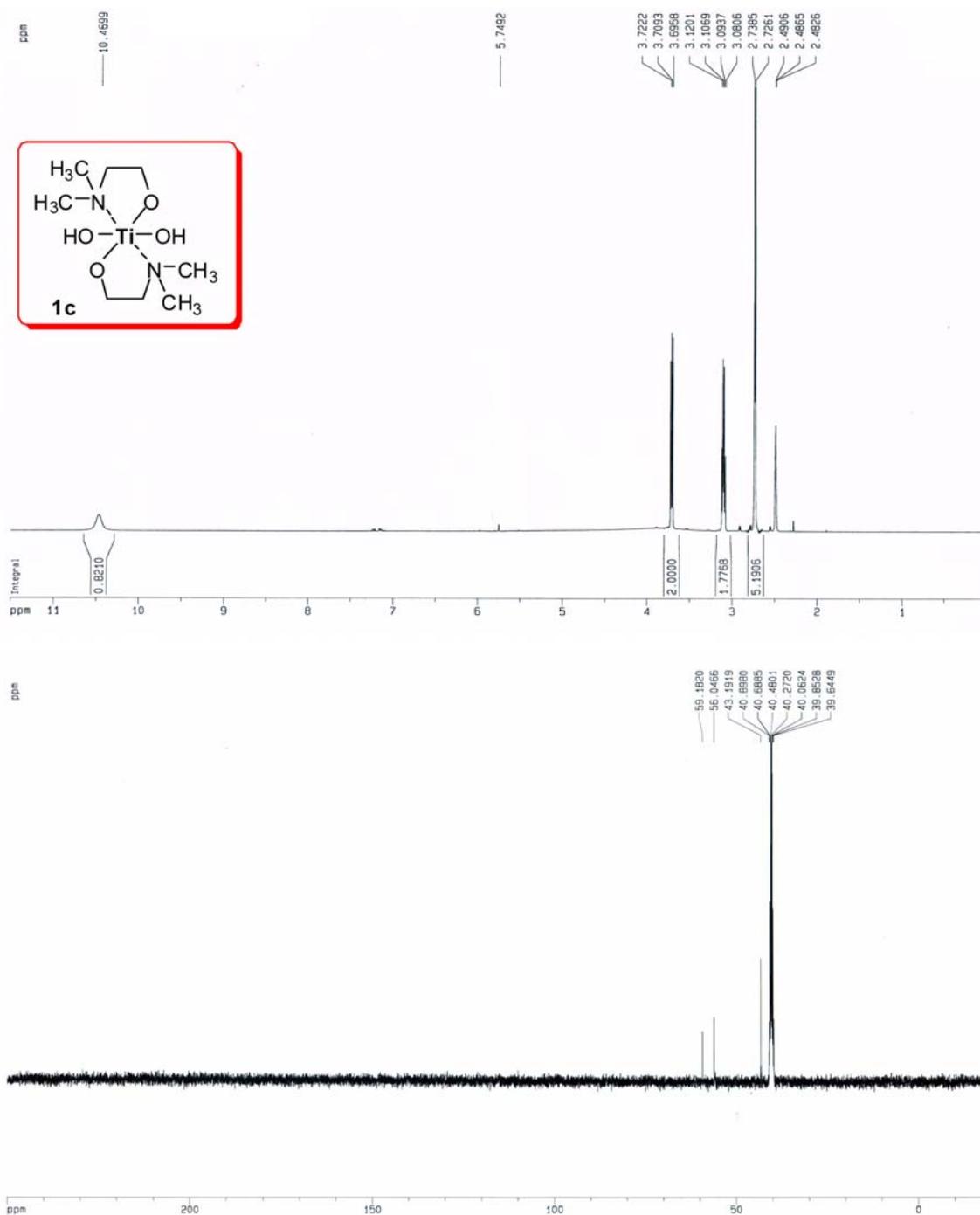


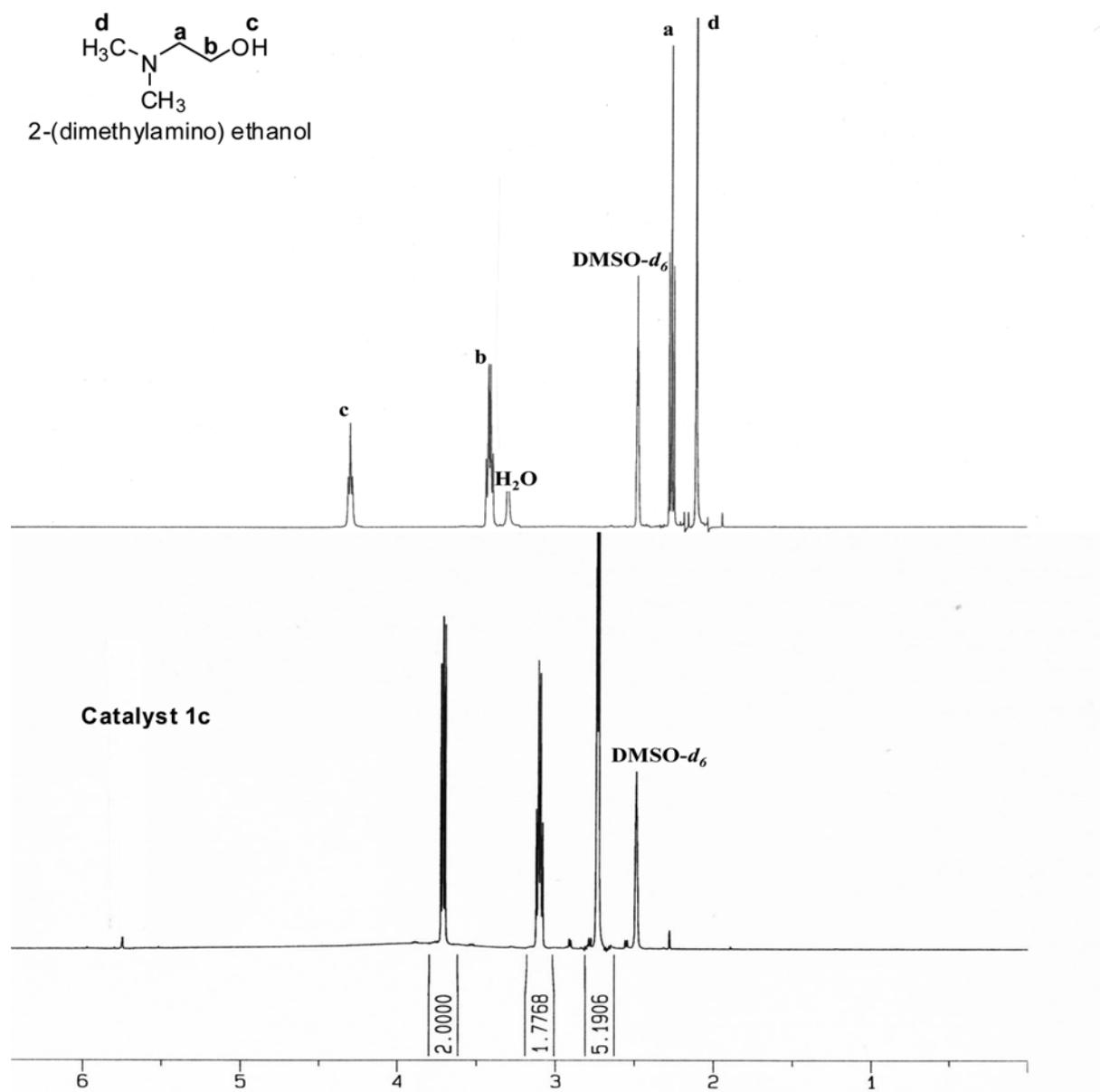
In a typical synthesis, to a solution of terephthalic acid (7.0 kg, 42.135 mol) in monoethylene glycol (3.21 kg, 52.875 mol) were introduced into the 7 L reactor. The mixture was heated at 150 °C under stirring at atmospheric pressure. Then the temperature was raised to 260 °C. During this period, esterification proceeded till the complete distillation of H<sub>2</sub>O for 3.3 h, dried under vacuum to give compound bis(2-hydroxyethyl) terephthalate (BHET, oligomer) as a white solid.



Plots of the internal reaction temperature versus esterification time for the reaction by the catalyst **1c** with no added catalyst. The temperature at 135 °C is complete esterification reaction.

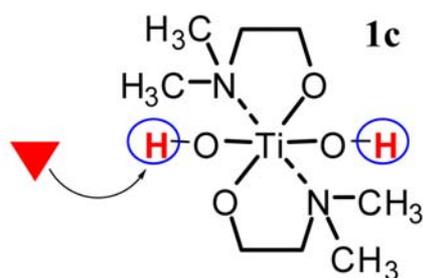
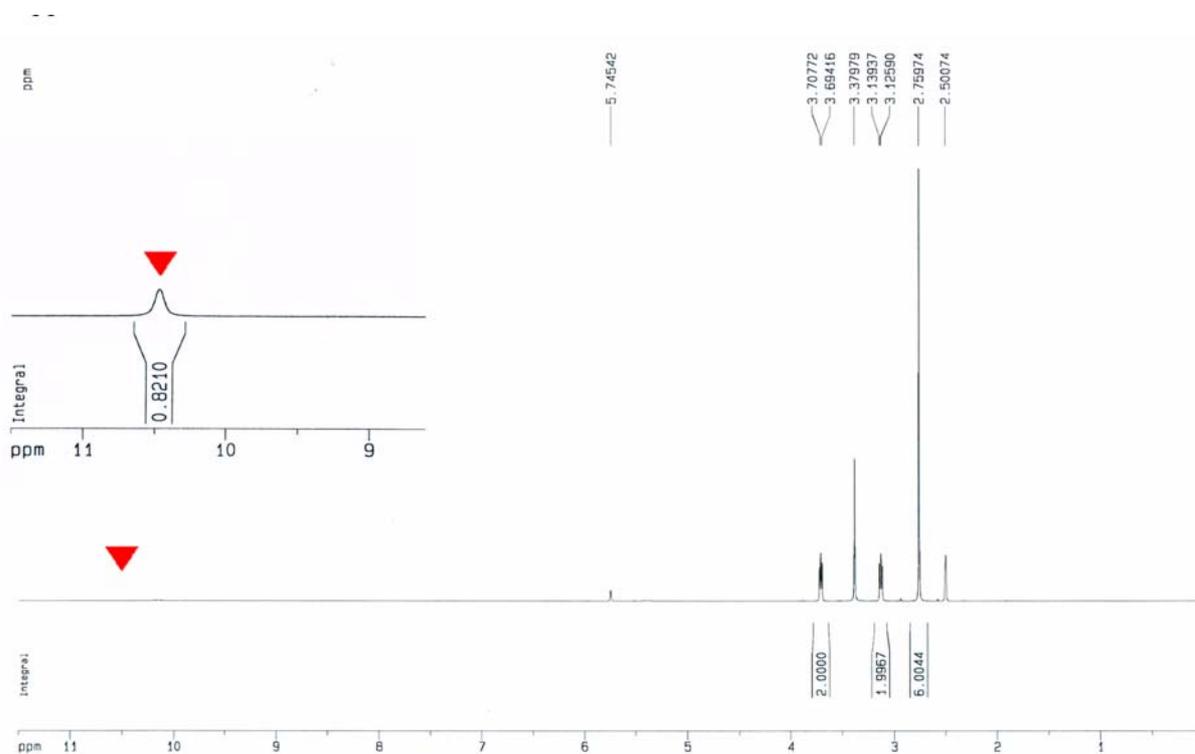
### Synthesis and Characteristics of PET Resin

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra of 1c

Compared 1c with 2-(dimethylamino)ethanol chemical shifted for  $^1\text{H}$  NMR

**$^1\text{H}$  NMR spectra of **1c** with  $\text{H}_2\text{O}$** 

$^1\text{H}$  NMR was performed with a  $\text{DMSO-}d_6$  solution of **1c** (0.014 M) and a  $\text{DMSO-}d_6$  solution of  $\text{H}_2\text{O}$  (0.140 M). The  $\text{H}_2\text{O}$  solution was introduced in portion (80 mL; 40 mL corresponds to 1.0 equiv.) and, after addition, the solution was maintained for 5 min at 25 °C. Hydroxide proton ( $\blacktriangledown$ ) disappeared.



IR spectra of **1c**