Supplementary information for:

Kinetic Studies on Lewis Acidic Metal Polyesterification Catalysts - Hydrolytic degradation is a Key Factor for Catalytic Performance

Lukas A. Wolzak [a,c], Rogier van Gemert [b], Keimpe J. van den Berg [b], Joost N. H. Reek [c]*, Moniek Tromp [a,d]*, Ties J. Korstanje [a]*

* Corresponding authors: t.j.korstanje@uva.nl; moniek.tromp@rug.nl; j.n.h.reek@uva.nl

Table of contents

Materials and Methods

General

Chemicals were obtained from Merck or Acros Organics and were used without further purification. For experiments with an azeotropic reflux, xylene (mixture of isomers) 99% ACS with b.p. 136 – 140 °C was applied. Titanium(triethanolaminato)acetate was synthesized following a reported procedure.[1] Acid values (AV) were determined via titration, with samples dissolved in a 1:1 mixture of xylene/ethanol, and titrated with a 0.1 M KOH in MeOH solution on a Metrohm 716 DMS Titrino station. The AV is proportional to the carboxylic acid concentration and is defined as milligrams of potassium hydroxide (KOH) required to neutralize one gram of sample. The AV (in mg KOH g^{-1}) was calculated via the formula:

$$\mathrm{AV} = \frac{5.611 * \mathrm{V}}{\mathrm{m}}$$

where V is the required volume (in mL) of a 0.1 M KOH solution and m the mass of the sample (in g). *In-situ* infrared spectra were collected with a Mettler Toledo ReactIR 15 equipped with an air-cooled Art Photonics FlexiSpec® diamond *in-situ* FTIR-ATR probe for harsh conditions. Conversion was followed by the peak height of the $\nu_{c=o}$ of the carboxylic acid (1712 cm^{-1}) with a two point baseline from 1790 to 1630 cm^{-1}. Water concentrations measurements were performed on a Metrohm 831 KF coulometer without diaphragm. Polyester hydrolysis experiments were conducted in a 1 L autoclave (in-house built) equipped with an overhead stirrer, a thermocouple and a heating mantle controlled by a Parr 4848 reaction controller.

Neat polyesterification

Polyesterification of 1,6-hexanediol and adipic acid

In a 1 L four-necked round bottom flask, equipped with an overhead stirrer and thermocouple, 1,6-hexanediol (327.77 g, 2.77 mol) and adipic acid (322.22 g, 2.20 mol) were heated to 170 °C while the stirring speed was slowly increased to 200 rpm. Water formed during polyesterification was collected in an empty Dean-Stark receiver via evaporation. After 1 h reaction time at 170 °C, catalyst (5.5 mmol, 0.1 mol% relative to -OH groups) was added (over a time period of 1 min. in small fractions as powder or liquid) to the reaction mixture and samples for acid value determination were taken every 30 minutes.

Polyesterification of oligomers of 1,6-hexanediol and adipic acid

In a 1 L four-necked round bottom flask, equipped with an overhead stirrer and thermocouple, oligomers (650.00 g, AV = 105 mg KOH g^{-1}) of 1,6-hexanediol (1.26 eq) and adipic acid (1.0 eq) and catalyst (5.5 mmol, 0.1 mol% relative to -OH groups) were heated to 170 °C while the stirring speed was slowly increased to 200 rpm. Water formed during polyesterification was collected in an empty Dean-Stark receiver via evaporation. Samples for acid value determination were taken every 30 minutes.

Polyesterification of oligomers of 1,6-hexanediol and Pripol 1009

In a 1 L four-necked round bottom flask, equipped with an overhead stirrer and thermocouple, oligomers (589.94 g, AV = 60 mg KOH g^{-1}) of 1,6-hexanediol (1.47 eq) and Pripol 1009 (1.0 eq) and catalyst (2 mmol, 0.2 mol% relative to -OH groups) were heated to 170 ^{o}C while the stirring speed was slowly increased to 200 rpm. Water formed during polyesterification was collected in an empty Dean-Stark receiver. Samples for acid value determination were taken every 30 minutes.

Azeotropic polyesterification

Polyesterification of 1,6-hexanediol and adipic acid

In a 250 mL five-necked round bottom flask, equipped with an overhead stirrer, thermocouple and *in-situ* ATR-IR probe, 1,6-hexanediol (49.62 g, 0.42 mol), adipic acid (48.71, 0.33 mol) and xylene (80 mL) were heated to 140 ^{o}C or 150 ^{o}C while the stirring speed was slowly increased to 285 rpm. When the reaction mixture reached 130 ^{o}C, catalyst (2.1 mmol, 0.25 mol% relative to -OH groups) was added (catalyst was suspended or dissolved in 2 mL xylene and supplied over a time period of 1 min.) and the ATR-IR measurement was started (5 minutes waiting time, 250 spectra averaged). Water formed during polyesterification was collected in a pre-filled (10 mL of xylene) Dean-Stark receiver.

Hydrolysis of polyester

A 1 L autoclave, equipped with an overhead stirrer and thermocouple, was charged with polyester (250 g, AV = 24.6 mg KOH g^{-1}) of 1,6-hexanediol (1.26 eq) and adipic acid (1.0 eq), water (50 mL) and catalyst (2.11 mmol). The reaction temperature was set at 150 ^{o}C and the stirring speed at 250 rpm. After 2 h at 150 ^{o}C the temperature was decreased to 25 ^{o}C and a sample for acid value determination was taken.

Figure S1. (A) Reaction set-up for neat polyesterification. (B) Reaction set-up for azeotropic polyesterification and in-situ FTIR-ATR.

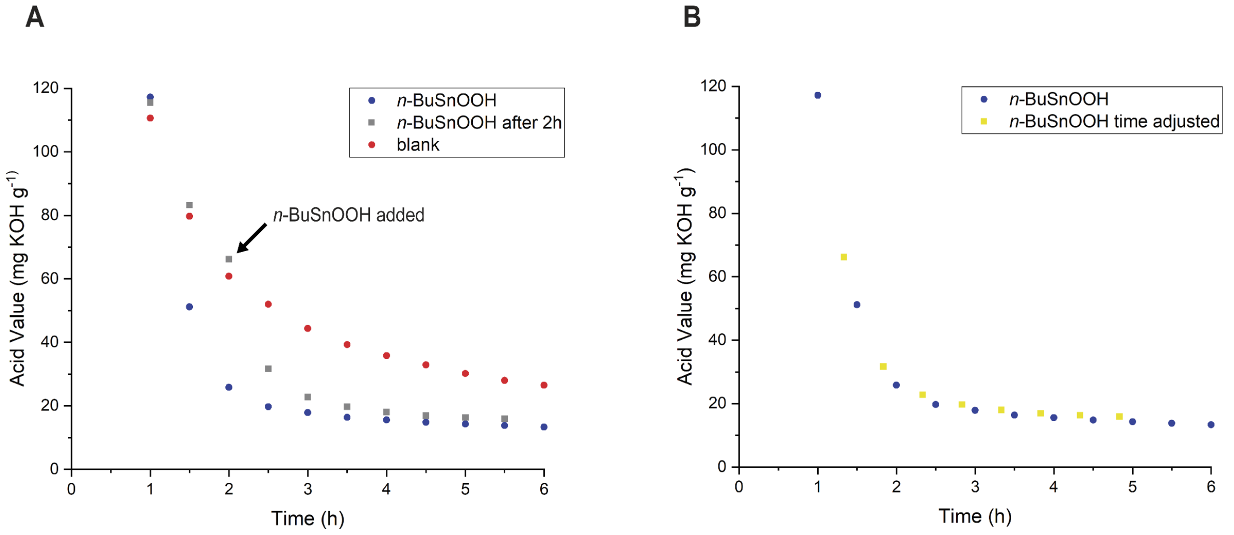
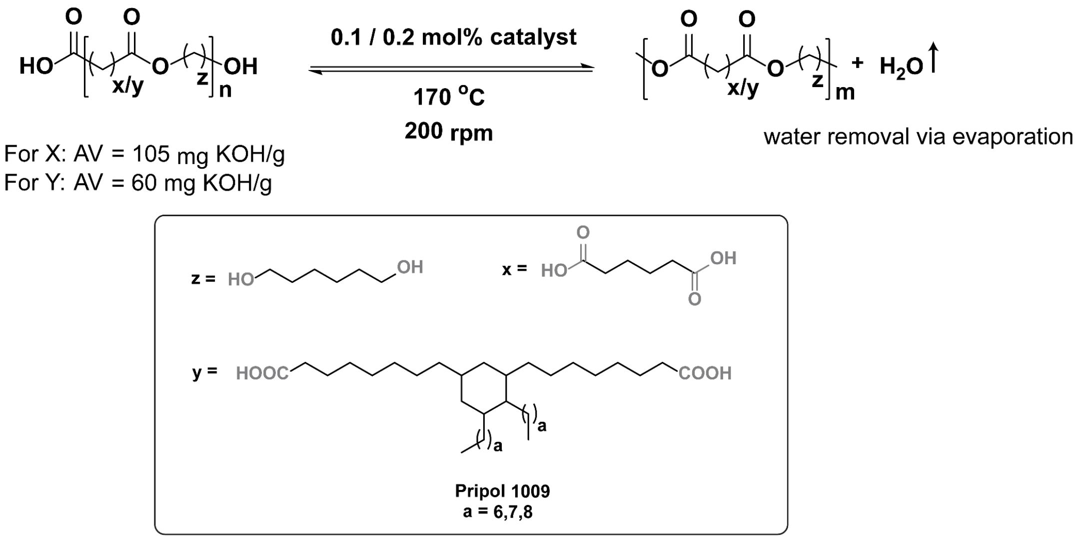


Figure S2. (A) Polyesterification of 1,6-hexanediol and adipic acid in the presence of 0.1 mol% *n*-BuSnOOH (on -OH groups) at 170 °C with *n*-BuSnOOH added after 1 h (blue trace), 2 h (grey trace) and blank (red). (B) Time adjusted kinetic profile (yellow trace).

Neat polyesterification



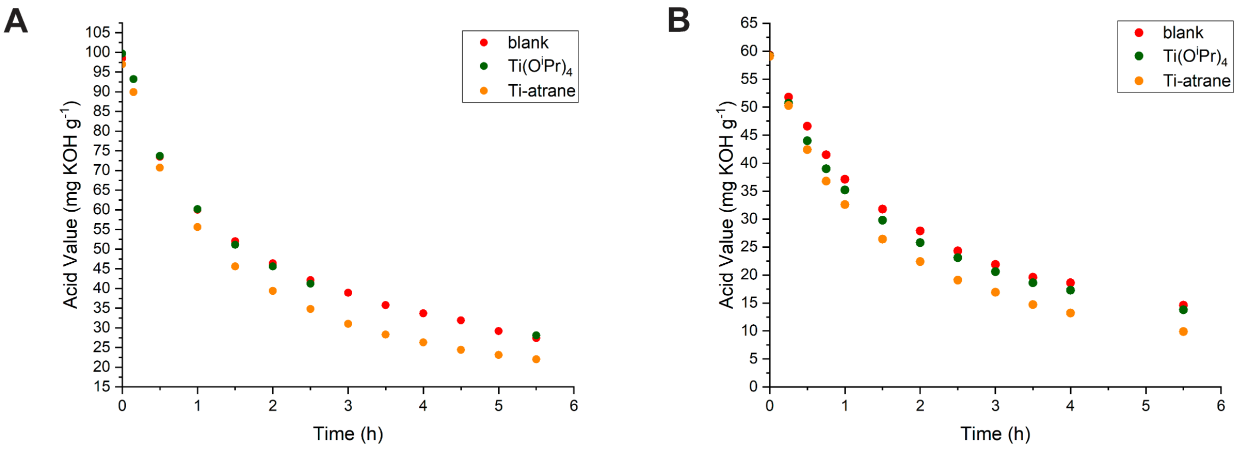
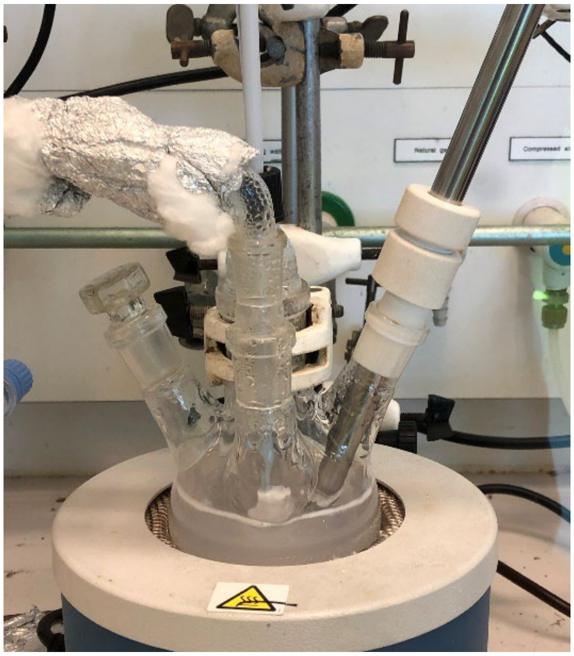


Figure S3. (A) Polyesterification of oligomers (AV = 105 mg KOH g^{-1}) of 1,6-hexanediol and adipic acid in the presence of 0.1 mol% catalyst (relative to -OH groups) at 170 °C. (B) Polyesterification of oligomers (AV = 60 mg KOH g^{-1}) of 1,6-hexanediol and Pripol 1009 in the presence of 0.2 mol% catalyst (relative to -OH groups) at 170 °C

Table S1. Water concentrations of neat polyesterification reactions.

Entry[a]		H_2O concentration (ppm) Polyesterification of 1,6-hexanediol and adipic acid	H_2O concentration (ppm) Polyesterification of oligomers of 1,6-hexanediol and Pripol 1009
1	blank	15077	5320
2	Ti(O^{i}Pr)$_4$	8378	4308
3	*n*-BuSnOOH	1527	-
4	Ti-atrane	5523	3870

[a] Water concentrations of the reaction mixture after 6 h reaction time.



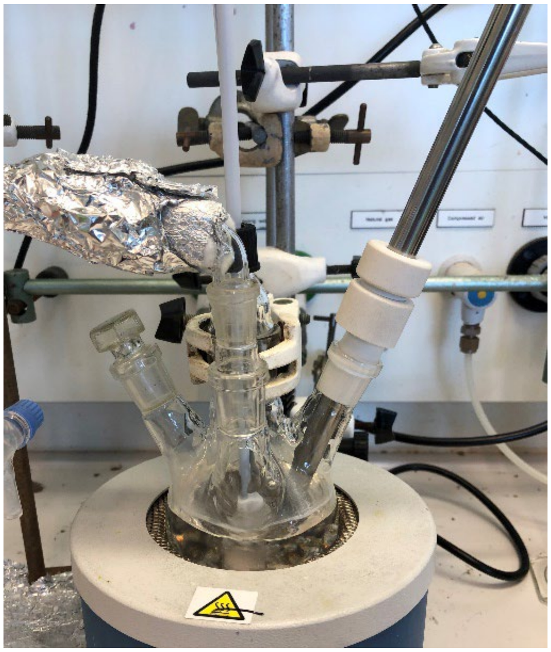


Table S2. Water concentrations of azeotropic polyesterification reactions

Entry[a]		H_2O concentration (ppm) Polyesterification of 1,6-hexanediol and adipic acid at 140 °C	H_2O concentration (ppm) Polyesterification of 1,6-hexanediol and adipic acid at 150 °C
1	blank	4669	1866
2	$Ti(O^iPr)_4$	4382	523
3	*n*-BuSnOOH	3772	514
4	Ti-atrane	2286; 2690[b]	158
5	$Zr(O^iPr)_4$-^iPrOH	-	293

[a] Water concentrations of the reaction mixture after 6 h reaction time. [b] Duplo experiment.

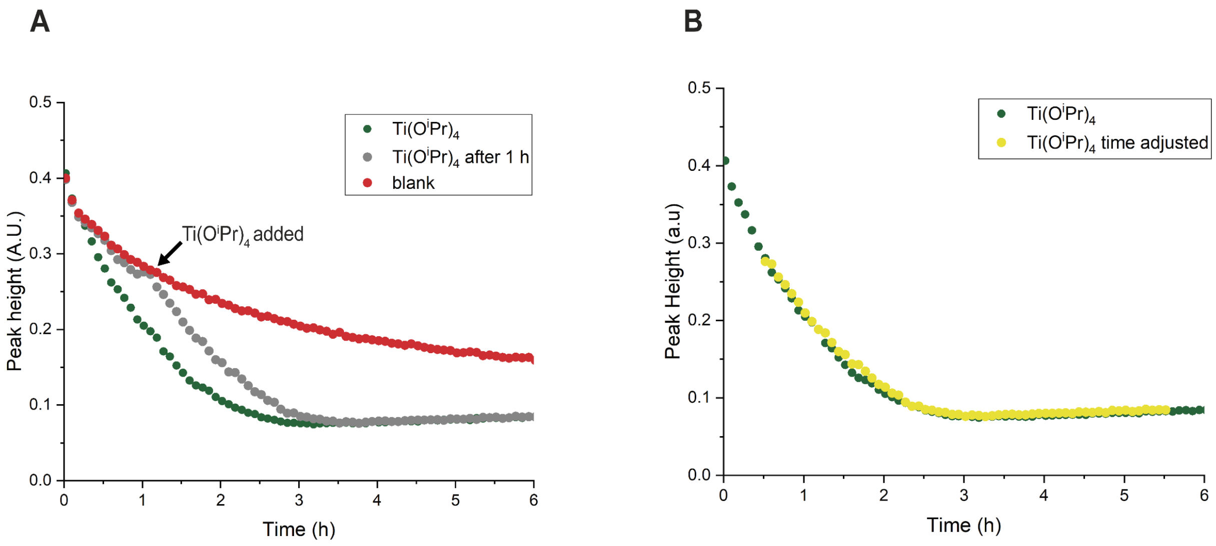


Figure S5. Kinetic profile of polyesterification of 1,6-hexanediol and adipic acid in the presence of 0.25 mol% Ti(O^{i}Pr)$_4$ (relative to -OH groups) at 150 °C (green trace) and Ti(O^{i}Pr)$_4$ added after 1 h (grey trace). (B) Time adjusted kinetic profile (yellow trace). Peak height at 1712 cm^{-1} ($\nu_{c=o}$ vibration of the carboxylic acid).

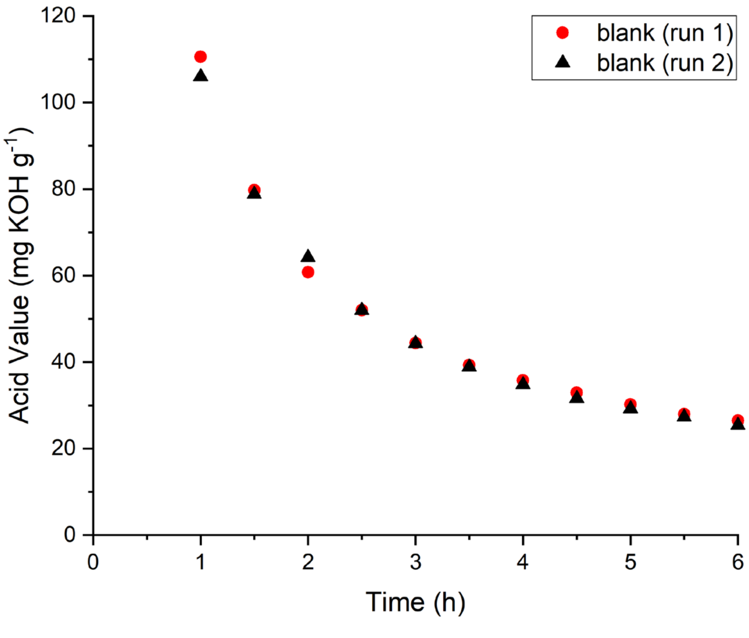


Figure S6. Reproducibility of polyesterification of reaction of 1,6-hexanediol and adipic acid of blank reaction (in the absence of a Lewis acidic metal catalyst) at 170 °C.

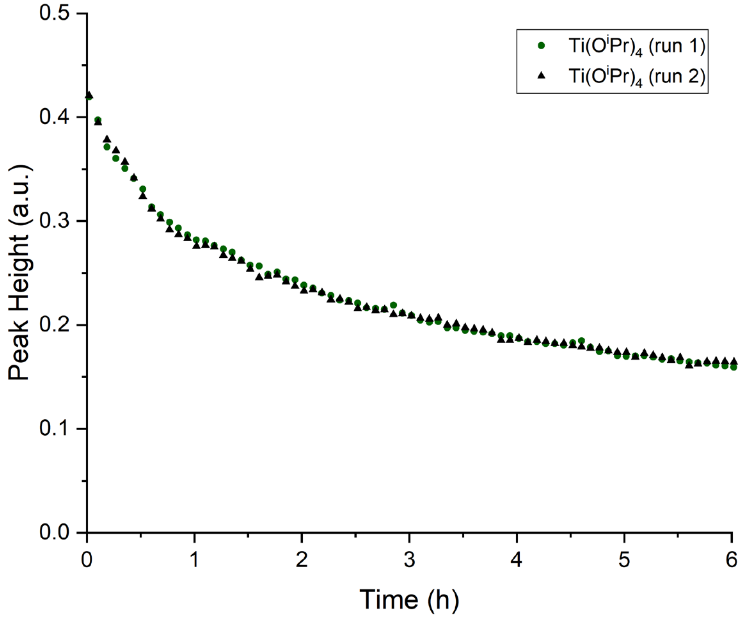


Figure S7. Reproducibility of polyesterification reaction of 1,6-hexanediol and adipic acid in the presence of 0.25 mol% $Ti(O^iPr)_4$ (relative to -OH groups) with xylene at 140 °C. Peak height at 1712 cm^{-1} ($\nu_{c=o}$ vibration of the carboxylic acid).

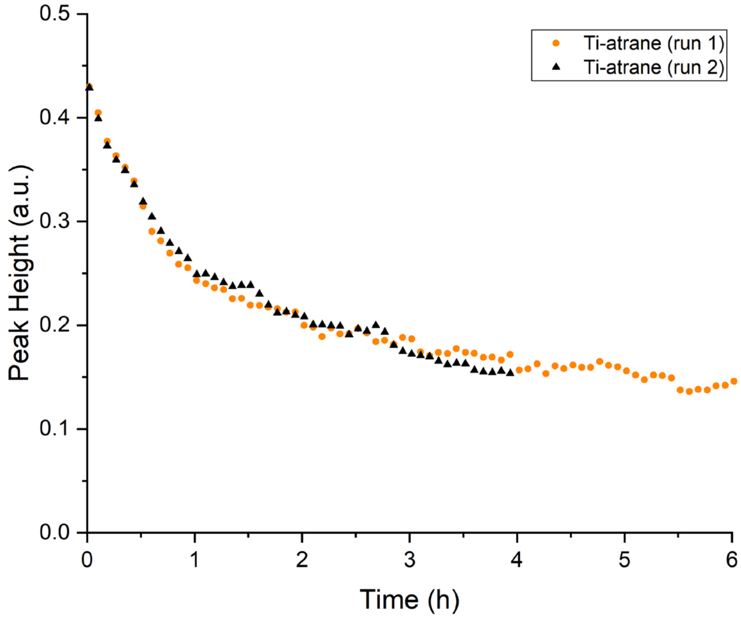


Figure S8. Reproducibility of polyesterification reaction of 1,6-hexanediol and adipic acid in the presence of 0.25 mol% Ti-atrane complex (relative to -OH groups) with xylene at 140 °C. Peak height at 1712 cm^{-1} ($\nu_{c=o}$ vibration of the carboxylic acid).

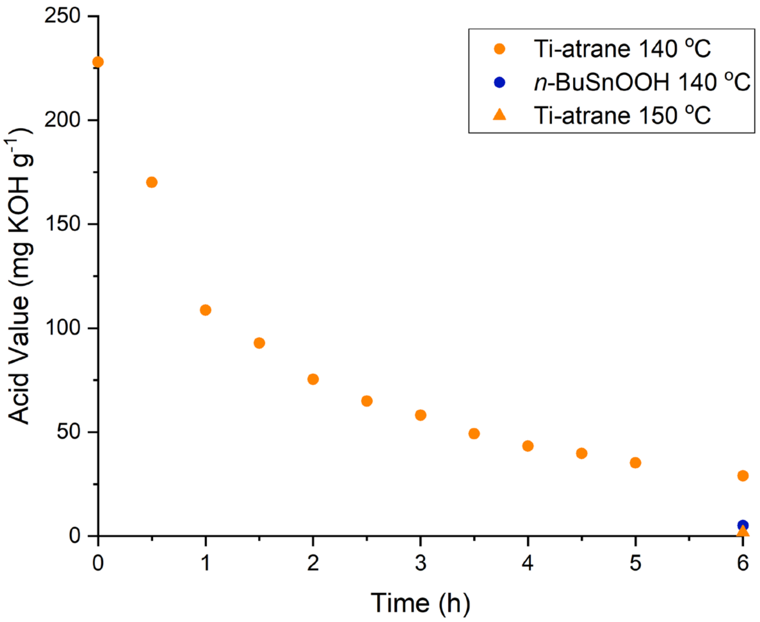


Figure S9. Acid Values of azeotropic polyesterification reactions of 1,6-hexanediol and adipic acid in the presence of 0.25 mol% catalyst (relative to -OH groups).

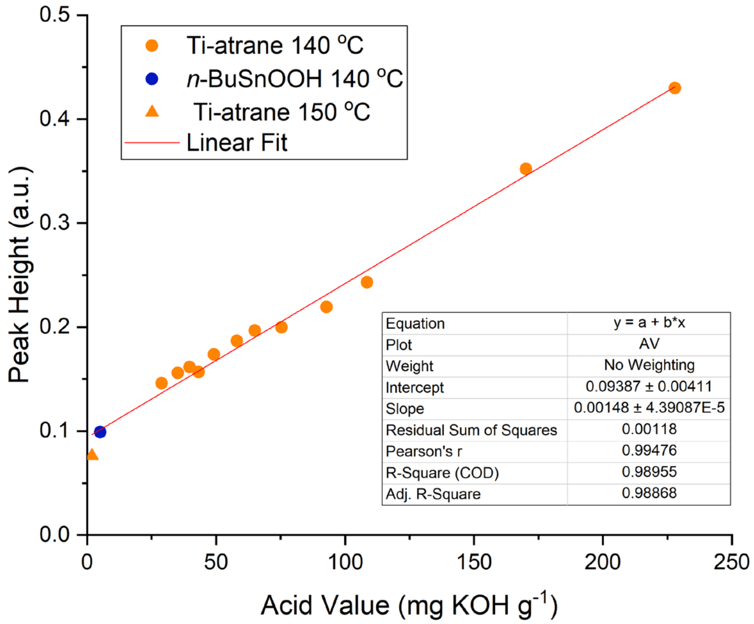


Figure S10. Correlation between peak height at 1712 cm^{-1} ($\nu_{c=o}$ vibration of the carboxylic acid) (x-axis) and Acid Value (y-axis).

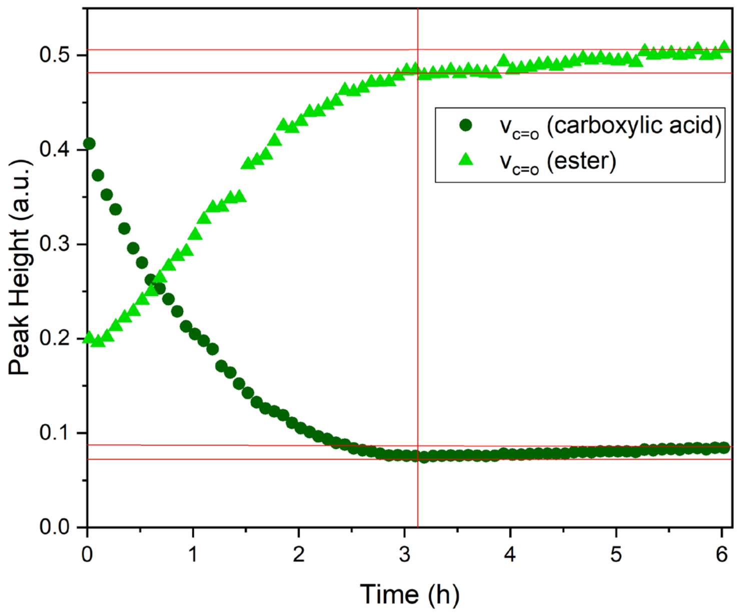


Figure S11. Peak height at 1712 cm^{-1} ($\nu_{c=o}$ vibration of the carboxylic acid) and peak height at 1736 cm^{-1} ($\nu_{c=o}$ vibration of the ester) of TiO^{i}Pr$_4$ catalyzed reactions at 150 ^{o}C.

The intensity (peak height) of the $\nu_{c=o}$ vibration of the carboxylic acid (at 1712 cm^{-1}) has a minimum at 3.12 hours. However, the increase in peak height, after this point in time is caused by an increase in the intensity of the 1736 cm^{-1} vibration ($\nu_{c=o}$ vibration of the ester) (see Figure 2A for the overlap between the $\nu_{c=o}$ vibration of the carboxylic acid and ester). Since this effect is rather small, we performed analysis on the peak height at 1712 cm^{-1} ($\nu_{c=o}$ vibration of the carboxylic acid) without peak deconvolution.

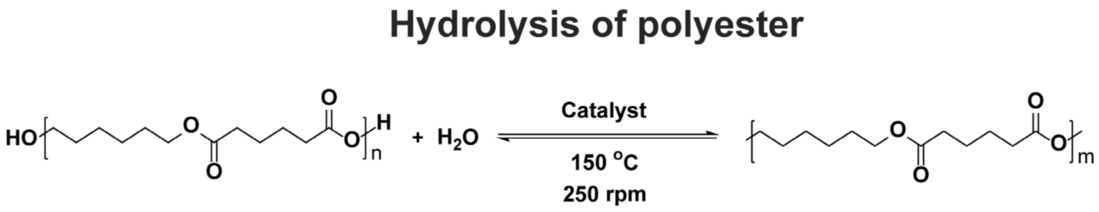


Table S3. Hydrolysis of polyester of 1,6-hexanediol and adipic acid.

Entry[a]		Acid Value[b] (mg KOH g^{-1})
1	blank	35.3
2	Ti-atrane	33.4
3	*n*-BuSnOOH	81.9

[a] Acid value of the reaction mixture at 0 h was 20.5 mg KOH g^{-1}. [b] Acid value of the reaction mixture after 2 h reaction time.

Figure S12. Reaction set-up for hydrolysis of polyester experiments.

References

1 *US Pat.*, US20120316316, 2012.