Electronic Supplementary Information (ESI)

Synthesis and characterisation of polyamides based on 2,5-furandicarboxylic acid as a sustainable building block for engineering plastics

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1 Experimental

1.1 Materials

Unless otherwise stated, all laboratory reagents and solvents were used as received. The present study was conducted only with 2,5-furandicarboxylic acid isomer of FDCA and will be termed simply as FDCA from here onwards. FDCA was kindly provided by Corbion B.V, Netherlands. 1,6-hexamethylenediamine (HMDA, 99.5+%) and m-cresol (99%) were purchased from Acros Organics. Titanium (IV) isopropoxide (TIPT, 97%), sodium carbonate (Na_2CO_3), sulphuric acid (H_2SO_4,98%), triflouroacetic acid-d1 (TFA-d_1), dimethyl sulfoxide-d6 (DMSO-d_6), sodium trifluoroacetate (Na-TFA, 98%), potassium trifluoroacetate (KTFA,98%) were all acquired from Sigma-Aldrich. Titanium citrate, CTL Ti638 UP (TIC, 55 wt% solution in water) was kindly provided by Catalytic technologies Ltd, UK. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99%) was purchased from Fluorochem UK. Dichloromethane (DCM), methanol and toluene were purchased from VWR chemicals.

1.2 Synthesis of dimethyl 2,5-furandicarboxylate (DMFDC)

DMFDC was synthesised according to the procedure described in literature with slight modification.[1] In a typical procedure, 24 g FDCA and 1.2 mL H_2SO_4 were added to a round bottom flask with 250 ml methanol. The contents were reacted under reflux conditions at 80 °C for 15 hours. The resulting solution was cooled to ambient temperature and then stored at -20 °C for two days to facilitate the precipitation. The mixture was then filtered through a Buchner funnel and washed with cold methanol three times. In the next step, the product was mixed with 300 mL of de-ionized water to form a suspension to be neutralized with a Na_2CO_3 solution (5 w/v %). After neutralization, the suspension was again filtered and washed with 200 mL de-ionized water three times before leaving it to dry in ambient conditions. Finally, the DMFDC powder collected, was recrystallized from a 50/50 v/v mixture of methanol/de-ionized water, dried overnight at 50 °C in vacuum oven, before any further use.

^{1}H NMR (500 MHz, DMSO-d_6, δ ppm, 298 K) (Figure S1 A):

7.44 (2H, =C***H***- of furan), 3.87(6H, -O-C***H$_3$***).

Yield after recrystallization = 76 %

1.3 General procedure for the synthesis of poly(hexamethylene furanamide) (PA6F) by melt polymerisation

1.3.1 Synthesis of PA6F in thin-film reactor

In a typical run, 150 mg (0.81 mmol) DMFDC and 94.66 mg (0.81 mmol) hexamethylenediamine (HMDA) were carefully weighed into a vial with magnetic stirrer. Calculated amount of TIPT catalyst was injected from a stock solution in toluene (20 µL mL^{-1}). After transferring the reactants and catalyst, vials were sealed, evacuated and purged with dry argon at least three times. Sealed vials were then placed into the reactor heating block. For the oligomerisation step, the reaction was performed at 65 °C. Stirring was started once HMDA was completely melted and formed a slurry with DMFDC. This mixture gradually turned transparent with stirring, reflecting complete solubility of DMFDC in HMDA. Reaction was continued for 3 hours and the oligomeric PA6F samples were obtained as white solids. Vials were then removed from the block and dried in vacuum oven at 60 °C for 2 hours.

PA6F oligomer ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm, 298 K) (Figure S2 A): 8.51 (2H, -N***H***-CO-), 7.16 (2H, =C***H***- of furan), 3.90 (6H, -OC***H$_3$*** of DMFDC), 3.30 (4H, -NH-C***H$_2$***-$(CH_2)_4$-C***H$_2$***-NH-), 1.57 (4H, -NH-CH_2-C***H$_2$***-$(CH_2)_2$-C***H$_2$***-CH_2-NH-), 1.38 (4H, -NH-$(CH_2)_2$-$(CH_2)_2$-$(CH_2)_2$-NH-).

In the polycondensation step, the vials were placed within the same reactor but fitted with an external argon / vacuum distillation set-up. After sealing the reactor, cycles of vacuum and argon were applied to ensure no oxygen was left in the system. Heating was started initially under argon. The contents were quickly heated to 190 °C after which stirring was started and the pressure was reduced to less than 1 mbar when a temperature 205 °C was reached. The temperature was then further increased to 230 °C. Reaction was carried out under these conditions for 5 hours. At the end, argon was introduced into the reactor and PA6F sample vials were then removed.

PA6F polymer ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm, 298 K) (Fig. 2 A): 8.51 (2H, -N***H***-CO-), 7.16 (2H, =C***H***- of furan), 3.31 (4H, -NH-C***H$_2$***-$(CH_2)_4$-C***H$_2$***-NH-), 1.56 (4H, -NH-CH_2-C***H$_2$***-$(CH_2)_2$-C***H$_2$***-CH_2-NH-), 1.38 (4H, -NH-$(CH_2)_2$-$(CH_2)_2$-$(CH_2)_2$-NH-).

1.3.2 Synthesis of PA6F in a 250 mL glass reactor

With an objective to increase the synthesis scale, a custom made 4-neck round bottom flask fitted with a condenser and vacuum trap, was used with an overhead stirrer. Flask was evacuated and filled with argon several times before charging the reactants. As a representative example of PA6F synthesis, procedure for the run listed in Table 1 entry 4 will be described. 16.40 g (0.089 mol) DMFDC, 10.39 g (0.089 mol) HMDA and 400 ppm of catalyst were introduced into the flask under argon atmosphere. In the oligomerisation step performed under argon, the reactor was heated to 65 °C by monitoring the reaction mixture temperature. Stirring was initiated once all the HMDA was melted and formed a slurry with DMFDC. The reaction was continued under these conditions until white solid agglomerate was formed after subsequent increase in the viscosity. At this point, stirring was stopped and removal of methanol, formed as a by-product, was started by slowly opening the flask contents to the vacuum line. Vacuum was continuously applied for an hour at 50 °C to ensure most of the methanol has been removed and collected.

The dried PA6F-oligoamide was then crushed and heated again to 200 °C under argon atmosphere. At this stage, stirring was started and pressure was reduced to less than 1 mbar in 5-8 minutes. The temperature of the melt was allowed to further increase to 230 °C, while constantly increasing the stirring speed to 100 rpm. The reaction was carried out for 3 hours at these conditions. At the end of the reaction, stirring was stopped and polymer was removed while still molten.

For the purification of as-synthesised PA6F, samples were dissolved in a mixture of DCM/HFIP (80/20 v/v) and precipitated using an excess of DCM.2 After stirring the mixture for 2 hours, the precipitates were allowed to settle down and remaining solvent was then carefully decanted. The same process was repeated three times while washing with fresh DCM each time. The purified polymer was then dried in vacuo at 60 °C overnight.

1.4 Characterisation

NMR spectra were recorded at 298 K on 500 MHz Bruker Avance II+ instruments using DMSO-d_6 or TFA-d_1 as a solvent. Samples were slightly heated in some cases to facilitate the dissolution.

Differential scanning calorimetry (DSC) analyses were conducted using a TA-instruments Q20 differential scanning calorimeter. All runs were performed under nitrogen atmosphere, with a constant flow rate of 18 mL min^{-1}. 4-6 mg of sample was weighed into the DSC pan. In the first heating scan, samples were cooled to 10 °C, and then heated to 325 °C at 10 °C min^{-1}. Samples were maintained at this temperature for 2 minutes before starting the cooling ramp. Samples were cooled to 10 °C at the same rate and reheated again to 325 °C at 10 °C min^{-1} to construct the thermogram for the second heating scan. Glass transition temperature (T_g) was recorded on the second heating scan. In some cases, melting temperature (T_m) was measured on the first heating scan.

Films for dynamic mechanical analysis (DMA) were produced by compression moulding on a hydraulic press (40 T, JBT engineering, UK). Press was first heated to 240 °C. Pre-crushed polymer granules were placed between two PTFE sheets (Bola, 1000 mm x 300 mm x 0.5 mm). The polymer was first placed between the heating plates of the press for 8 minutes to allow it to soften. Then final press was performed under 20 bar pressure for 4 minutes. Film thickness varied between 120 – 150 microns. DMA measurements were carried out on a Mettler Toledo DMA1 instrument operated in tension mode. Frequency of oscillation 1 Hz and a displacement amplitude of 10 µm (0.1 % strain) was employed. Sample size of 10 mm x 2.5 mm (length x width) was cut from the polymer film and mounted on the sample holder using a pre-load force of 1.5 N. Specimens were heated from 25 to 250 °C at a heating rate of 5 °C min-1, while data for storage modulus (E'), loss modulus (E'') and tan delta was collected. For each polymer, three parallel samples were tested.

For wide angle x-ray diffraction (WAXD) studies, STOE STADI P diffraction system equipped with pure Cu-Kα1 (λ = 0.154 nm) radiation at 40 kV and 40 mA, was used. Samples films pressed earlier were subjected to WAXD measurements in the transmission mode for 2θ= 2° to 70°.

Thermogravimetric analysis (TGA) was performed on a Setsys Evolution TGA 16/18 from Setaram. 12-15 mg sample, pre-dried at 100 °C in vacuum oven overnight, was loaded into a 170 µL alumina crucible. In the analysis program, the furnace was first purged with argon for at least 30 minutes at room temperature, samples were then heated from room temperature to 150 °C at 10 °C min^{-1}, maintained there for 20 minutes to remove any residual water and then heated again to 700 °C at 10 °C min^{-1}, all under a constant flow of argon.

Uniaxial tensile testing was performed on an Instron 3369 universal testing machine equipped with 1 kN load cell. Tests were conducted on compression moulded films of dimensions 45 mm x 10 mm x 0.2 mm. At least three replicates were tested and average values were reported alongside the standard deviation.

Inherent viscosity measurements were performed on crude polymer samples at 25 °C in m-cresol solvent using Ubbelohde viscometer (type 1B) at a concentration of 0.5 g dL^{-1}. For this purpose, 50 mg of polyamide sample was dissolved in 10 mL of m-cresol and heated at 60 °C for 4 hours to facilitate the dissolution. Samples were filtered using 0.45 µm PTFE syringe filters before analysis to remove any undissolved polymer and impurities. For blank solvent, only m-cresol was used. Efflux times for both polymer solution and solvent were measured three times and the average value was reported.

Inherent viscosity (dL g^{-1}) was calculated using following relationship:

$$\eta_{inh} = \frac{\ln\left(\frac{t}{t_o}\right)}{C}$$

where η_{inh} is the Inherent viscosity at 25 °C (dL g^{-1}), t and to are the efflux time for the sample solution (sec) and blank solvent respectively and C is the polymer solution concentration in g dL^{-1}.

Matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) mass spectrometry was performed on a Bruker Autoflex speed instrument in linear positive mode. The polymer sample (10 mg mL^{-1}), matrix 1,8,9-anthracenetriol (dithranol) (10 mg mL^{-1}) and Na-TFA (0.1 M), all in HFIP solvent, were combined in the ratio 20:50:2 µL respectively. The solution was then centrifuged and 1 µL of the solution was dropped onto the MALDI plate and allowed to dry under ambient conditions. The remaining mass of different end-groups was calculated from following equation:

$$M_{eg} = M_{ps} - \{(M_{ru} \times n) + M_{cation}\}$$

where M_{eg} is the mass of end-group, M_{ps} is the mass of polymer species, M_{ru} is the mass of repeating unit, n is number of repeat units in the polymer species and M_{cation} is the mass of cation.

Gel permeation chromatography (GPC) was performed on an Agilent-1260 GPC/SEC system equipped with a TDA 305- triple detector array from Viscotek. The three detectors used to evaluate absolute molecular weight of PA6F samples were the refractive index (RI), low angle

and right-angle light scattering detector (LALS, RALS) and a viscosity detector. For molecular weight separation, two analytical columns (PSS PFG analytical linear M, 300 x 8.00 mm, 7µm) were employed. HFIP with 0.02 M K-TFA was used as mobile phase at a flow rate of 0.70 mL min^{-1}. Samples were prepared in HFIP at 2 mg mL^{-1} concentration and an injection volume of 50 µL was employed.

2 NMR assignments for dimethyl 2,5-furandicarboxylate (DMFDC)

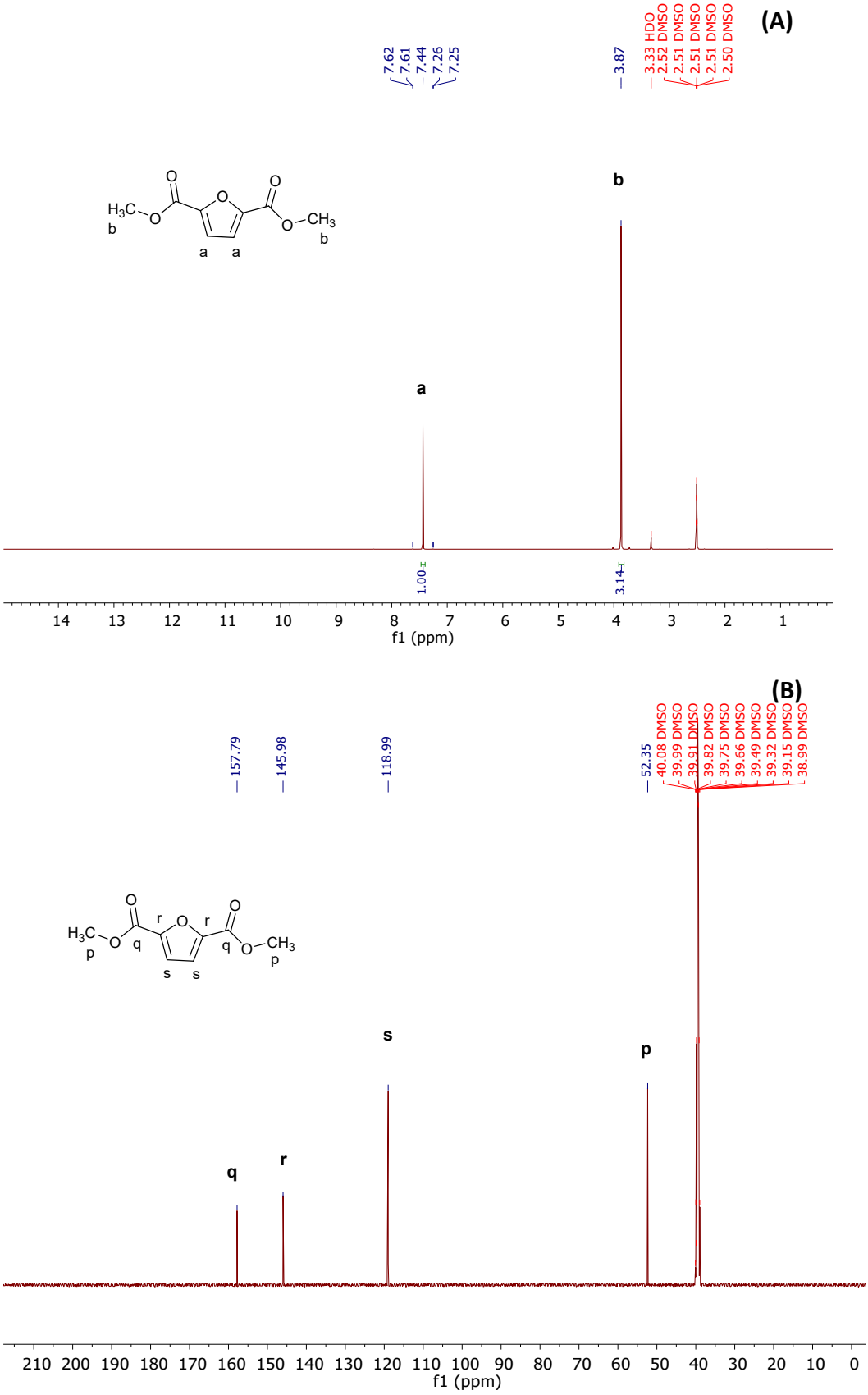


Figure S1. NMR spectra for DMFDC monomer recorded in DMSO-d_6 at 298 K **(A)** ^{1}H NMR and **(B)** {H^{1}} ^{13}C NMR.

3 NMR analysis of PA6F oligomer

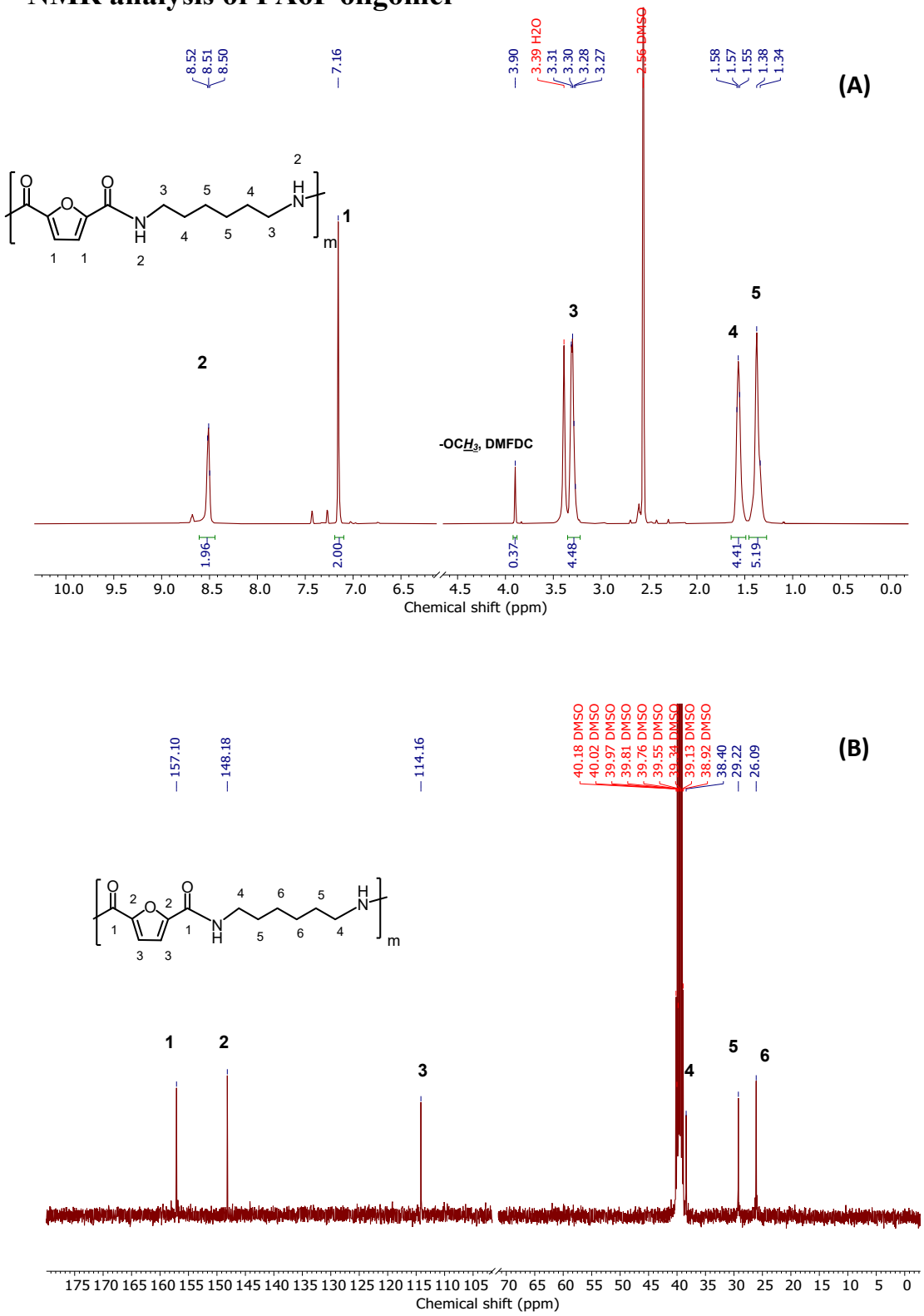


Figure S2. A typical example of NMR spectra for PA6F oligomer recorded in DMSO- d_6 at 298 K **(A)** ^{1}H NMR and **(B)** $\{H^{1}\}$ ^{13}C NMR.

4 Synthesis of PA6F by melt polycondensation and reaction condition optimisation using thin-film reactor

4.1 Synthesis of PA6F by catalytic melt polycondensation

We initiated the study by synthesising PA6F polyamide using different titanium-based catalysts due to their excellent performance in the polycondensation reaction of polyester and amides, whereas, dibutyltin(IV) oxide (DBTO) was included for a comparison as it has been cited as an active catalyst for polyester synthesis (Figure S3).[3–8] Initially, the melt phase polycondensation using stoichiometric amounts of DMFDC and HMDA was carried out at 250 mg scale thin-film reactor.

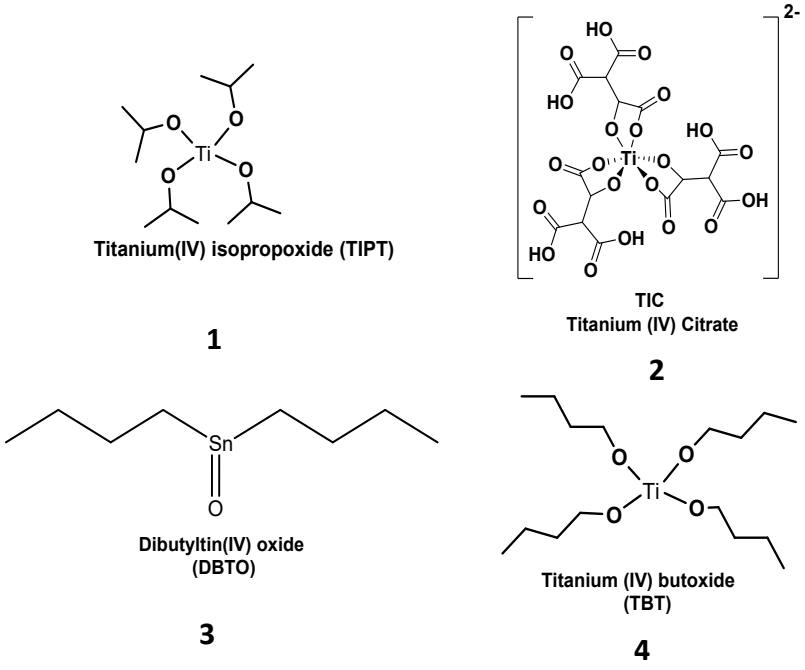


Figure S3. Chemical structures of the catalysts used in the synthesis of PA6F

The reaction was conducted following a two-stage process analogous to one used for the polyester synthesis. As a starting point, reaction conditions already reported by *Grosshardt et al.* were employed.[9] In the first stage of the reaction, designated as oligomerisation, stoichiometric amounts of DMFDC and HMDA were reacted in the presence of a catalyst under inert atmosphere at 140 °C for up to 3 hours. In the second stage, the reaction temperature was raised to 230 °C to start the polycondensation under vacuum which was carried out for 5 hours. The catalytic activity was mainly assessed by evaluating the solution inherent viscosities measured in *m*-cresol at 25 °C (see experimental). Table S1 and Figure S4 summarise the main outcomes of these experiments.

Table S1: Analysis of PA6F samples synthesised following catalytic melt polycondensation using different catalysts and loadings.

Entry	Catalyst	Catalyst loading [a] (ppm)	Inherent viscosity [b] (dL/g)	T_{g1} [c] (°C)	T_{m1}, $T_{m1'}$ [c] (°C)	T_{g2} [d] (°C)	T_{m2} [d] (°C)
1	Control	0	0.26	60	141, 303	103	- [e]
2		50	0.30	- [f]	- [f]	- [f]	- [f]
3	**TIPT**	100	0.33	67	164, 304	111	- [e]
4	**1**	200	0.35	65	153, 314	112	- [e]
5		400	0.37	67	151, 313	114	- [e]
6		50	0.25	- [f]	- [f]	- [f]	- [f]
7	**TIC**	100	0.31	63	144, 307	110	- [e]
8	**2**	200	0.27	- [f]	- [f]	- [f]	- [f]
9		400	0.26	62	143, 299	106	- [e]
10		50	0.24	- [f]	- [f]	- [f]	- [f]
11	**DBTO**	100	0.29	61	137, 304	107	- [e]
12	**3**	200	0.26	- [f]	- [f]	- [f]	- [e]
13		400	0.34	97	162, 301	110	- [e]
14		50	0.30	- [f]	- [f]	- [f]	- [f]
15	**TBT**	100	0.32	- [f]	- [f]	- [f]	- [e]
16 [g]	**4**	200	0.30	123	308	110	- [e]
17 [g]		400	0.15	91	157, 303	103	- [e]

Synthesis conditions: DMFDC: HMDA = 1:1, oligomerisation at 140 °C, 3 hours under argon; polycondensation at 230 °C, 5 hours under vacuum.

[a] Calculated on the basis of metal weight in the catalyst relative to the weight of DMFDC in feed

[b] Measured at 25 °C using m-cresol solvent for polymer sample concentration of 0.5 g/dL

[c] Measured on the first heating scan of the DSC thermogram

[d] Measured on the second heating scan of the DSC thermogram

[e] Not detected following second heating scan of the DSC

[f] Sample not analysed

[g] Sample was dried and annealed in the temperature range of 100-140 °C before DSC analysis

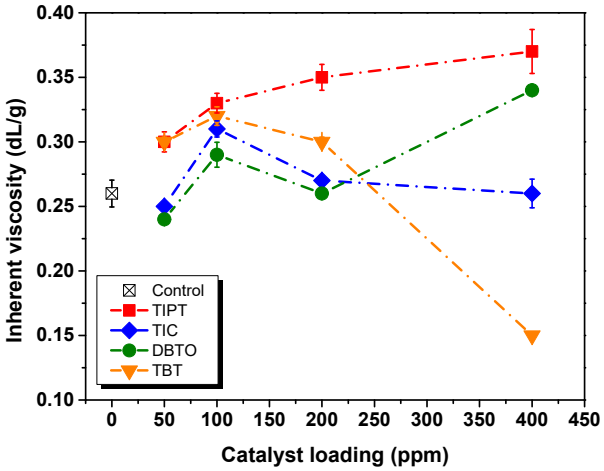


Figure S4: Inherent viscosity of PA6F samples synthesised using different catalysts and loadings.

It can be realised from Figure S4 that overall, catalyst incorporation had a positive impact on the inherent viscosity of the polymer compared to the sample synthesised without catalyst. In particular, TIPT and DBTO showed considerable improvements in the inherent viscosity with increase in catalyst concentration, with an exception for DBTO at 200 ppm, when the viscosity dropped slightly. For the TIC and TBT catalysts, viscosity improvement was obvious until 100 ppm of the catalyst, after which it decreased, more in the case of TBT and less in case of TIC. The decreased in viscosity at higher catalyst concentrations suggest possible depolymerisation under these conditions.

4.1.1 MALDI-TOF mass spectrometry analysis

Further characterisation of PA6F chemical structure, in particular the end-groups, was performed using MALDI-ToF mass spectrometry. As an example, Figure S5 depicts the MALDI spectrum recorded for the sample synthesised with 200 ppm TIPT. The figure illustrates a single repeat unit of 236.9 Da which corresponds to the repeating unit already confirmed by NMR analysis. Furthermore, different series of end-groups can also be observed, reflecting deviation of end-groups from the expected amino and ester groups. These end-groups were assigned to the chemical structures presented in Table S2.

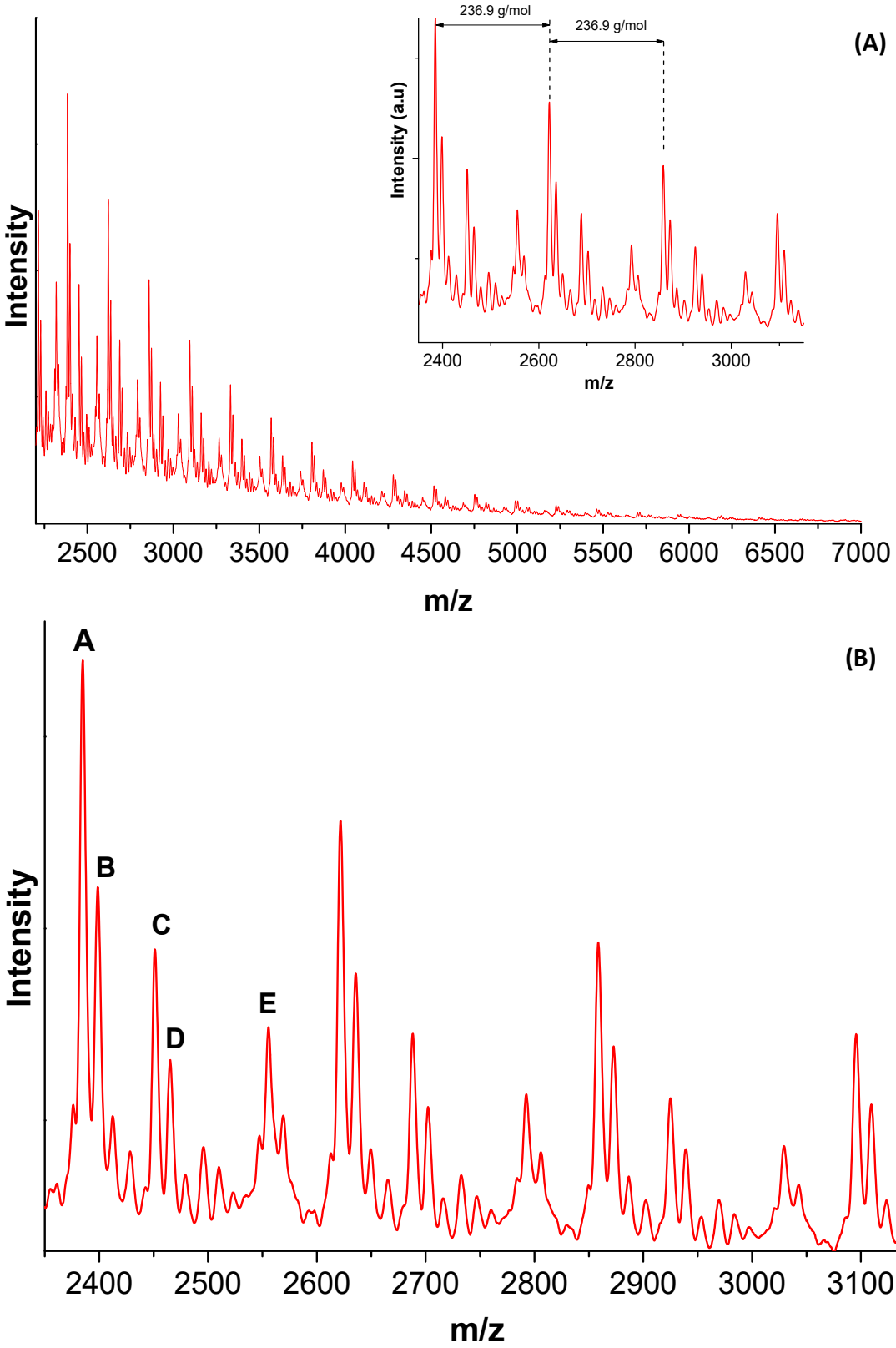
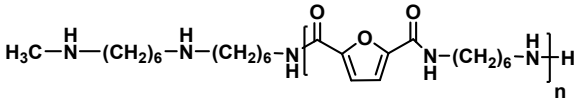
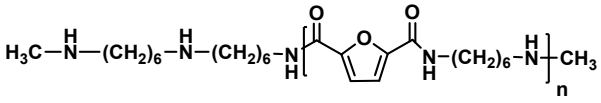
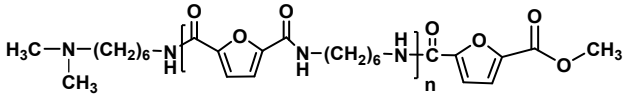
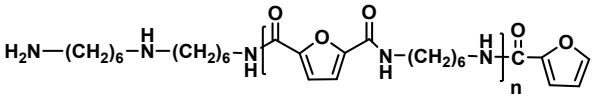
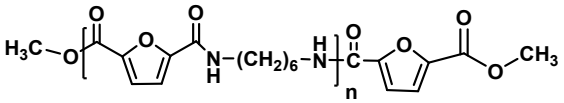


Figure S5: MALDI-TOF MS analysis of PA6F sample synthesised with 200 ppm TIPT **(A)** full range spectrum and **(B)** spectrum in the range of 2350 to 3150 m/z.

Table S2: MALDI-TOF MS for PA6F sample synthesised using 200 ppm TIPT catalyst

Series	m/z (n)	Proposed end-groups	M_{EG} (cation) Assigned	M_{EG} (cation) Observed
A	2384.8 (9)		229.4 (Na^+)	229.7 (Na^+)
B	2398.7 (9)		243.4 (Na^+)	243.6 (Na^+)
C	2451.3 (9)		296.4 (Na^+)	296.4 (Na^+)
D	2465.1 (9)		309.5 (Na^+)	310.0 (Na^+)
E	2555.6 (10)		184.1 (H^+)	185.6 (H^+)

From Table S2, three abundant series of end-groups i.e. A, B and C contain terminal methyl groups were observed. The methylation of amino end-groups, termed as *N*-methylation, is a major concern during ester amidation reactions, and has been highlighted in the literature previously. Flannigan *et al.* encountered similar issue while studying the direct thermal condensation of aromatic methyl esters with aromatic amines.[10] Malluche and co-workers probed the ester/amine reaction system with the help of a model reaction between methyl benzoate and hexylamine.[11] They were able to confirm the presence of several alkylated species in the product mixture. Both of these studies excluded the possibility of methanol produced as by-product being responsible for the alkylation. Instead, it was proposed that alkylation of terminal amino groups to be a competing reaction to the amidation of ester.

It is apparent that *N*-methylation is an undesirable side reaction. Methyl end-groups act as chain terminators and are incapable of taking part in the condensation reaction, thus, upsetting the reaction stoichiometry. This side reaction greatly lowers the possibility of polymer chain growth, which in turn results in a lower molecular weight product. Therefore, in order to synthesise PA6F polyamide with a higher molecular weight, *N*-methylation of the end-groups must be curtailed.

4.1.2 Extent of N-methylation estimation using ^{1}H NMR spectroscopy and its dependence on oligomerisation temperature

In their patent application, Duursma *et al.* have showed that minor variations in oligomerisation temperature during the PA6F oligomer preparation can greatly affect the extent of *N*-methylation.[12] With the help of ^{1}H NMR analysis, they were able to compare the extent of *N*-methylation in samples prepared at different temperatures. This proposition was tested in the present system. Figure S6 shows a representative example of ^{1}H NMR spectrum recorded for a PA6F oligomer prepared using 200 ppm TIPT catalyst. The relative concentration of different functional groups was estimated following the ^{1}H NMR chemical shifts described in the patent using following equations (See Figure S6 and Table S3).[2]

$$\%\ ester = \left(\frac{integral\ at\ 4.14\ ppm}{3}\right) \times 100\%$$

$$\%\ acid = (ingeral\ at\ 7.55\ ppm) \times 100\%$$

$$\%\ N-methylation = \frac{(integra\ at\ 3.00\ ppm + integral\ at\ 3.09\ ppm + integral\ at\ 3.18\ ppm)}{3} \times 100\%$$

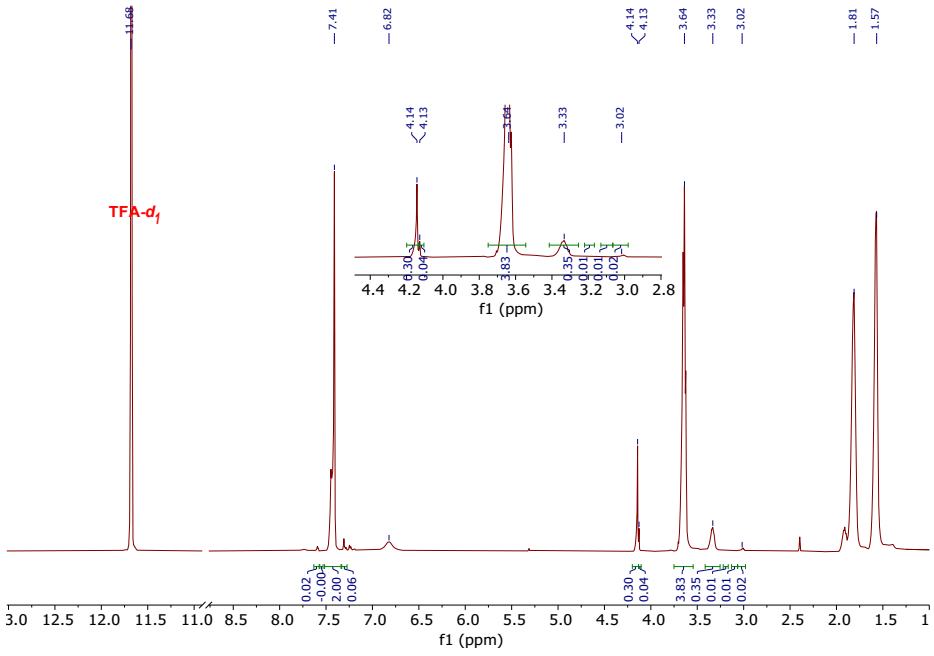


Figure S6: ^{1}H NMR spectrum of oligomer sample synthesised with 200 ppm TIPT (entry 884, Table S3) recorded in TFA-d_1 at 25 °C.

Table S3: Concentration of various functional groups calculated using ^{1}H NMR after oligomerisation stage conducted at different reaction conditions.

DMFDC: HMDA= 1:1, 140 °C, 3 h				
Entry	**TIPT (ppm)**	**% Ester**	**% Acid**	**% *N*-methylation**
9501	0	20.00	51	53.00
DMFDC: HMDA= 1:1, 65 °C, no solvent, 3 h				
Entry	**TIPT (ppm)**	**% Ester**	**% Acid**	**% *N*-methylation**
881	0	10.33	3	2.67
882	50	12.33	4	2.67
883	100	13.00	3	1.67
884	200	11.33	2	1.33
885	400	12.00	3	1.67
DMFDC: HMDA= 1:1, 65 °C, MeOH, 3 h				
Entry	**TIPT (ppm)**	**% Ester**	**% Acid**	**% *N*-methylation**
886	0	21.67	2	2.00
887	50	21.33	2	1.33
888	100	20.33	3	3.00
889	200	16.67	2	1.67
8810	400	17.00	2	1.67
DMFDC: HMDA= 1:1.1, 65 °C, no solvent, 3 h				
Entry	**TIPT (ppm)**	**% Ester**	**% Acid**	**% *N*-methylation**
911	0	17.33	3	2.00
912	50	13.33	5	3.67
913	100	11.00	4	2.00
914	200	10.33	4	2.00
915	400	10.00	4	2.67
DMFDC: HMDA= 1:10, 65 °C, MeOH, 3 h				
Entry	**TIPT (ppm)**	**% Ester**	**% Acid**	**% *N*-methylation**
916	0	10.33	4	2.00
917	50	8.00	4	2.00
918	100	8.67	4	2.67
919	200	10.67	4	1.67
9110	400	9.00	3	2.00

In conclusion, when oligomerisation was conducted at the temperature employed in our initial experiments (140 °C), the extent of *N*-methylation was significantly higher. These observations also complement our previous findings regarding several *N*-methylated end-groups witnessed during MALDI-ToF analysis. Whereas, *N*-methylation was considerably lower (1-2%) when oligomerisation was conducted at 65 °C. Though, contrary to the claim put forward by the inventors, we were unable to see any significant impact of incorporating methanol as a solvent for the oligomerisation step to counter the *N*-methylation.

4.1.3 PA6F melt polycondensation with optimised reaction parameters

A series of experiments was conducted using TIPT catalyst, where oligomerisation was performed at 65 °C, followed by polycondensation step, which was carried out using previously mentioned conditions. The results of PA6F synthesised using these modified conditions are summarised and compared with earlier results, in Figure S6. It is evident that significant improvements in both inherent viscosity and glass transition temperatures (T_g) were observed after adjusting the oligomerisation conditions to the lower temperature regime. For the catalytic samples, a nearly two-fold increase in inherent viscosity was observed, whereas, the T_g values increased by almost 18 °C. Even for the uncatalysed samples, an increase of 65% in the inherent viscosity was observed. This positive impact could be attributed to the considerable decrease in the extent of *N*-methylation of amino end-groups following the lower oligomerisation temperature. This will ensure an appropriate balance between the two reactive end-groups (amino, ester) that will effectively allow the polymer chains to grow further during the polycondensation stage of the reaction.

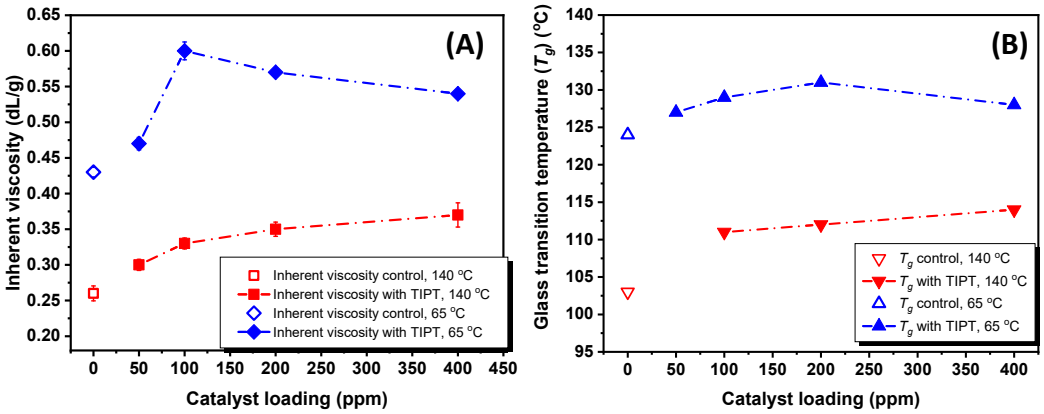


Figure S7: Effect of oligomerisation temperature on the final polymer properties, improvement in **(A)** Inherent viscosity and **(B)** glass transition temperatures T_g as a function of TIPT catalyst concentration when oligomerisation was conducted at 65 °C compared with earlier samples where oligomerisation temperature was 140 °C.

5 Properties of PA6F polymers synthesised in the thin-film reactor

Table S4. PA6F samples produced in thin-film reactor

Monomer molar ratio	Catalyst loading		Inherent Viscosity [c]	Thermal properties [d]		GPC data [e]		
	(ppm) [a]	(mol %) [b]	dL g^{-1}	T_g (°C)	T_m (°C)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	$Đ$
	0	0	0.47	118	nd	5	18	3.41
	50	0.0096	0.47	126	nd	8	18	2.20
DMFDC:HMDA = 1:1	100	0.0192	0.58	126	nd	9	23	2.22
	200	0.0384	0.66 [f]	128	nd	13	26	2.01
	400	0.0769	0.59 [f]	129	nd	14	43	3.06

[a] Calculated on the basis of metal (Ti) weight in the catalyst relative to the weight of DMFDC in feed

[b] Calculated on the basis of moles of catalyst to the total moles of feed

[c] Measured at 25 °C using *m*-cresol solvent for polymer sample concentration of 0.5 g dL^{-1}

[d] Measured on the second heating curve of DSC thermogram

[e] Performed using HFIP as mobile phase and evaluated using triple detection method to obtain absolute molecular weights

[f] Some insoluble fraction of the polymer was left in solution after 4 hours at 60 °C

nd Not detected following second heating scan of the DSC

6 DSC thermograms for PA6F synthesised in thin-film reactor

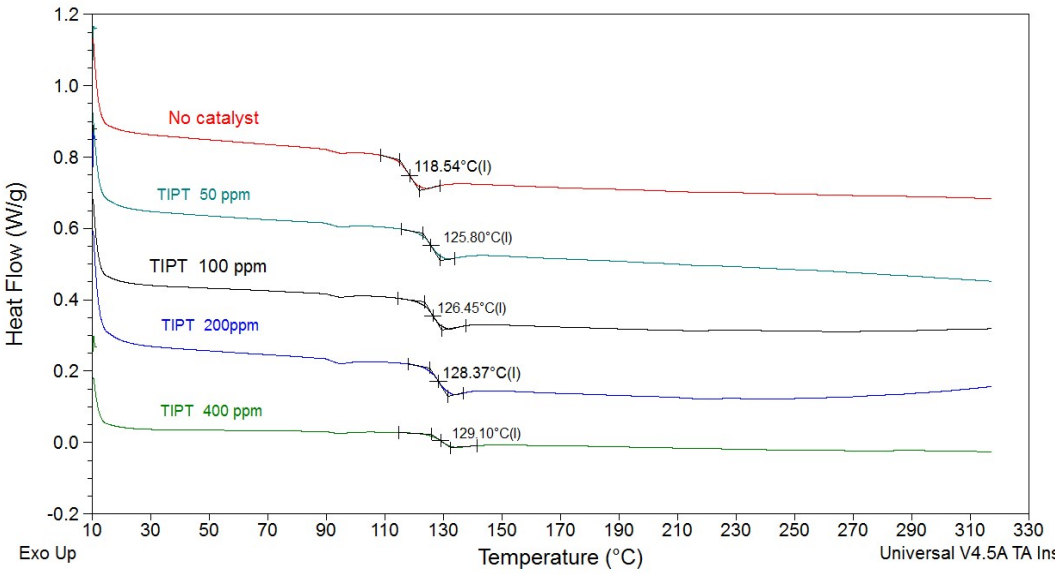


Figure S8. DSC second heating curves for samples synthesised in the thin-film reactor at different loadings of TIPT catalyst.

7 ^{1}H NMR analysis of oligomer samples from glass reactor

Selected samples of PA6F oligomers synthesised in glass reactor were subjected to ^{1}H NMR analysis using TFA-d_1 at 298 K . All chemical shifts were referenced to furanic protons assigned at 7.41 ppm (2H, =C***H***- of furan).

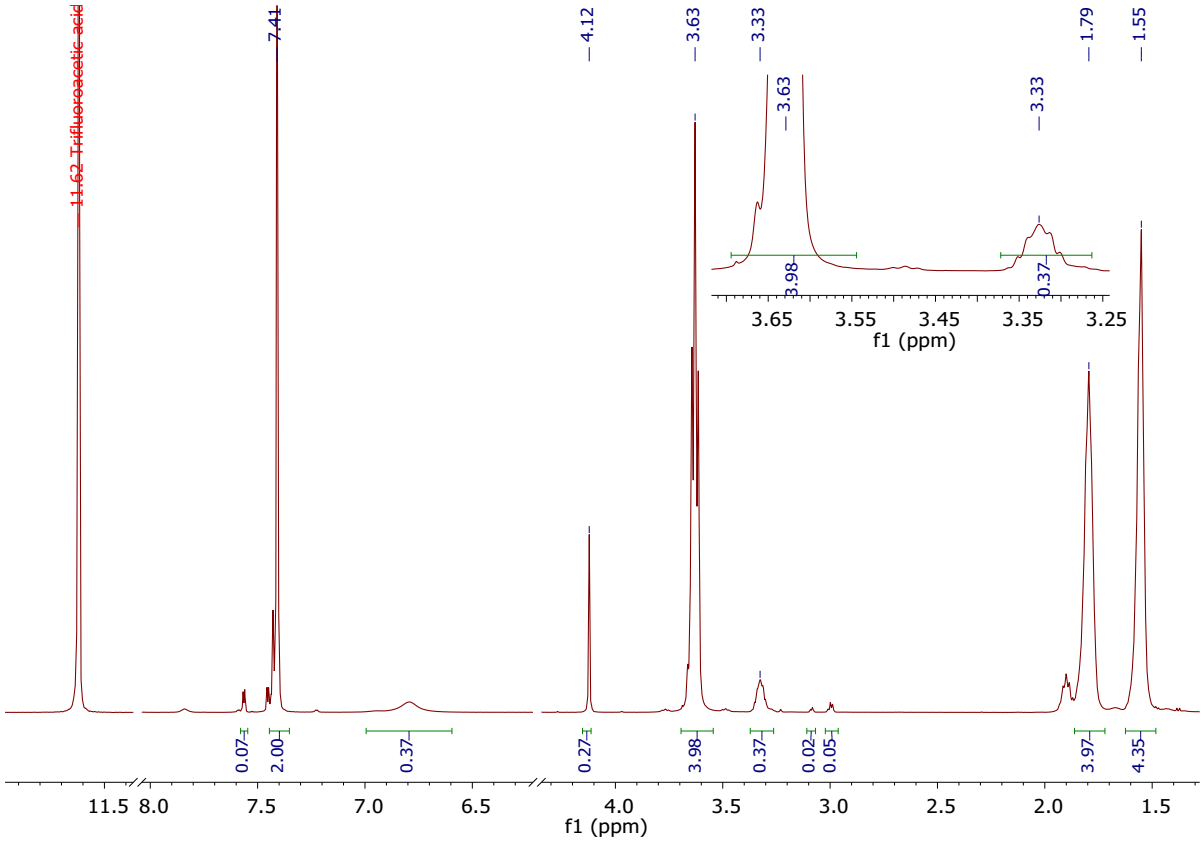


Figure S9. ^{1}H NMR spectrum example of a PA6F oligomer recorded after first stage of oligomerisation in TFA-d_1 at 298 K.

Table S5. Degree of polymerisation (DP) and number average molecular weight (M_n) of selected oligomer samples synthesised in the glass reactor (see Table 1, main article)

Entry	Catalyst	Cat loading [a] (ppm)	Unreacted ester [b] (%)	DP [c]	M_n [d] (g mol^{-1})
1	No cat.	0	3.38	11.10	2,600
2	TIPT	200	4.67	13.67	3,200
3	TIPT	300	4.50	10.75	2,500
4	TIPT	400	4.83	11.62	2,700

[a] Calculated on the basis of metal (Ti) weight in the catalyst relative to the weight of DMFDC in the feed

[b] Calculated by ^{1}H NMR (Figure S9) using relation :

$$unreacted\ ester\ (\%) = \left(\frac{Integral\ value\ at\ \delta\ 4.12\ ppm}{6}\right) \times 100$$

[c] Calculated by ^{1}H NMR signals and based on amino end-groups only (Figure S9), using formula [13]:

$$DP = \frac{Integral\ value\ at\ \delta\ 3.63\ ppm}{Integral\ value\ at\ \delta\ 3.33\ ppm}$$

[d] Calculated using formula: $M_n = DP \times Repeating\ unit\ mass\ (236.3\ \frac{g}{mol})$

8 DSC thermograms for PA6F synthesised in the glass reactor

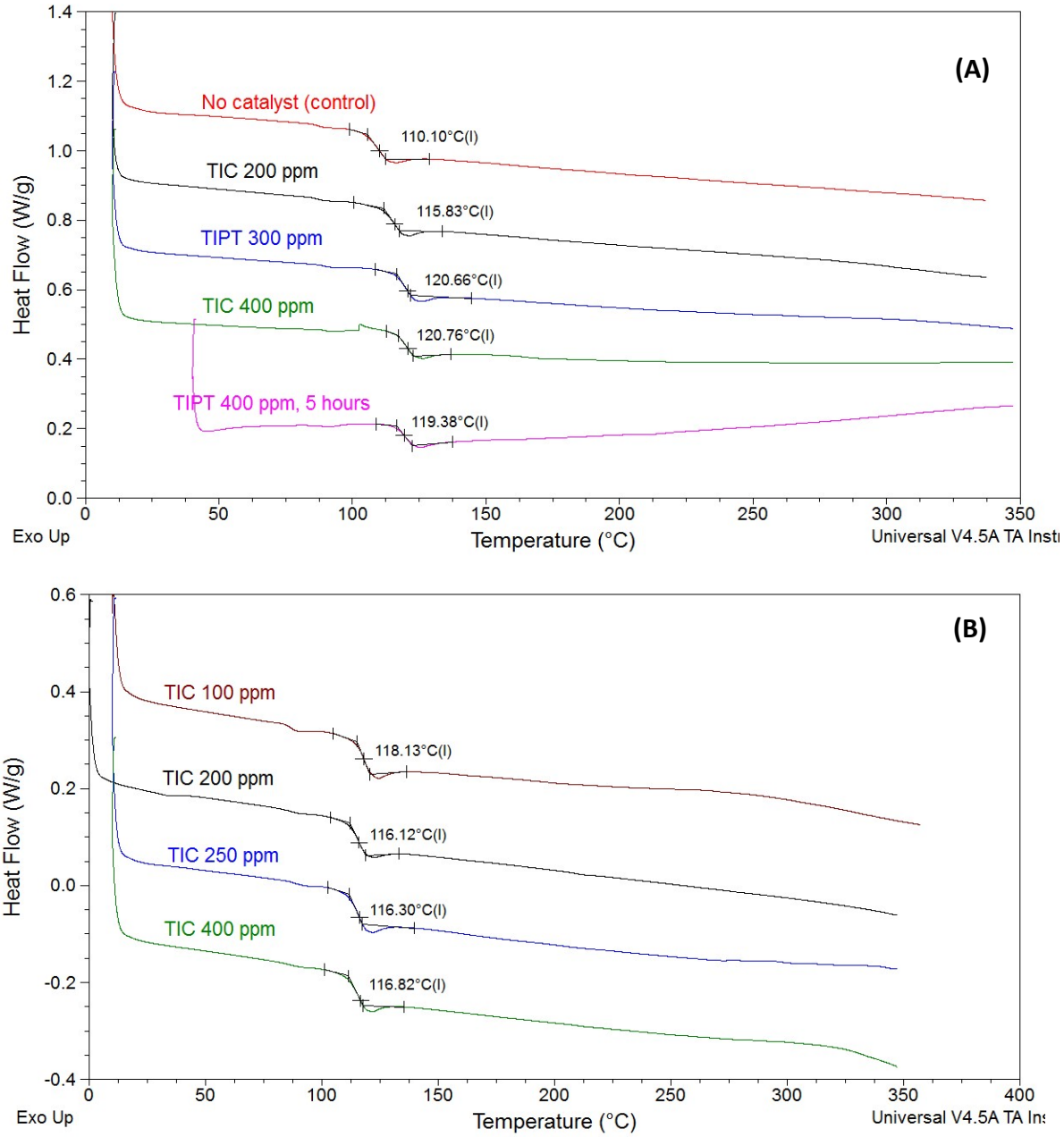


Figure S10. DSC second heating curves for the as-synthesised samples of PA6F polymers using **(A)** TIPT catalyst and **(B)** TIC catalyst

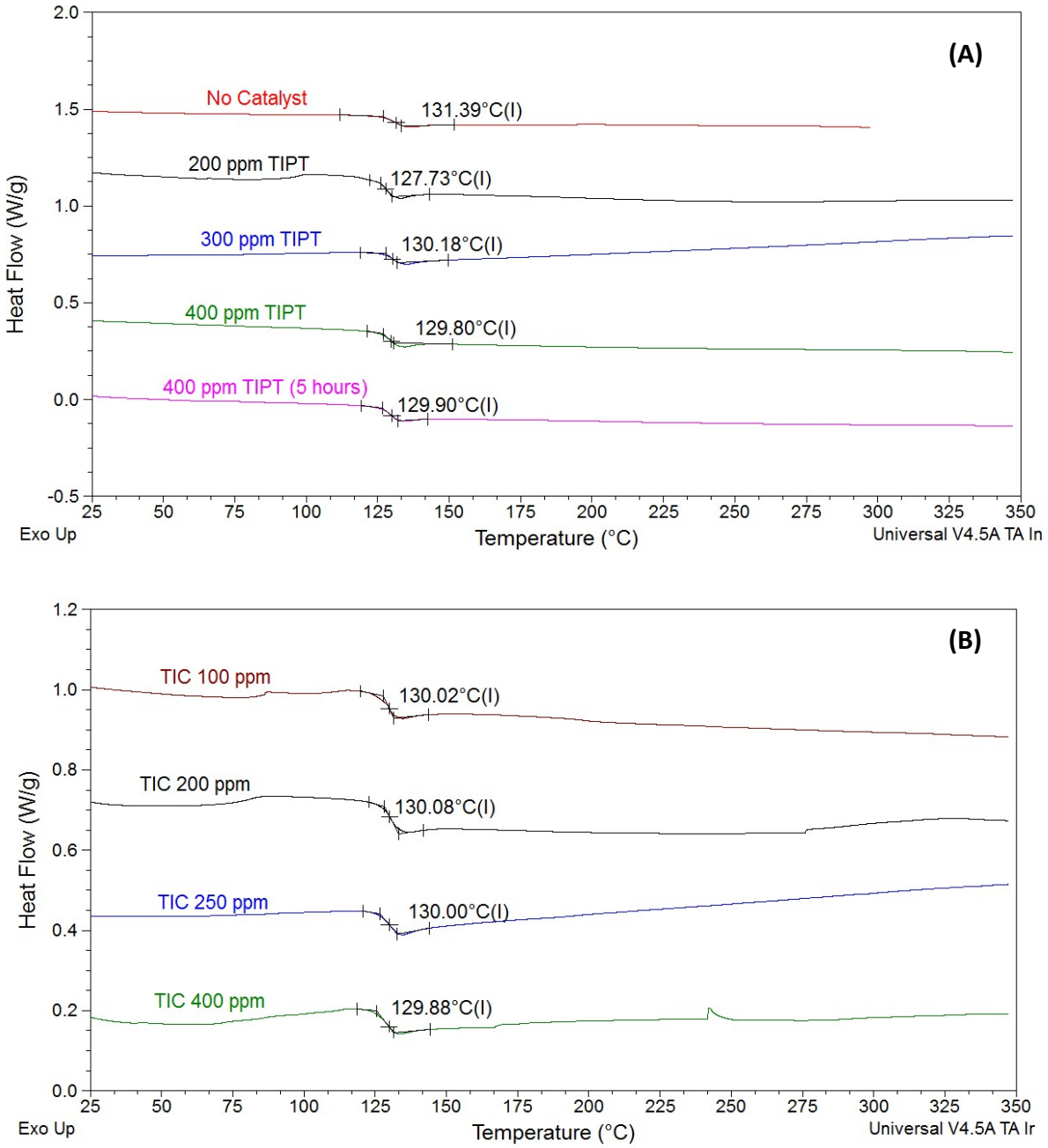


Figure S11. DSC second heating curves for solvent purified samples of PA6F polymers synthesised earlier using **(A)** TIPT catalyst and **(B)** TIC catalyst

9 Colour analysis by CIELAB for PA6F samples

The colour of polymer samples was evaluated in solution using Avantes Starline AvaSpec-2048L UV/VIS spectrometer. For this purpose, PA6F samples were dissolved in HFIP solvent at a concentration of 50 mg mL^{-1}. The International Commission on Illumination (CIE)'s L*a*b* colour space system (CIELAB) was used to evaluate the colour. In this system, the lightness of the sample is represented by L* (L* = 100 for white, L * = 0 for black). a* represents the red-green (positive values indicate red, negative values indicate green and zero represents neutral grey). b* represents the yellow-blue axis (positive values indicate yellow, negative values indicate blue and zero represents neutral grey).

Table S6. Colour values on CIELAB space system and sample pictures for PA6F synthesised at varying HMDA excess in the feed.

Entry	DMFDC: HMDA	Catalyst	Catalyst loading (ppm)	Colour values			Sample Pictures
				L*	a*	b*	
1	1:1	No cat.	0	99.48	-0.91	18.92	
2	1:1	TIPT	400	99.06	0.21	9.12	
3	1:1.02	TIPT	400	87.02	1.17	15.51	
4	1:1.045	TIPT	400	89.93	0.26	10.43	

5	1:1.10	TIPT	400	98.00	-1.00	19.77	
6	1:1.045	No catalyst	0	98.10	-7.29	57.39	

10 MALDI-ToF MS end-group analysis of PA6F polymers

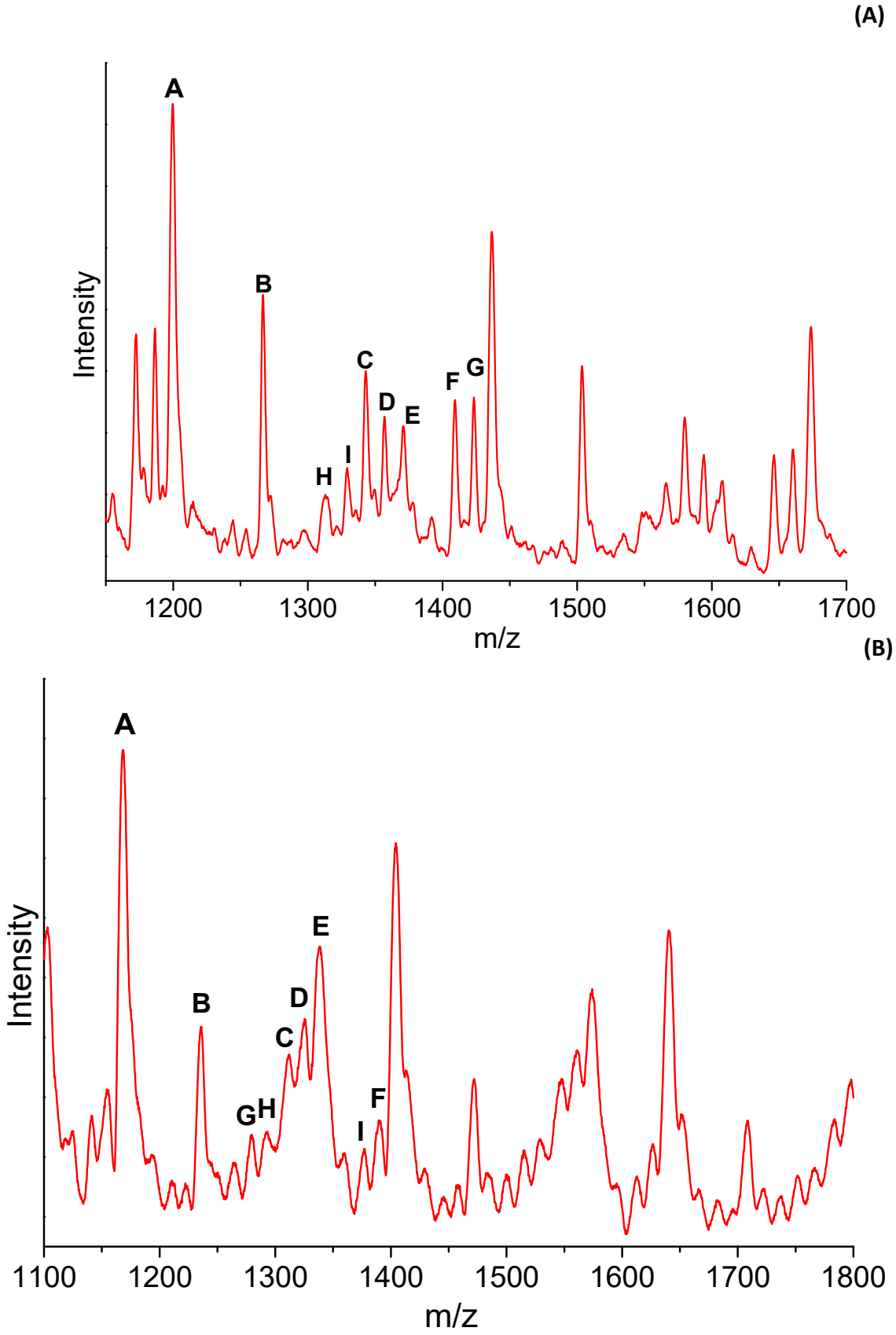


Figure S12. MALDI-ToF MS spectra for PA6F polymers series assignments **(A)** without catalyst and **(B)** with 400 ppm TIPT catalyst.

Table S7. MALDI-ToF end-groups analysis of PA6F polymer synthesised without any catalyst (Table 1, entry 1).

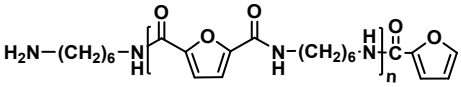
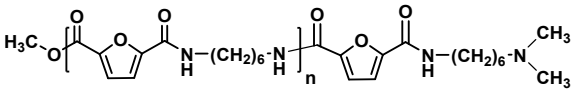
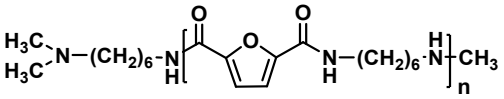
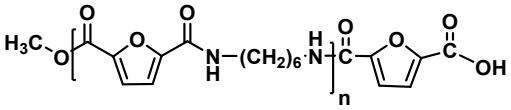
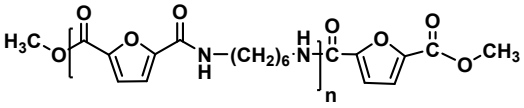
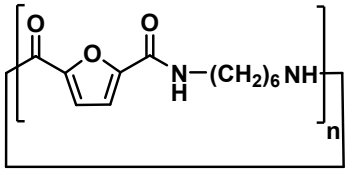
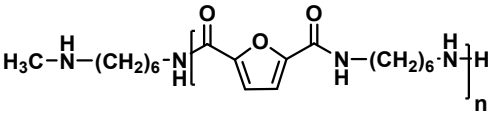
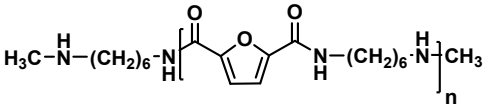
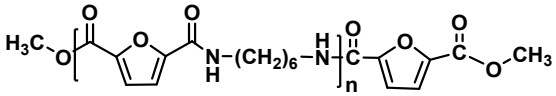
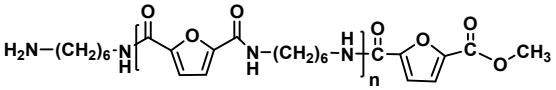
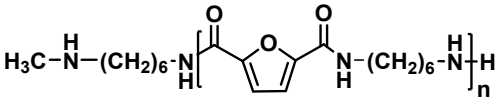
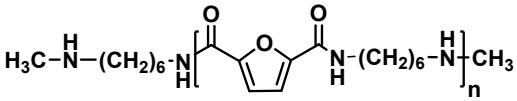
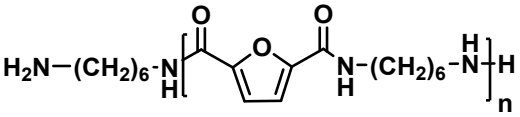
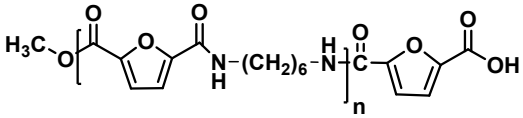
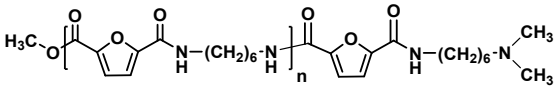
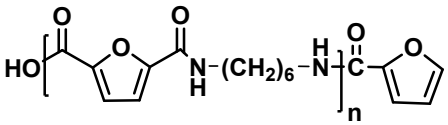
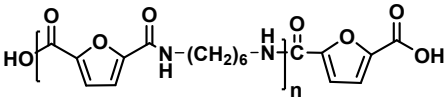
Series	m/z (n)	Proposed end-groups	M_{EG} (cation) Calculated	M_{EG} (cation) Observed
A	1199.6 (4)		210.1 (K^+)	213.0 (K^+)
B	1266.7 (4)		296.4 (Na^+)	296.1 (Na^+)
C	1343.0 (5)		158.3 (H^+)	157.6 (H^+)
D	1356.9 (5)		170.1 (H^+)	171.4 (H^+)
E, F	1371.0 (5), 1409.3 (5)		184.1 (H^+), 184.1 (K^+)	185.4 (H^+), 185.8 (K^+)
G	1423.3 (6)		0 (H^+)	0.9 (H^+)
H	1312.9 (5)		130.2 (H^+)	127.4 (H^+)
I	1329.0 (5)		144.3 (H^+)	143.5 (H^+)

Table S8. MALDI-ToF end-group analysis of PA6F polymer synthesised with 400 ppm TIPT catalyst (Table 1, entry 4).

Series	m/z (n)	Proposed structure	M_{EG} (cation) Calculated	M_{EG} (cation) Observed
A	1168.4 (4)		184.1 (K^+)	184.0 (K^+)
B	1235.5 (4)		268.3 (Na^+)	267.4 (Na^+)
C	1312.2 (5)		130.2 (H^+)	117.2 (H^+)
D	1325.3 (5)		144.3 (H^+)	143.0 (H^+)
E	1338.3 (5)		116.2 (K^+)	117.2 (K^+)
F	1390.0 (5)		170.1 (K^+)	169.4 (K^+)
G	1279.6 (4)		296.4 (K^+)	295.4 (K^+)
H	1292.4 (5)		112.1 (H^+)	110.8 (H^+)
I	1376.8 (5)		156.1 (K^+)	157.1 (K^+)

11 MALDI-ToF MS end-group analysis of PA6F oligomers

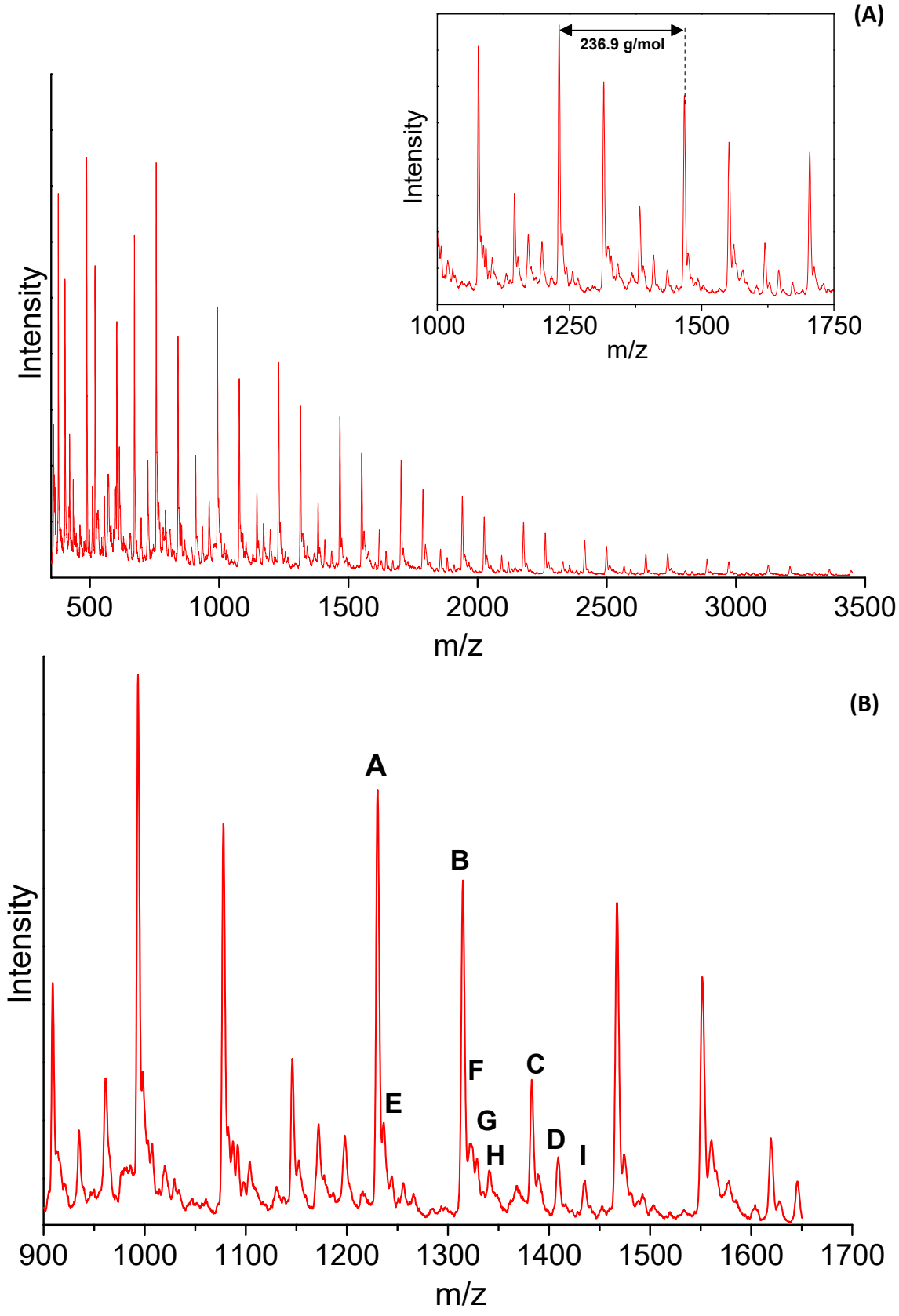
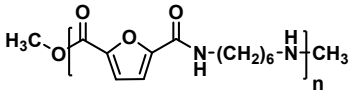
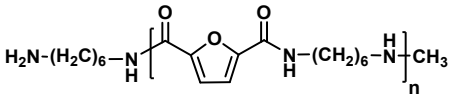
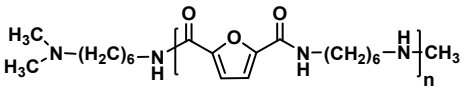
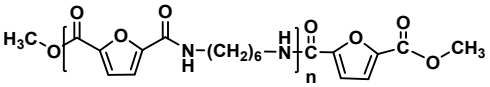
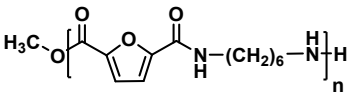
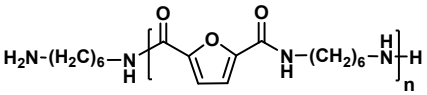
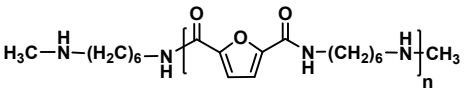
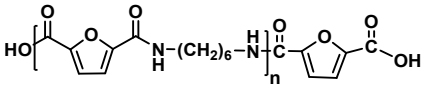
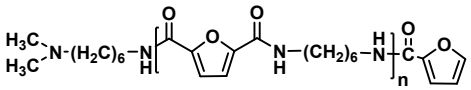


Figure S13. MALDI-ToF MS spectra for PA6F oligomer synthesised without catalyst **(A)** full range and **(B)** in the range 900-1650 m/z (see Table S9 for assignments).

Table S9. MALDI-ToF MS end-groups analysis of PA6F oligomer synthesised without catalyst.

Series	m/z (n)	Proposed end-groups	M_{EG} (cation) Assigned	M_{EG} (cation) Observed
A	1230.4 (5)		46.0 (H^+)	45.0 (H^+)
B	1314.8 (5)		130.2 (H^+)	129.3 (H^+)
C	1382.9 (5)		158.3 (K^+)	159.6 (K^+)
D	1409.1 (5)		184.1 (K^+)	185.7 (K^+)
E	1236.7 (5)		32.0 (Na^+)	29.1 (Na^+)
F	1323.2 (5)		116.2 (Na^+)	114.6 (Na^+)
G	1328.8 (5)		144.3 (H^+)	143.2 (H^+)
H	1341.1 (5)		156.1 (H^+)	155.2 (H^+)
I	1434.6 (5)		210.3 (K^+)	212.2 (K^+)

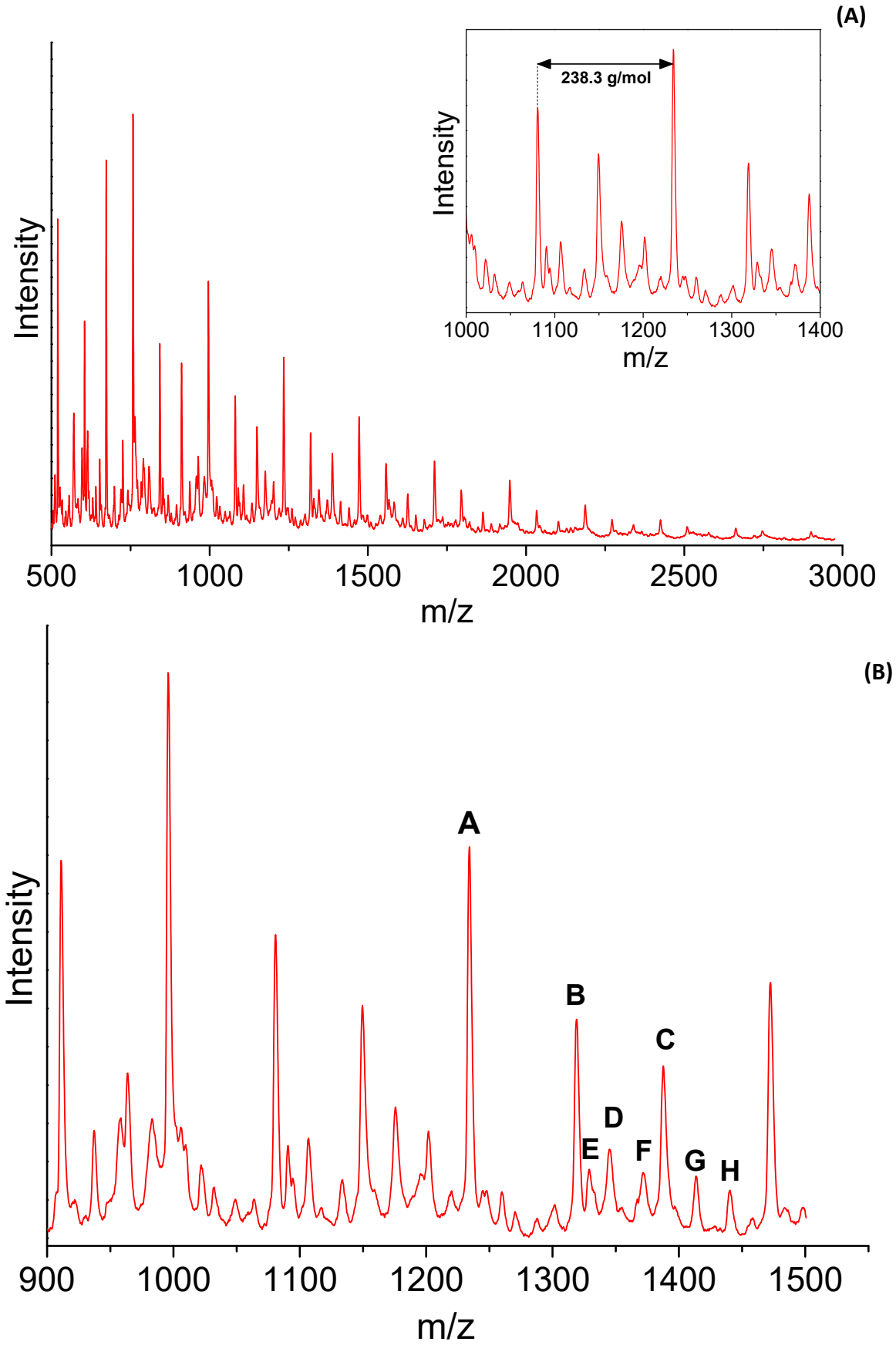
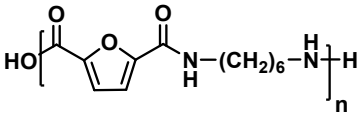
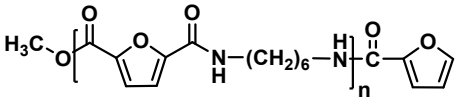
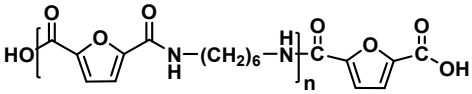
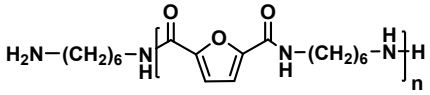
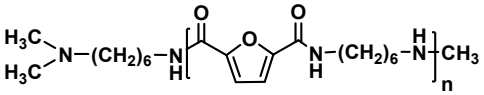
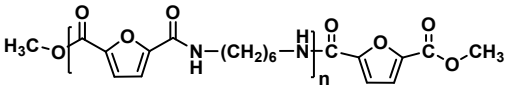
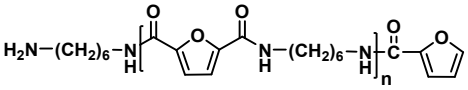


Figure S14. MALDI-ToF MS spectra for PA6F oligomer synthesised with 400 ppm TIPT **(A)** full range and **(B)** in the range 900-1650 m/z (see Table S10 for peak assignments).

Table S10. MALDI-ToF MS end-groups analysis of PA6F oligomer synthesised with 400 ppm TIPT.

Series	m/z (n)	Predicted end group	M_{EG} (cation)	M_{EG} (cation)
			Assigned	**Observed**
A	1234.2 (5)		18.0 (Na^+)	19.9 (Na^+)
B	1319.0 (5)		126.1 (H^+)	126.7 (H^+)
C	1387.7 (5)		156.1(K^+)	157.4 (K^+)
D,E	1345.6 (5), 1329.0 (5)		116.2 (K^+), 116.2 (Na^+)	114.9 (K^+), 115.1 (Na^+)
F	1372.1 (5)		158.2 (Na^+)	157.5 (Na^+)
G	1414.1 (5)		184.1 (K^+)	183.2 (K^+)
H	1440.4 (5)		210.3 (K^+)	209.9 (K^+)

12 PA6F compression moulded films

Figure S15. Compression moulded films of PA6F.

13 Stress-strain curves from PA6F tensile testing

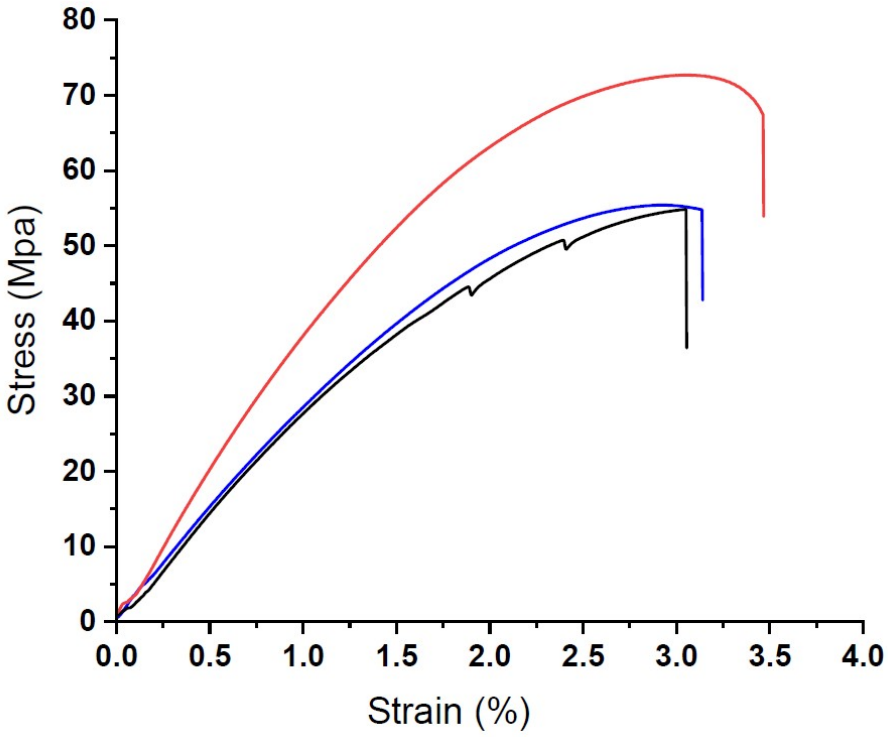


Figure S16. Stress-strain curves for PA6F compression moulded specimens.

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