Supporting Information: Aminolytic upcycling of poly(ethylene terephthalate) wastes using thermally-stable organocatalyst

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Experimental Part

Materials

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, Sigma, 98%), Methanesulfonic acid (MSA, Sigma, >99%), 1,8-Diazabicyclo[5.4.0]undéc-7-ène (DBU, Fisher, 98%), Benzoïc acid (BA, Sigma, >99.5%), Ethanolamine (EA, Fisher, 99%), N-Methylethanolamine (NMEA, Sigma, >98%), 2-(2-Aminoethylamino)ethanol (AEAE, Fisher, 99%), 2,2-Amino(ethoxy) ethanol (AEE, Sigma, 98%), 2-Amino-2-methyl-1-propanol (AMP, Fisher, 99%), Dimethyl Succinate (DMS, Fisher, 98%), Acetone (extra dry, Fisher, 99.8%) were all used as received. Acetone, dichloromethane (DCM), dietheyl ether, ethyl acetate, hexane, chloroform, dimethylsulfoxide, methanol, water either used for precipitation or recrystallization of depolymerization products or solubility tests were technical grade furnished by Scharlab. Poly(ethylene terephtalate) (PET) samples were provided by EkoREC in San Sebastian.

Formation of TBD:MSA catalyst

A Schlenck tube of 100 ml was dried under vacuum with a flame before placing it in the glovebox. The organocatalyst was prepared in Schlenck tube in the glovebox with the addition of TBD (1g, 7.18 mmol) followed by the MSA (0.466 ml, 7.18 mmol), during which acidic vapors are observed in the Schlenck. A magnetic stirrer is loaded in the Schlenck and the mixture is stirred during 5 min. Then, 60 ml of dry acetone is transferred in the tube and closed with a rubber cap. The Schlenck is removed from the glovebox and place in a pre-heated oil-bath at 57°C. Once the catalyst is completely solubilized, the agitation and the heating is stopped until room temperature is reached in order slowly crystallized the TBD:MSA protic ionic liquid salt. The tube is then transferred at +6°C during 72h. White needles were obtained in the Schlenck and filtered and washed with fresh acetone. The product (1.55 g, yield = 92 %) is finally dried under vacuum at 40°C and stored in desiccator to avoid the protonation of the catalyst.

Typical procedure of PET depolymerization using various amino-alcohols.

Bis(2-hydroxyethyl) terephtalamide (BHETA): PET samples (0.5g, 2.6 mmol), TBD:MSA salt (0.061g, 0.26 mmol) and ethanolamine (EA, 3.18g, 51.04 mmol) were loaded in a 50 ml Schlenck tube with an oval magnetic stirrer. The solution was degassed during 30 min with N_2 under agitation. The Schlenck is then poured in a pre-heated bath at 180°C and the

depolymerization is started. After 10 min, the mixture is completely clear and all PET pellets disappeared. The mixture was then cooled to rt. The solution slowly recrystallized in the mixture and 10 ml of DMSO was added to completely solubilize it and precipitated in DCM. After the white precipitate was filtrated and washed with DCM, Bis(2-hydroxyethyl) terephtalamide (BHETA, 0.61g, 2.42 mmol, yield = 93 %) was obtained as a fine white powder.
The calculation of the yield is based on the molar ratio between the product and the initial PET sample and relies on the statement that every mole of the repeating unit of the PET gives one mole of terephtalamide diol, as follows:

$$Yield\ (\%) = \frac{n_{BHETA}}{(m_{PET}/MM_{PET\ repeating\ unit})} * 100$$

with $MM_{\text{PET repeating unit}} = 192\ \text{g.mol}^{-1}$

Purification by recrystallization: Another procedure was followed for the purification of BHETA. At the end of the depolymerization, the oil bath was stopped and the mixture was slowly cooled down to rt overnight. Then, acetone was added over the solid white-yellow recrystallized solid, the mixture was filtrated and was with fresh acetone three times (3 x 20 ml). The white solid was the placed under vacuum overnight (yield = 73%).

Similar procedures have been performed using other amino-alcohols and different solvents for purification process. All ^{1}H and ^{13}C NMR characterizations of the diols were reported in SI (Figures S1-10).

Bis(2-hydroxyethyl)dimethylterephtalamide (BHEDMTA): PET samples (0.5g, 2.6 mmol), TBD:MSA salt (0.061g, 0.26 mmol) and N-methylethanolamine (NMEA, 3.91g, 51.04 mmol) were reacted during 15 min until the disappearance of PET pellets. At the end of the polymerization, the mixture was slowly cooled down to rt. Then, 10 ml of MeOH was added to completely solubilize it and precipitated in excess of Et_2O. Once the white precipitate was filtrated and washed with Et_2O. The white solid was placed under vacuum overnight (yield = 76%, 0.55g).
Purification by recrystallization: At the end of the depolymerization, the oil bath was stopped and the mixture was slowly cooled down to rt overnight. Then, the reactor was transferred to the fridge to allow a higher recrystallization at 6°C during 48h. The mixture was filtered and washed with acetone. The white solid was placed under vacuum overnight (yield = 73%).

Bis(2-((2-hydroxyethyl)amino)ethyl)terephthalamide (BHEAETA): PET samples (2 g, 10.42 mmol), TBD:MSA salt (0.245g, 1.04 mmol) and 2-(2-Aminoethylamino)ethanol (AEAE, 21.7g, 208 mmol) were reacted during 30 min until the disappearance of PET pellets. At the end of the depolymerization, the oil bath was stopped and the mixture was slowly cooled down to rt overnight. Then, the reactor was transferred to the fridge to allow a higher recrystallization at 6°C during 48h. The mixture was filtered and washed with acetone. The white solid was placed under vacuum overnight (yield = 55.4%, 1.95g).

Bis(2-(2-hydroxyethoxy)ethyl)terephthalamide (BHEETA): PET samples (2g, 10.4 mmol), TBD:MSA salt (0.245g, 1.04 mmol) and 2-(2-Aminoethoxy)ethanol (AEE, 21.88g, 208.1 mmol) were reacted during 30 min until the disappearance of PET pellets. At the end of the

polymerization, the mixture was slowly cooled down to rt. Then, 10 ml of DMSO was added to completely solubilize it and precipitated in excess of DCM. Once the white precipitate was filtrated and washed with DCM. The white solid was placed under vacuum overnight (yield = 92.2%, 3.26g).

Bis(1-hydroxy-2-methylpropan-2-yl)terephthalamide (BHMPTA): PET samples (2g, 10.42 mmol), TBD:MSA salt (0.245g, 1.04 mmol) and Aminomethyl propanol (AMP, 18.57g, 208.3 mmol) were reacted during 30 min. Then, the reactor was left during 1 day at room temperature and followed by 48h at +6°C to allow the crystallization of the product. The mixture was filtered and washed with water. The white solid was placed under vacuum overnight (yield = 60%, 1.93g).

Synthesis of Poly(ester-amide)s. BHETA (0.5g, 1.98 mmol), dimethyl succinate (0.29g, 1.98 mmol) and DBU:BA salt (0.027g, 0.1 mmol) were loaded in a 50 ml Schlenck tube with an oval magnetic stirrer. The mixture of solids was degassed during 30 min with N_2 under agitation. The Schlenck is then poured in a pre-heated bath at 200°C and the polymerization is started at 500 rpm. After 2h at 200°C under N_2, the mixture is then placed under a static vacuum during 1h. Vacuum is applied during 4 more hours at 200°C. After 5h at 200°C vacuum, the polymerization is stopped and the polymers analyzed by NMR, DSC and SEC.

This procedure was applied for BHEDMTA, BHEAETA, BHEETA and BHMPTA monomers at 180°C.

Characterizations

Nuclear Magnetic Spectroscopy (NMR) analysis. Terephtalamides-based diols and kinetics of the depolymerization were all runed on a Bruker Advance 300 (300 MHz) spectrometer in d_6-DMSO.

Melting point measurements. The melting points of the terephtalamide diols were determined using a Stuart Melting Point Apparatus SMP3.

Differential Scanning Calorimetry (DSC). The thermal behavior of the polymers was determined using a DSC 8500 (PerkinElmer). Experiments were carried out at heating and cooling rates of 10°C/min from -60 to 150°C and 20°C/min from 40 to 300°C under a nitrogen flow of 20 mL/min, employing samples of 4.5-5.5 mg. The instrument was calibrated with indium and tin standards. The values of melting temperature (T_m) and the latent heat of melting (ΔH_m) reported were taken from second heating scan.

Calculation of rate constant. The rate constants were calculated for all the organocatalysts (TBD:MSA, DBU:BA, TBD, no catalyst).

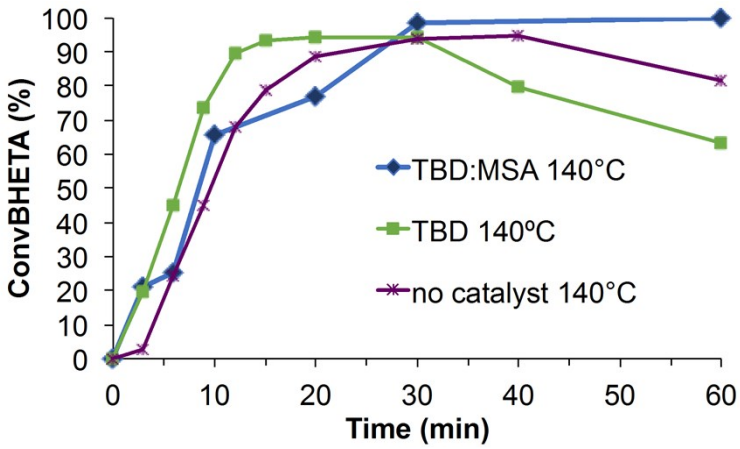


Figure S1. Depolymerization of PET powder using ethanolamine and different catalyst at 140°C.

PET concentration was calculated as follows: $[PET]_{initial}$ = 0.0026 mol / 0.0031L of ethanolamine = 0.826M. Concentration of BHETA over time was calculated taking into account the initial load of PET and conversion.

Reaction rate: $r = k[PET]^n[Ethanolamine]^m$

[Ethanolamine] being constant due to its large excess, $k_{app} = k[Ethanolamine]^m$ and the order of the reaction regarding to PET is equal to 1, as follows:

$r = -k_{app}[PET]^1$

$$\frac{dBHETA}{dt} = -\frac{dPET}{dt}$$

$$-\frac{dPET}{dt} = r$$

$$\frac{dPET}{dt} = -k_{app}[PET]$$

$$-\int \frac{dPET}{[PET]} = \int k_{app}\, dt$$

$$ln\,[PET] = -k_{app}\, t$$

$k = k_{app}/[Ethanoamine]$ (with [Ethanoamine]=16.53 M)

Table S1. Rate constant determination of PET depolymerization with ethanolamine.

Entry	Temp. (°C)	Catalyst (eq)	k_{app} (min^{-1})	k ($min^{-1}M^{-1}$)
1	180	TBD:MSA (0.1)	0.480	0.029
2	180	TBD:MSA (0.05)	0.272	0.016
3	180	DBU:BA (0.1)	0.318	0.019
4	180	TBD (0.1)	0.324	0.020
5	180	/ (none)	0.261	0.016
6	140	TBD (0.1)	0.194	0.012
7	140	/ (none)	0.117	0.007

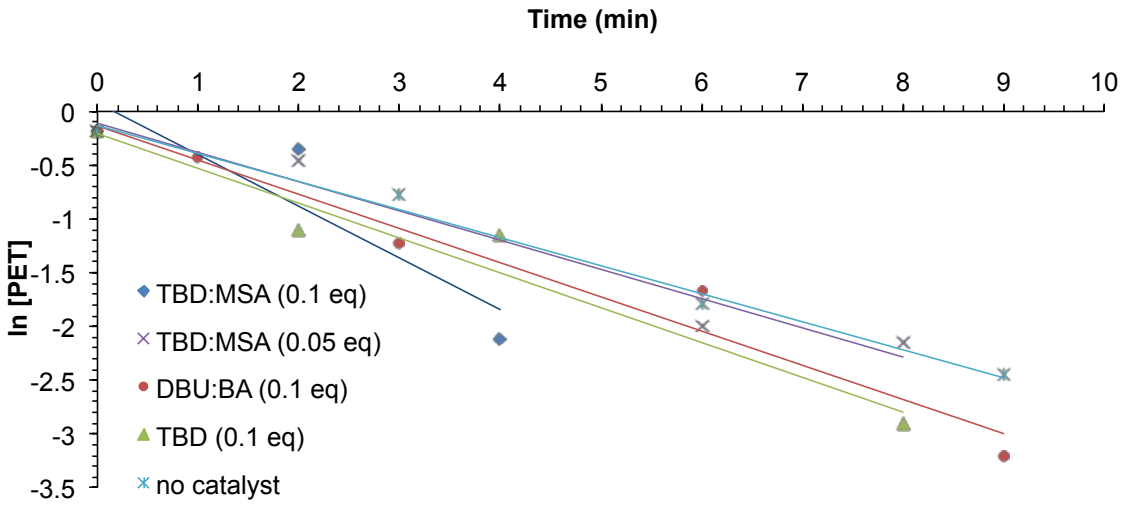


Figure S2. Kinetic plot of PET depolymerization with ethanolamine at 180°C.

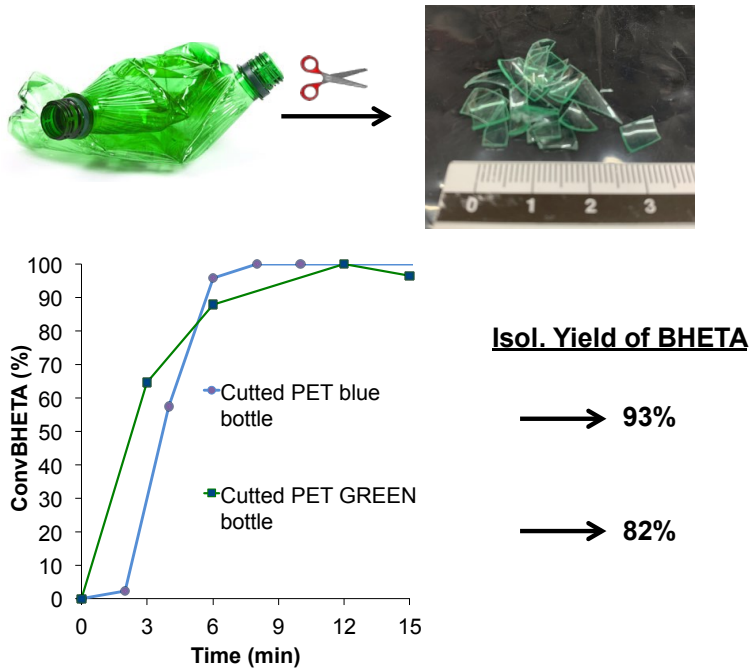
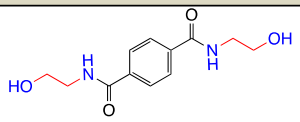
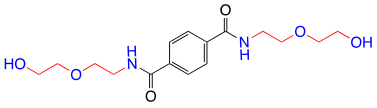
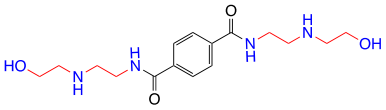
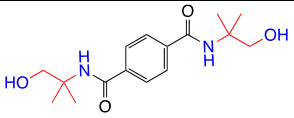
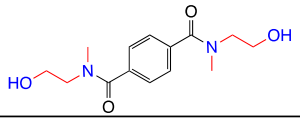


Figure S3. Depolymerization of green PET bottles using ethanolamine and TBD:MSA salt as catalyst.

Table S2. Solubility table of terephtalamide diols at 10mg/ml.

Entry	Terephtalamide monomer	Hexane	$CHCl_3$	EtOAc	Acetone	DMSO	MeOH	H_2O
1		- - -	- - -	- - -	- - -	+ + +	- - -	- - -
2		- - -	- - -	- - -	- - -	+ + +	+ + +	+ + +
3		- - -	- - -	- - -	- - -	+ + +	-	+ + +
4		- - -	- - -	- - -	- - -	+ + +	+ + +	- - -
5		- - -	- - -	- - -	- - -	+ + +	+	+ + +

- - - = not sol., - = slightly insol., + = slightly sol., + + + = soluble

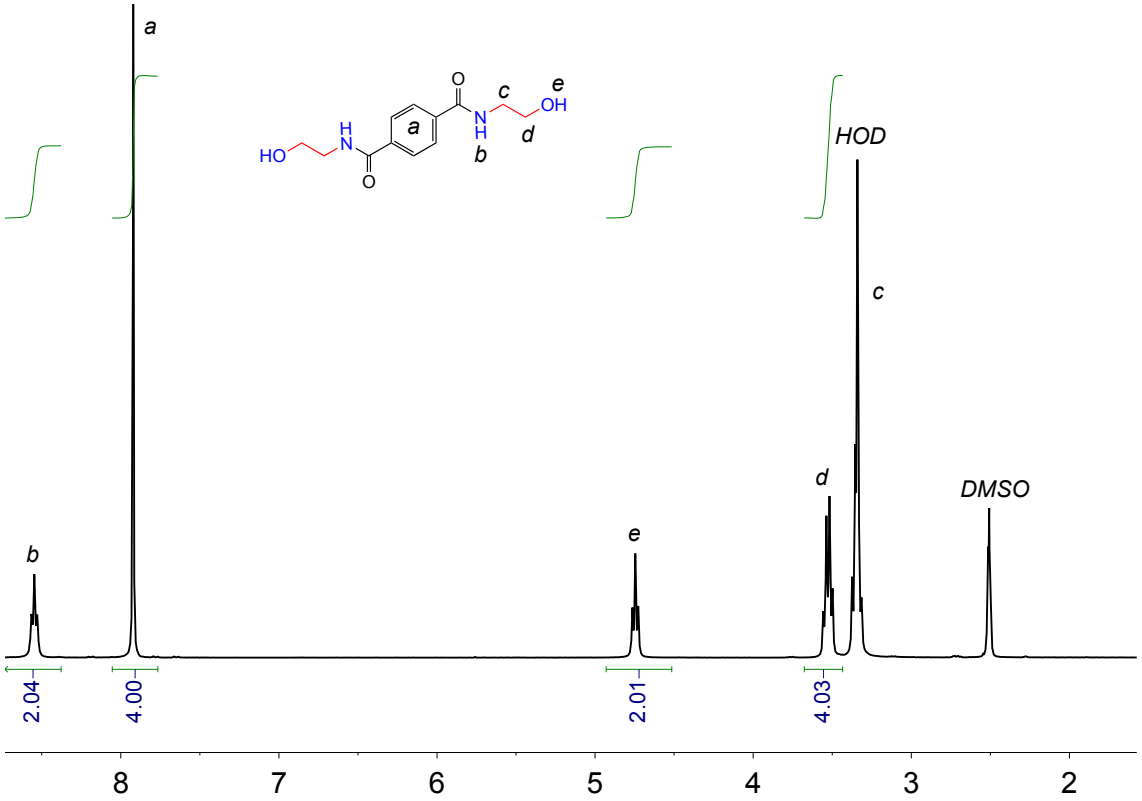


Figure S4. ^{1}H NMR (300MHz, d_6-DMSO) of BHETA.

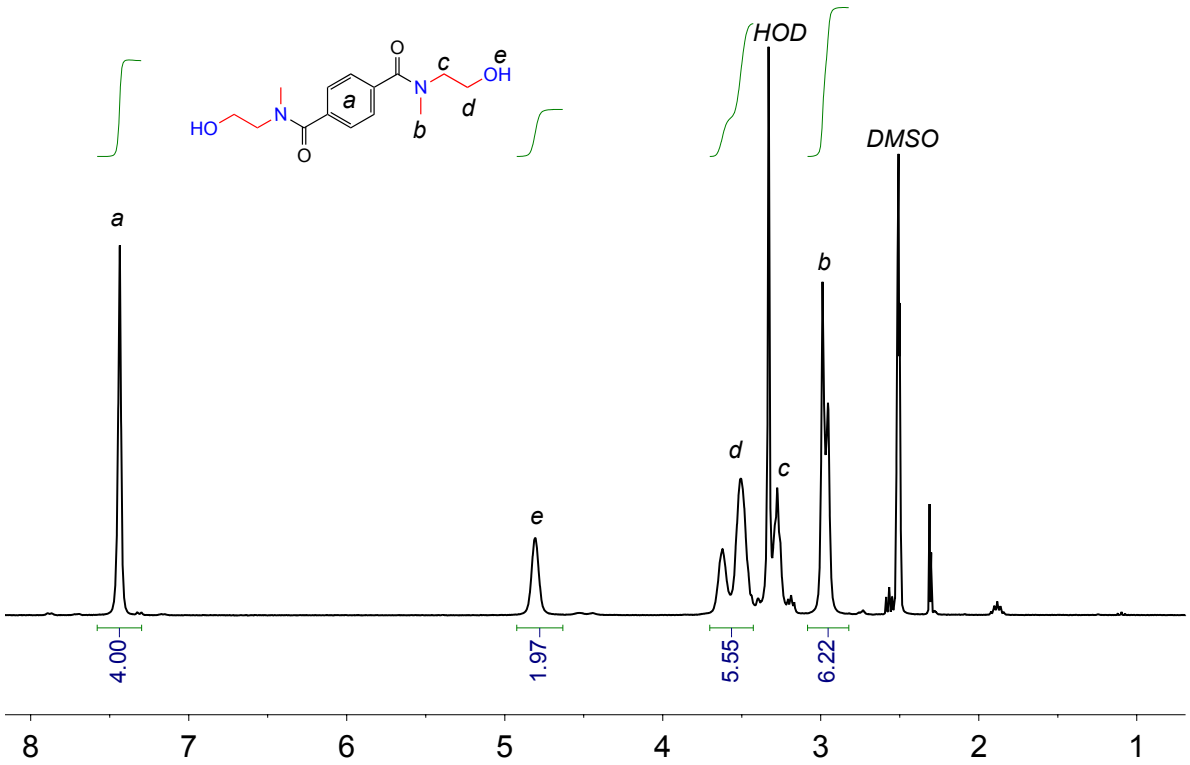


Figure S5. ^{1}H NMR (300MHz, d_6-DMSO) of BHEDMTA.

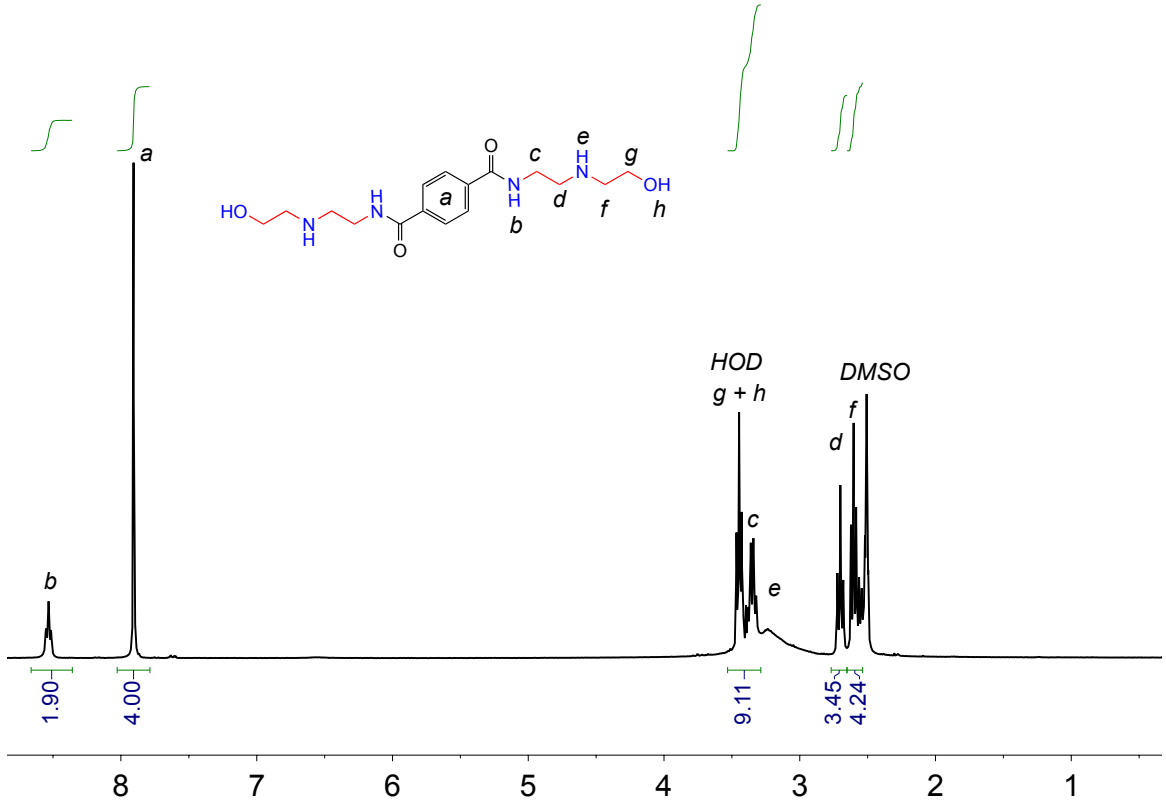


Figure S6. ^{1}H NMR (300MHz, d_6-DMSO) of BHEAETA.

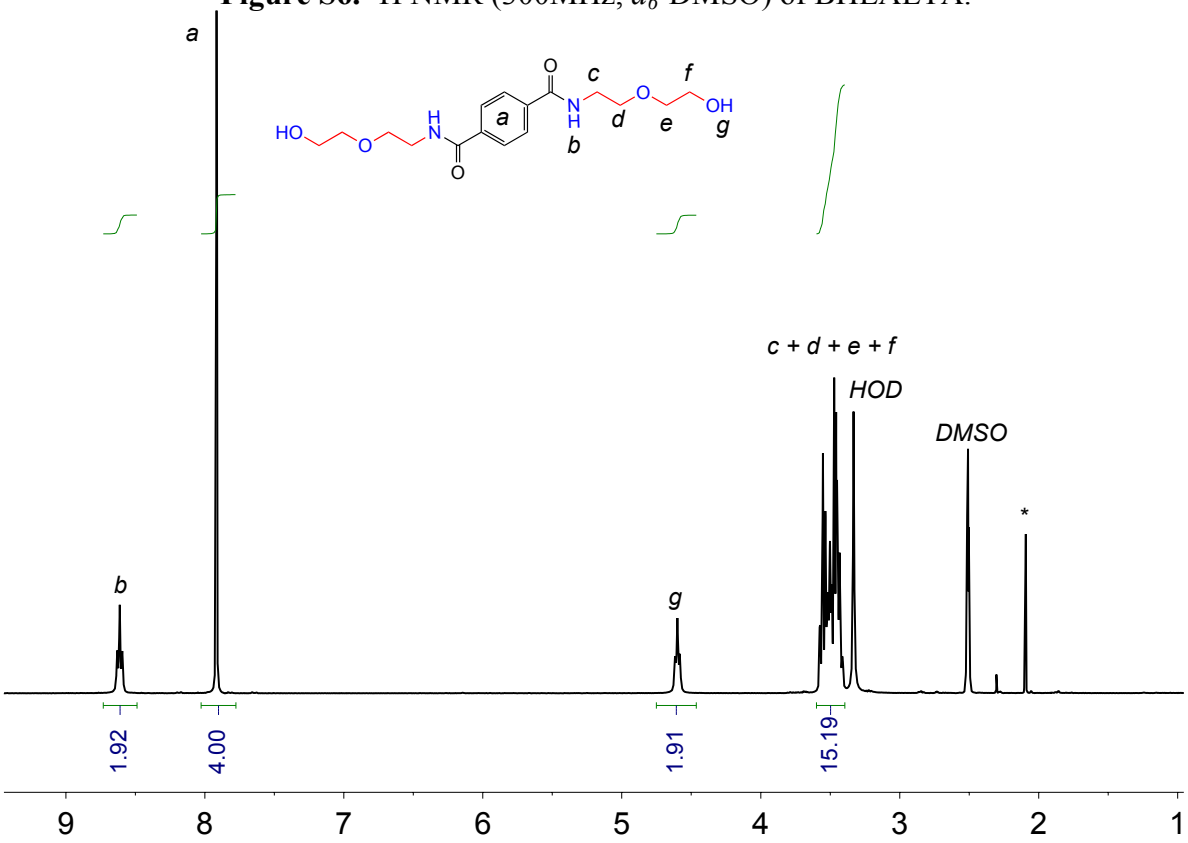


Figure S7. ^{1}H NMR (300MHz, d_6-DMSO) of BHEETA.

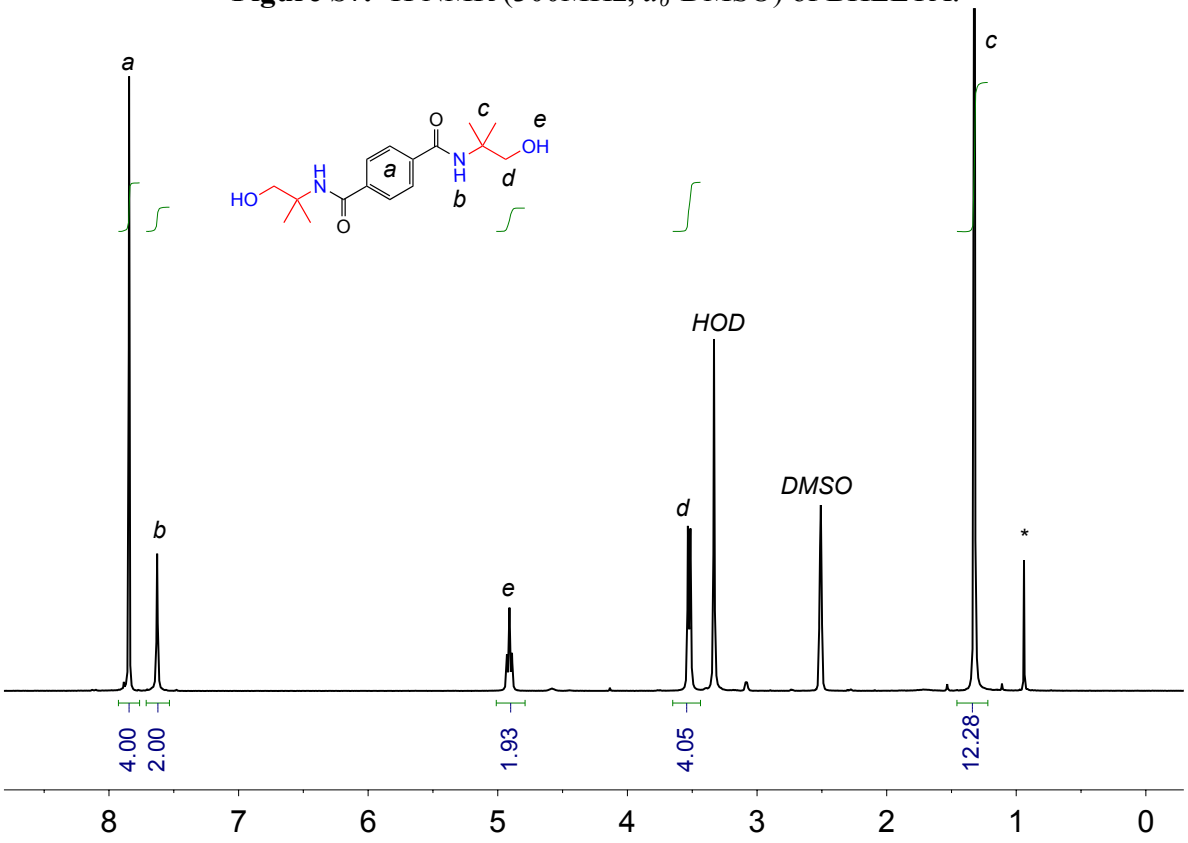


Figure S8. ^{1}H NMR (300MHz, d_6-DMSO) of BHMPTA.

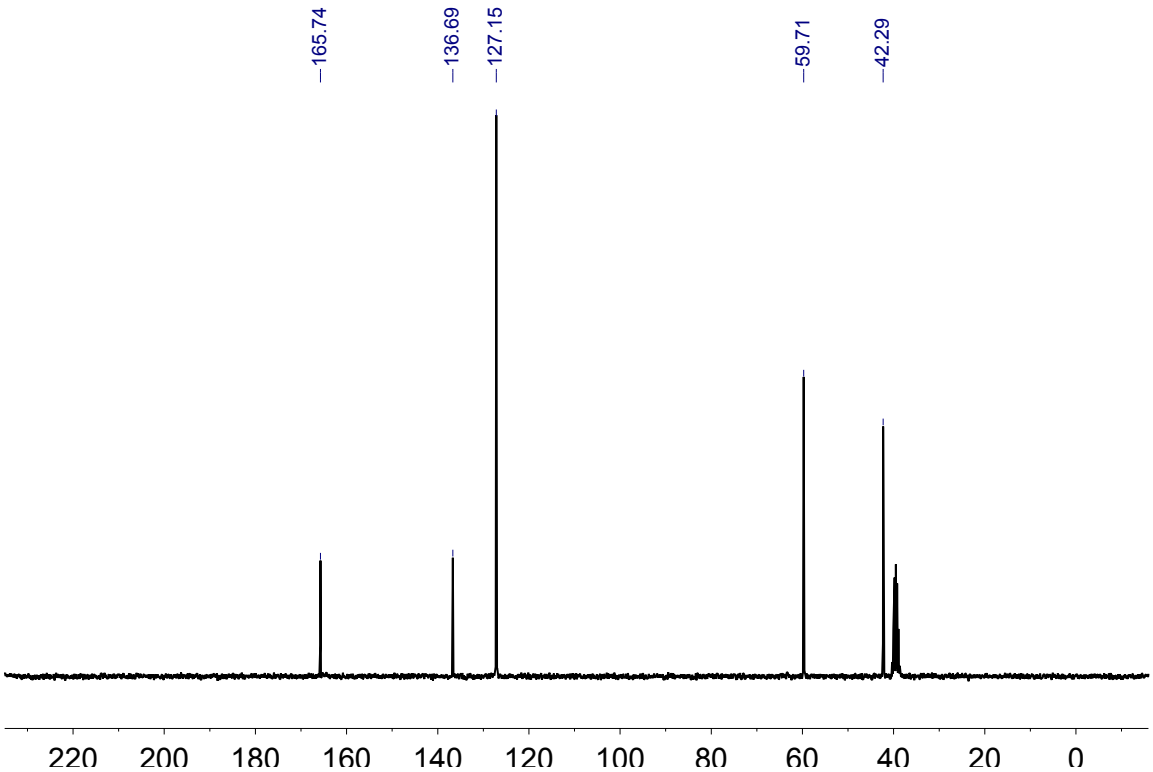


Figure S9. ^{13}C NMR (300MHz, d_6-DMSO) of BHETA.

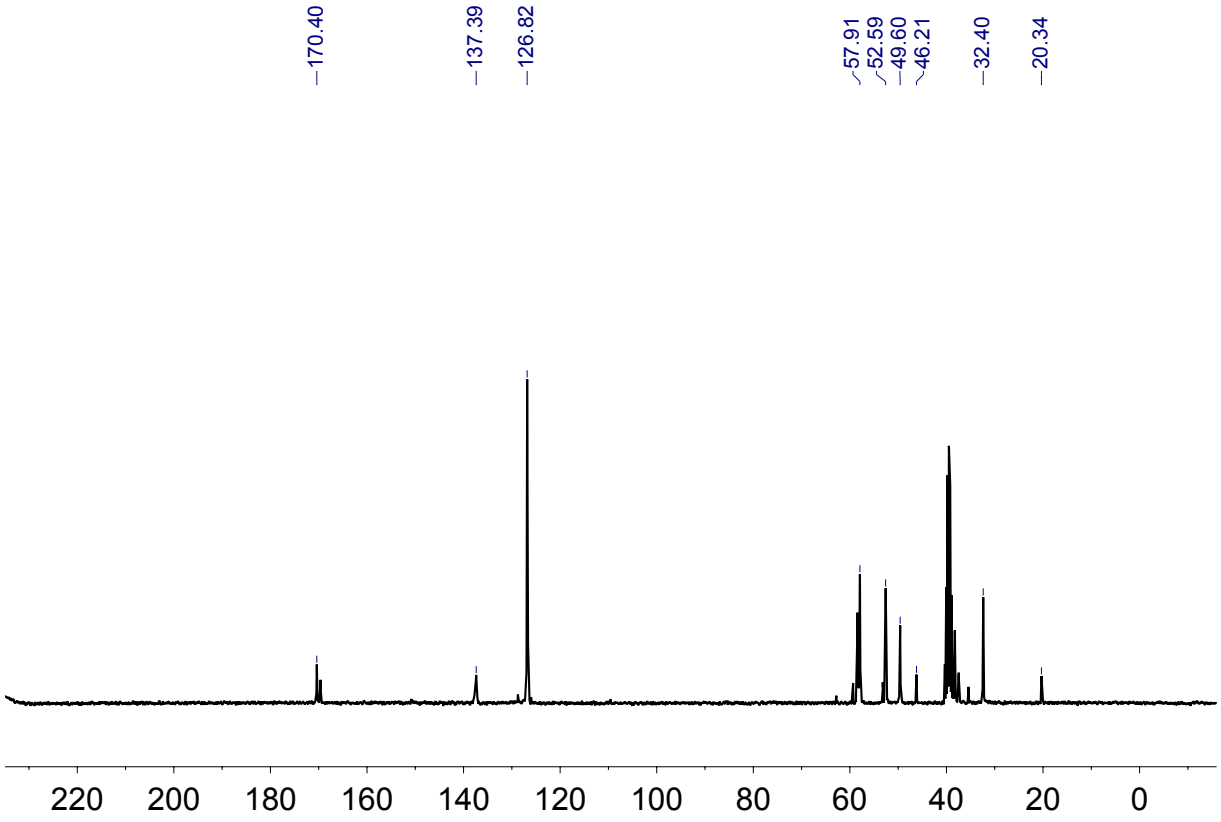


Figure S10. ^{13}C NMR (300MHz, d_6-DMSO) of BHEDMTA.

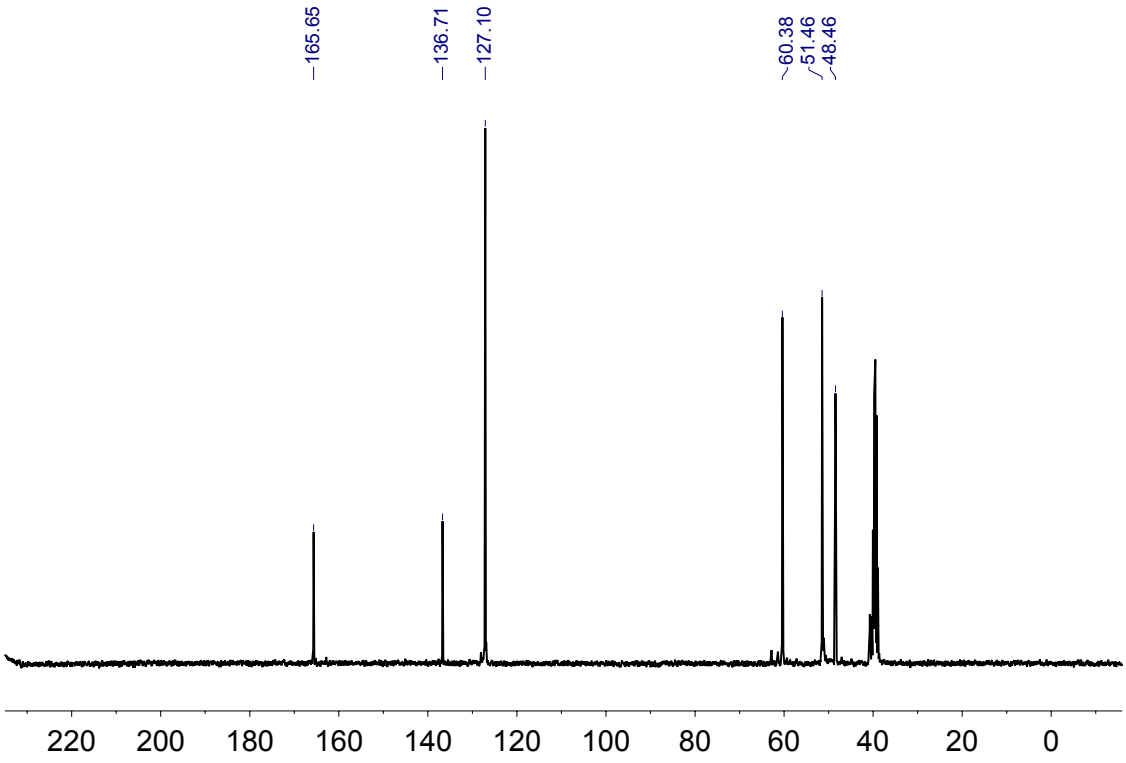


Figure S11. ^{13}C NMR (300MHz, d_6-DMSO) of BHEAETA.

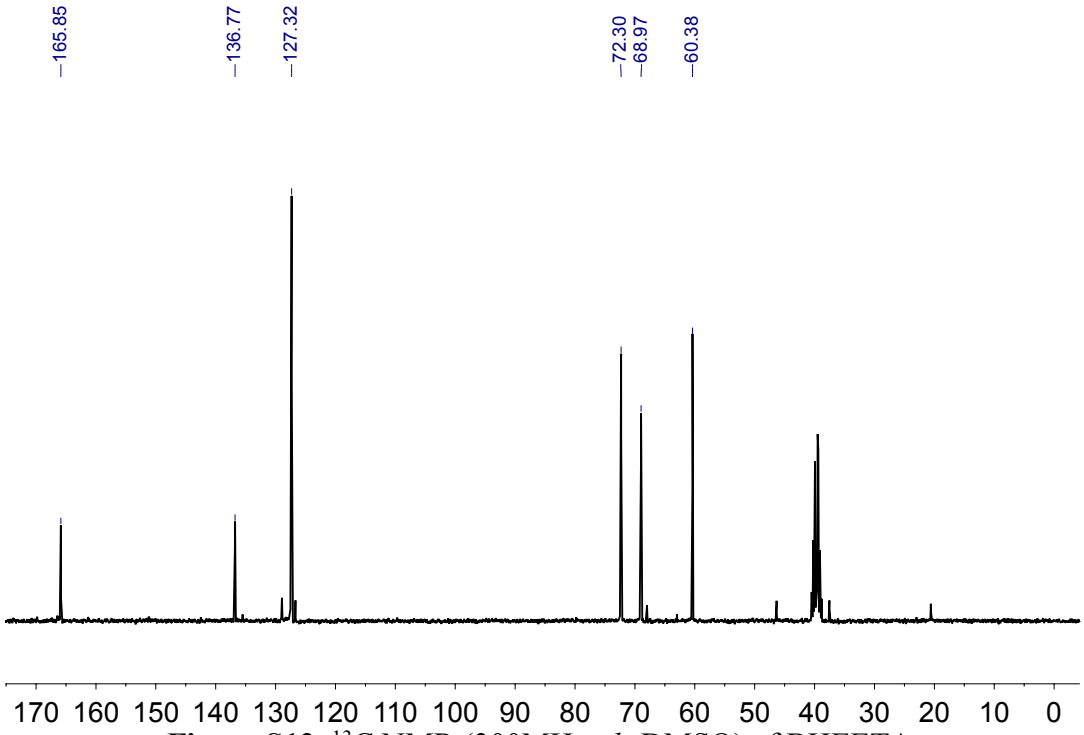


Figure S12. ^{13}C NMR (300MHz, d_6-DMSO) of BHEETA.

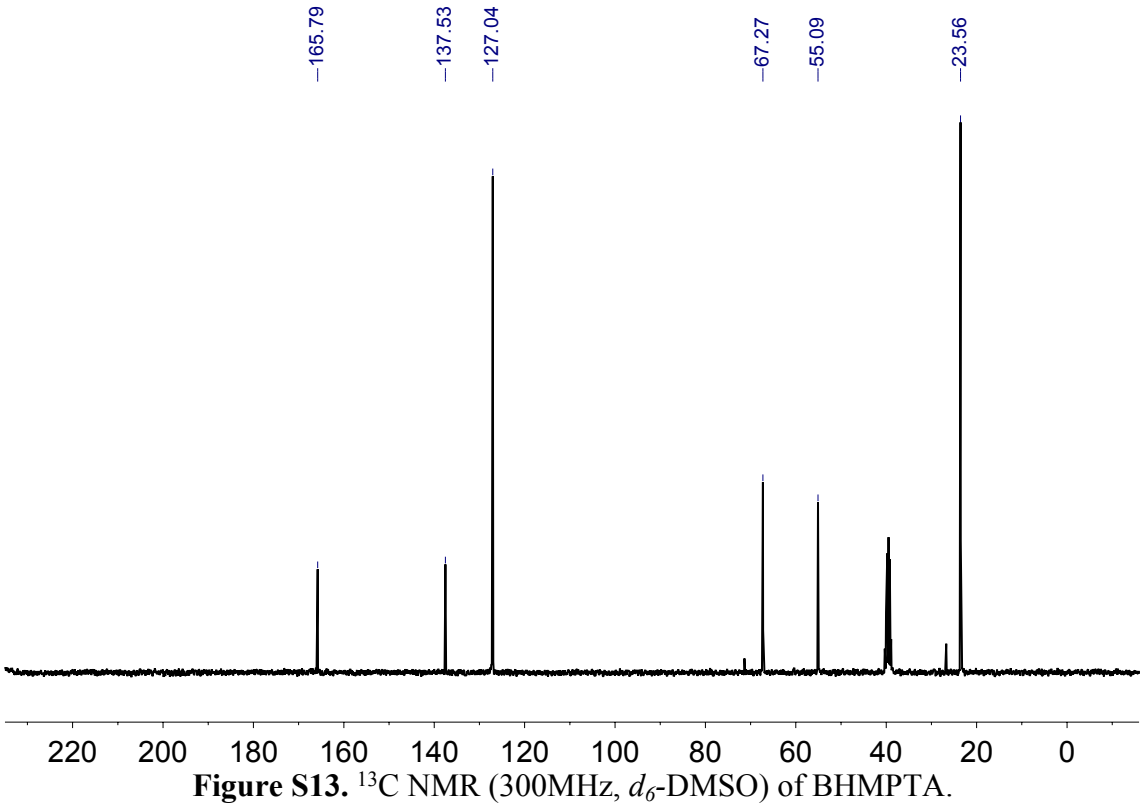


Figure S13. ^{13}C NMR (300MHz, d_6-DMSO) of BHMPTA.

Table S3. Polymerization of diesters with terephtalamides diols.

Entry[a]	Terephtalamide diol	Diester	Temp. (°C)	M_n (kDa)[b]	M_w (kDa)[b]	M_w/M_n[b]	T_g (°C)[c]
1	BHETA	DMS	200	1.6	2.2	1.34	7
2	BHETA	DMA	200	1.9	2.8	1.46	18
3	BHEETA	DMS	180	/[d]	/[d]	/[d]	/[d]
4	BHMPTA	DMS	180	/[d]	/[d]	/[d]	/[d]
5	BHEAETA	DMS	180	/[e]	/[e]	/[e]	-11

[a] 1 eq. of diol and 1 eq. of diester (in total) were used with 0.1 eq of DBU:BA as catalyst, at 180°C.
[b] Determined by GPC in DMF (LiBr)
[c] Determined by DSC

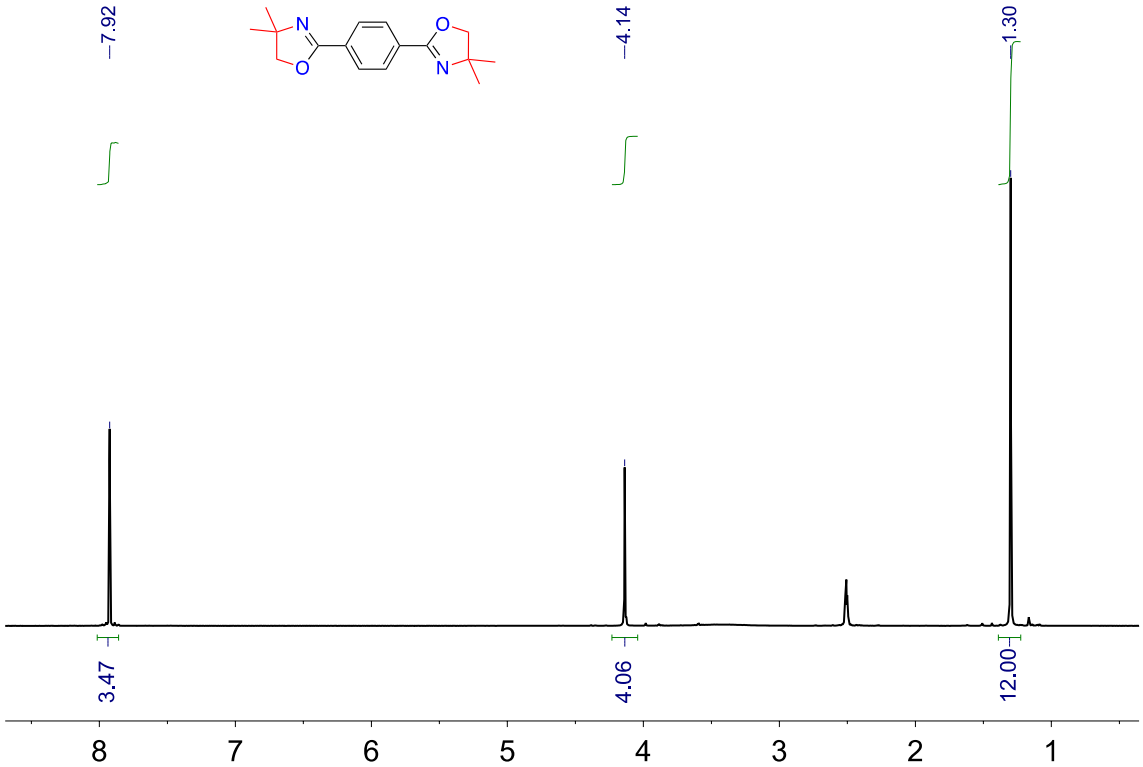


Figure S14. ^{1}H NMR (300MHz, d_6-DMSO) of 2,2'-(1,4-phenylene)-bis-(4,4-dimethyl-2-oxazoline) (PBDMO).

Calculation of PET crystallinity.

The differences observed in terms of reactivity between the bottle grade amorphous PET and commercial PET pellets can be explained taking into account the degree of crystallinity. Since both are the same polymer to analyses the influence of the processing on the degree of crystallinity, DSC measurements were carried out at a constant heating rate of 20ºC under N_2 flow. As expected, the 2nd heating and the cooling were identical because their intrinsic properties are equal since they are the same material. However, during the first heating rate in the case of the amorphous bottle grade PET a characteristic cold crystallization could be observed due to the relaxation of the material during the heating. Thus, the new crystals formed contribute to the enthalpy observed on the melting point. Therefore, to calculate the starting crystallinity the enthalpy of cold crystallization was discounted from the melting enthalpy employing the following equation[1]:

$$Degree\ of\ crystallinity = \frac{\Delta H_m - \Delta H_c}{\Delta H_0} x\ 100$$

Where $^{\Delta H_m}$ is the melting enthalpy, $^{\Delta H_c}$ is the cold crystallization enthalpy and $^{\Delta H_0}$the enthalpy of the 100% percent crystalline PET which is equal to 135J/g.[2]

Thus, taking into account the enthalpies obtained on DSC experiments and applying the previous equation, we concluded that bottle grade PET samples had 7.4% crystallinity degree while the pellet posses a higher value of 40%.

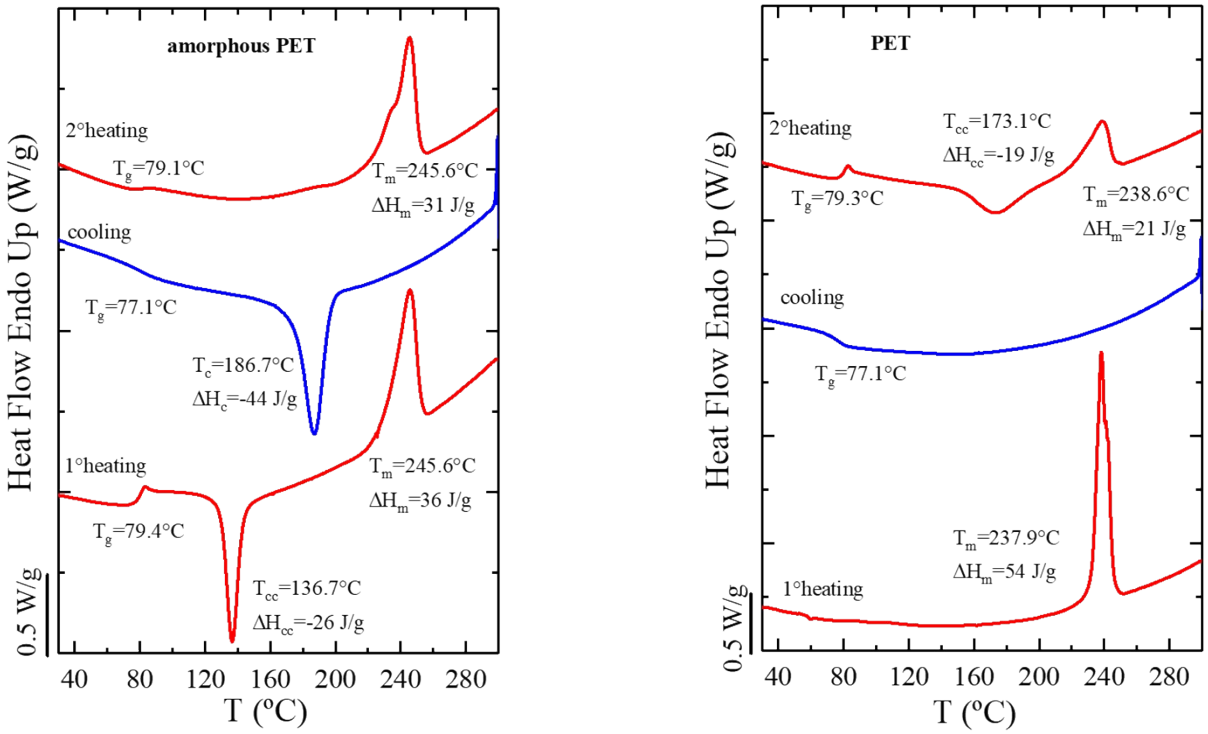


Figure S15. DSC analysis of amorphous PET bottle sheet (left) and PET white pellets (right).

References

1. Bruckmoser K, Resch K. Effect of processing conditions on crystallization behavior and mechanical properties of poly(lactic acid) staple fibers. *J Appl Polym Sci*. 2015;132(33):n/a-n/a. doi:10.1002/app.42432
2. Shieh Y-T, Lin Y-S, Twu Y-K, Tsai H-B, Lin R-H. Effect of crystallinity on enthalpy recovery peaks and cold-crystallization peaks in PET via TMDSC and DMA studies. *J Appl Polym Sci*. 2009;116(3):NA-NA. doi:10.1002/app.31570