SUPPORTING INFORMATION

Biobased Polyamide Thermosets: From a Facile One-Step Synthesis to Strong and Flexible Materials

Charalampos Pronoitis, Geng Hua, Minna Hakkarainen, and Karin Odelius*

Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

*Corresponding author: Email: hoem@kth.se, Tel: +46-8 790 80 76 (K.O.).

The SI contains 9 figures and 2 tables in 8 pages.

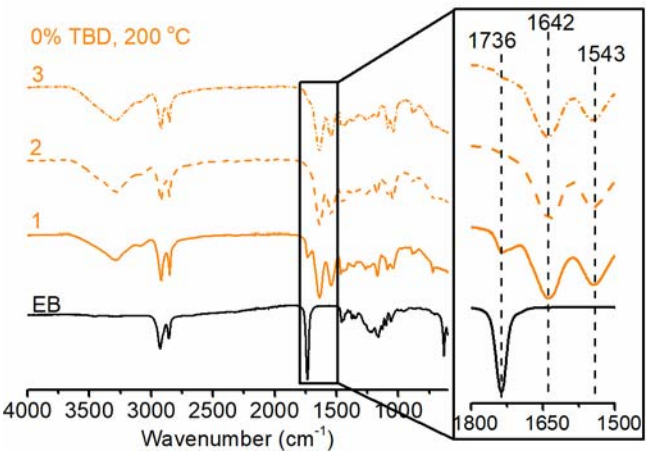

Figure S1. Compiled FTIR spectra of the three specimens named 1, 2, 3 respectively obtained from the mixture synthesized at 200 °C in the absence of TBD. The ECC (%) calculated using eq. 1 varies between 1 and 10% denoting an inhomogeneous product.

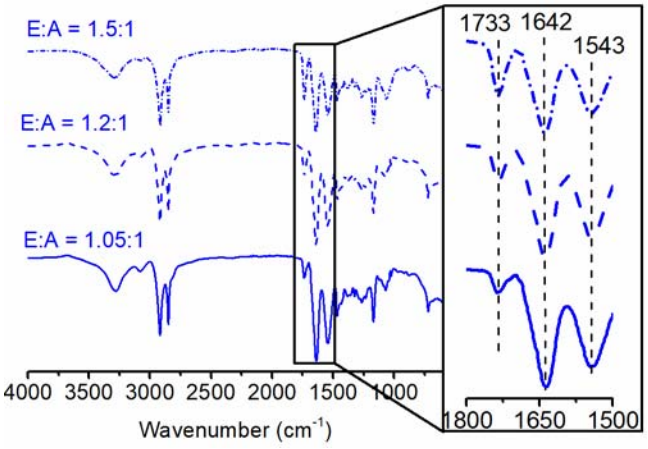

Figure S2. Compiled FTIR spectra of the thermosets synthesized with an excess of EB.

Table S1. Thermal and mechanical properties of the polyamide thermosets after drying under vacuum at 130 ˚C for 24 h.[a]

E:A[b]	T_g (˚C)[c]	T_m (˚C)[c]	ΔH_m (J g^{-1})[c]	T_c (˚C)[d]	ΔH_c (J g^{-1})[d]	E (MPa)	σ_b (MPa)	ε_b (%)
1:1	37 ± 0.4	68 ± 1.0	8 ± 0.5	48 ± 0.9	10 ± 0.4	510 ± 80	14 ± 3	46.5 ± 14
1:1.2	30 ± 0.6	66 ± 0.6	14 ± 0.2	45 ± 0.4	16 ± 0.4	322 ± 38	11.5 ± 1.0	72 ± 25
1:1.5	11.5 ± 0.4	64.5 ± 0.3	22 ± 0.6	40 ± 0.3	22 ± 1.0	126 ± 19	5.4 ± 0.4	47 ± 13
1:1[e]	29 ± 3.7	-	-	-	-	nd[f]	nd[f]	nd[f]

[a]The thermal properties are reported as averages from triplicate measurements. The mechanical properties are averages of at least five measurements. [b]Ester to amine stoichiometric ratio. [c]Calculated from the second heating scan. [d]Calculated from the cooling scan. [e]Prepared with DSEBAC instead of EB. [f]Not determined.

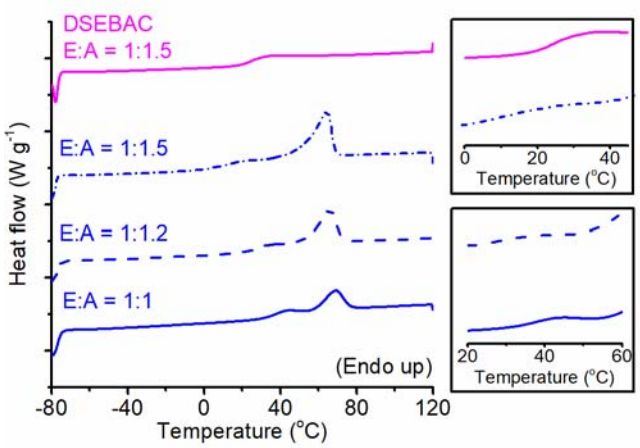

Figure S3. Typical DSC heating scans for the dried PA thermosets. The inset graphs present the glass transition of the respective thermosets.

In Figure S4 the ^{1}H NMR spectra of the extracted fractions in $CDCl_3$ of the PA thermosets with different ester to amine ratios are presented. Due to differences in the concentration of the solutions, the chemical shifts differ slightly among them.

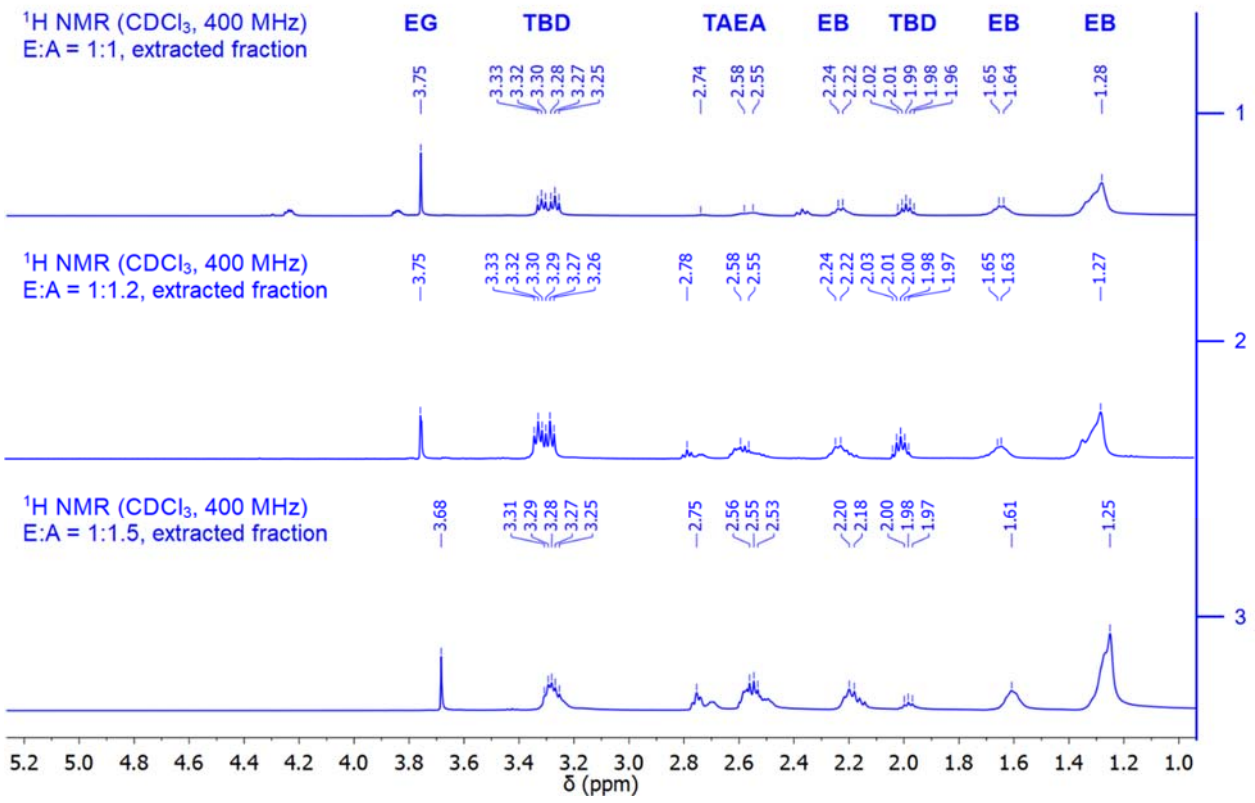

Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of the thermosets' extracted fractions; from top to bottom: 1) 1:1 ester to amine ratio; 2) 1:1.2 ester to amine ratio; 3) 1:1.5 ester to amine ratio.

In Figure S5 the stacked 1H NMR spectra of EB, TAEA and linear PEB synthesized using TAEA as initiator after 96 h of reaction are presented. The conversion was calculated from the ratio of the integrals of EB and PEB –COOCH_2 protons, 1 and 1', respectively.

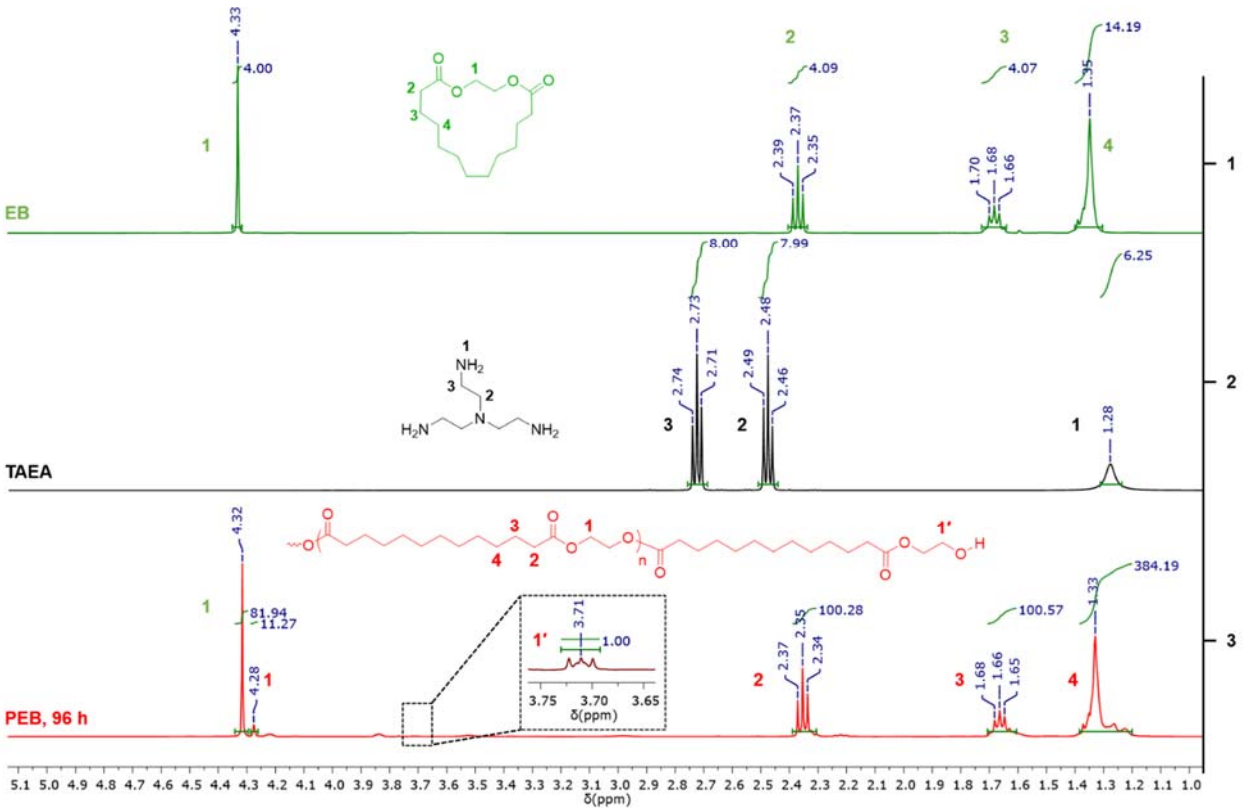

Figure S5. Stacked ^{1}H NMR spectra of pure EB (top), TAEA (middle) and linear PEB initiated by TAEA using 4 mol% of TBD as catalyst at 100 ˚C after 96 h of reaction (bottom). The conversion of EB after 96h of reaction is 13.7%.

Table S2. Thermal and mechanical properties of the polyamide thermosets prepared with an excess of EB.[a]

E:A[b]	T_g (°C)[c]	T_m (°C)[c]	ΔH_m (J g^{-1})[c]	T_c (°C)[d]	ΔH_c (J g^{-1})[d]	E (MPa)	σ_b (MPa)	ε_b (%)
1.05:1	22 ± 0.3	68 ± 0.1	27 ± 1.8	51 ± 1.0	26.5 ± 0.5	230 ± 30	20 ± 2.3	175 ± 27
1.2:1	10 ± 1.0	68 ± 1.3	36 ± 1.0	54 ± 0.7	35 ± 1.5	195 ± 20	17 ± 2.7	201 ± 24
1.5:1	7 ± 0.5	65 ± 0.5	42 ± 1.2	54 ± 0.3	39 ± 0.3	nd[e]	nd[e]	nd[e]

[a]The thermal properties are reported as averages from triplicate measurements. The mechanical properties are averages of at least five measurements. [b]Ester to amine stoichiometric ratio. [c]Calculated from the second heating scan. [d]Calculated from the cooling scan. [e]Due to a large excess of EB it was not possible to obtain homogeneous films, appropriate for tensile testing measurements.

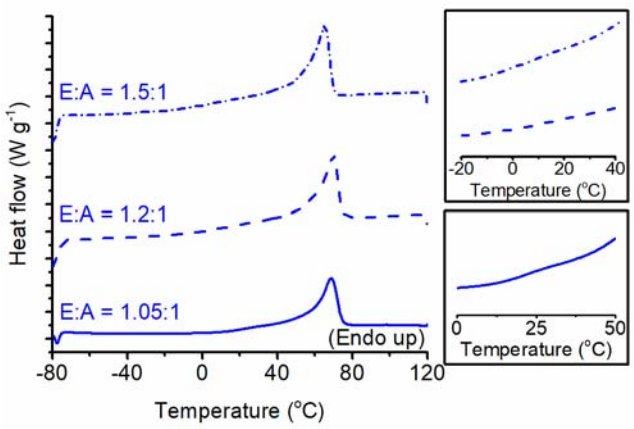

Figure S6. Typical DSC heating scans for the thermosets prepared with an excess of EB. The inset graphs present the glass transition of the respective thermosets.

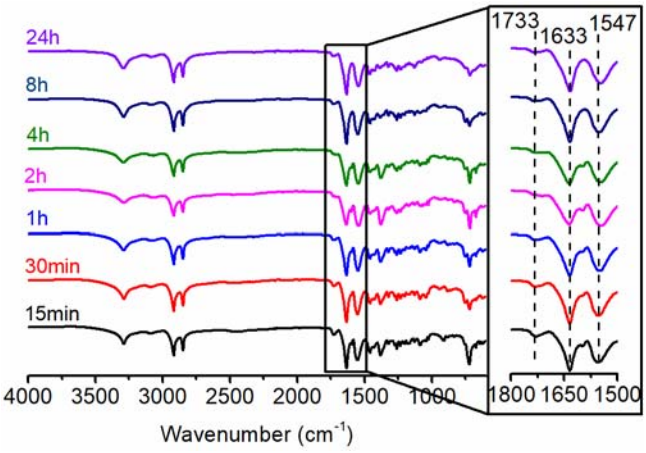

Figure S7. Stacked FTIR spectra at different time intervals of the products obtained from the reaction between EB and DETA for the synthesis of linear oligoamides.

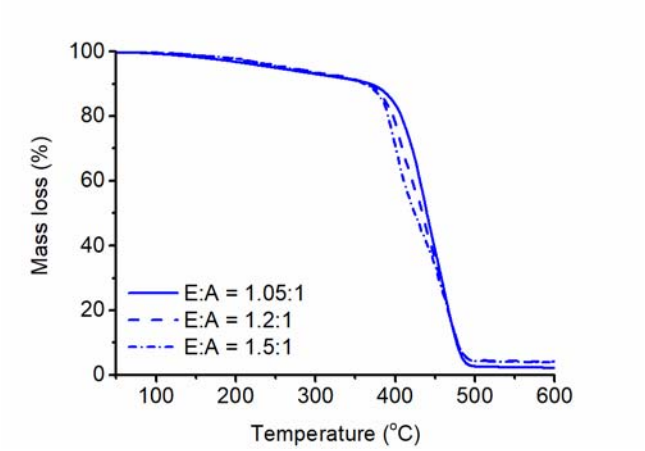

Figure S8. TGA curves of the PA thermosets synthesized with excess of EB. The initial mass loss until ~260 ˚C is due to evaporation of moisture and ethylene glycol.

A rectangular-shaped specimen with dimensions 67 × 5 × 0.6 mm was twisted and kept at 120 ˚C overnight in an oven. Once cooled down and the permanent twisted shape was fixed, it was heated with a conventional heating gun to soften it and made flat as a temporary shape. The specimen was reheated with the same equipment and the twisted and permanent shape was fully reobtained, Figure S9.

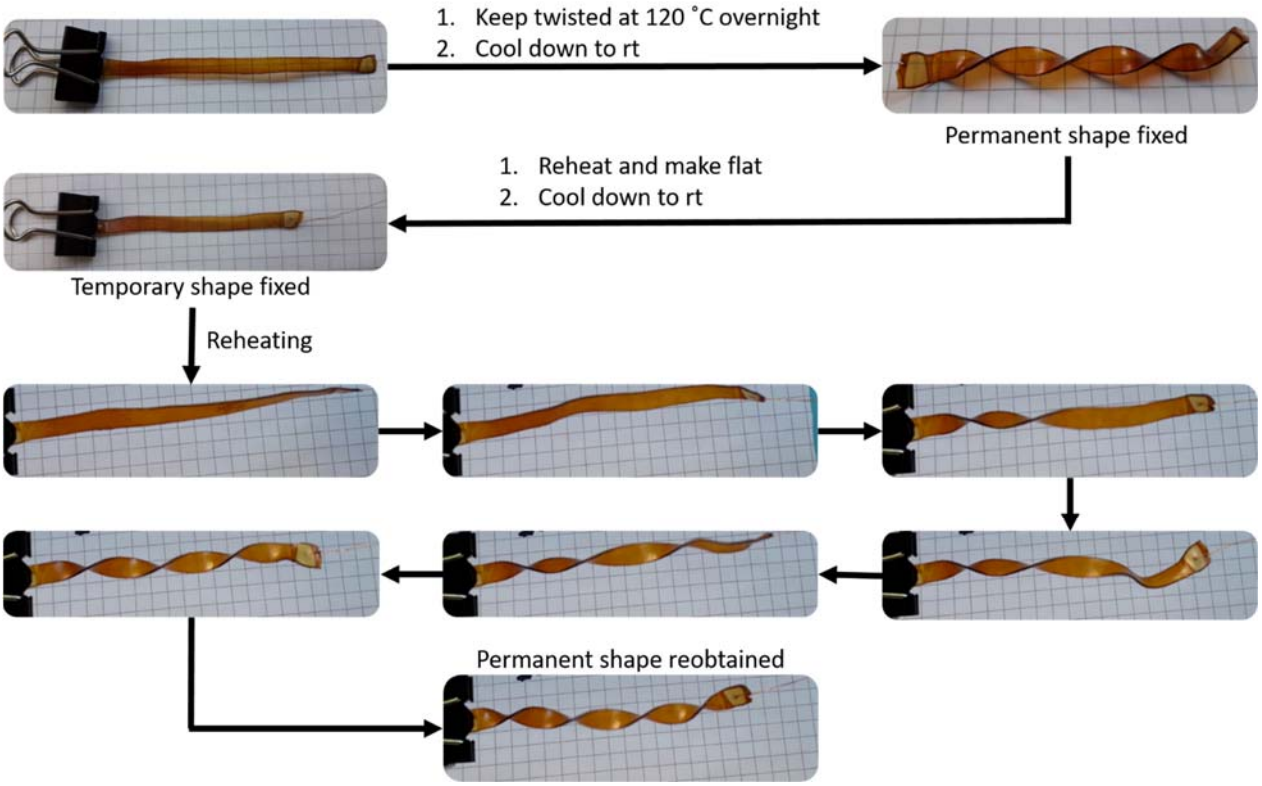

Figure S9. Shape-memory effect of the 1.5:1 ester to amine ratio PA thermoset. A conventional heating gun was used to elevate the temperature and the permanent shape was reobtained.