

SUPPORTING INFORMATION

Solid-State Polymerization of EDTA and Ethylenediamine as One-Step Approach to Monodisperse Hyperbranched Polyamide

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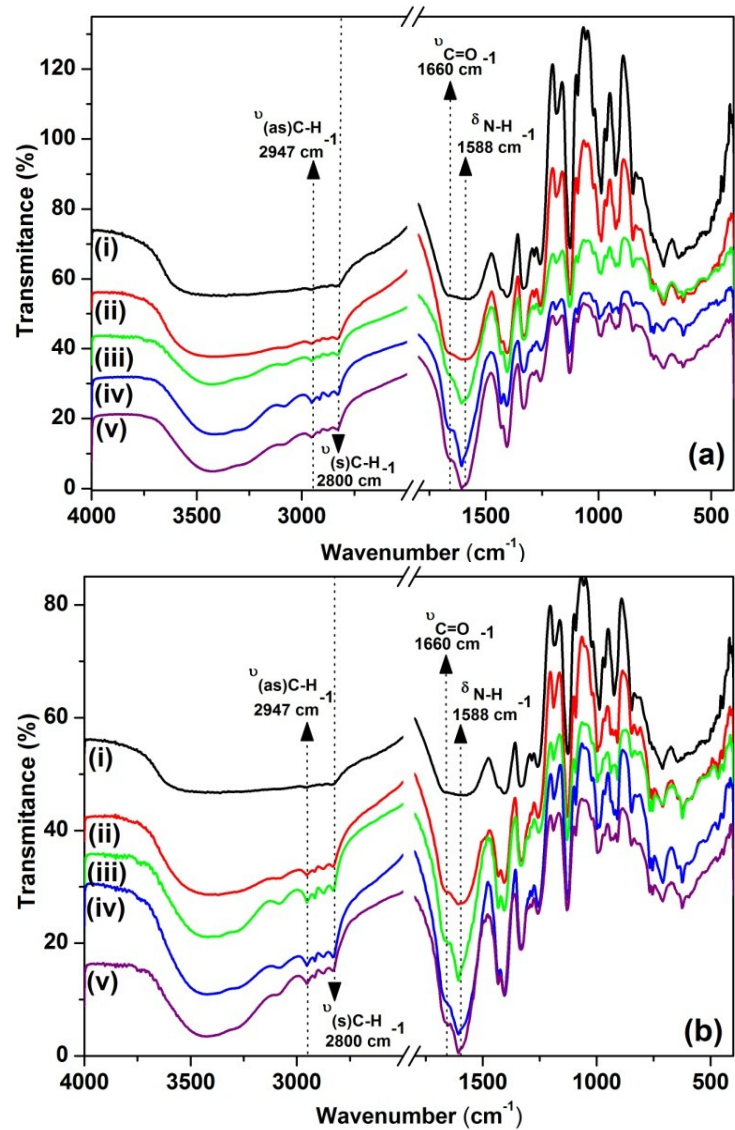


Figure S1. FTIR spectra of the precursor salt (prepared with EDTA:EDA ratio of (a) 1:1.5 and (b) 1:2) after thermal treatment at 120 °C for (i) 2, (ii) 4, (iii) 8, (iv) 12 and (v) 24 hours.

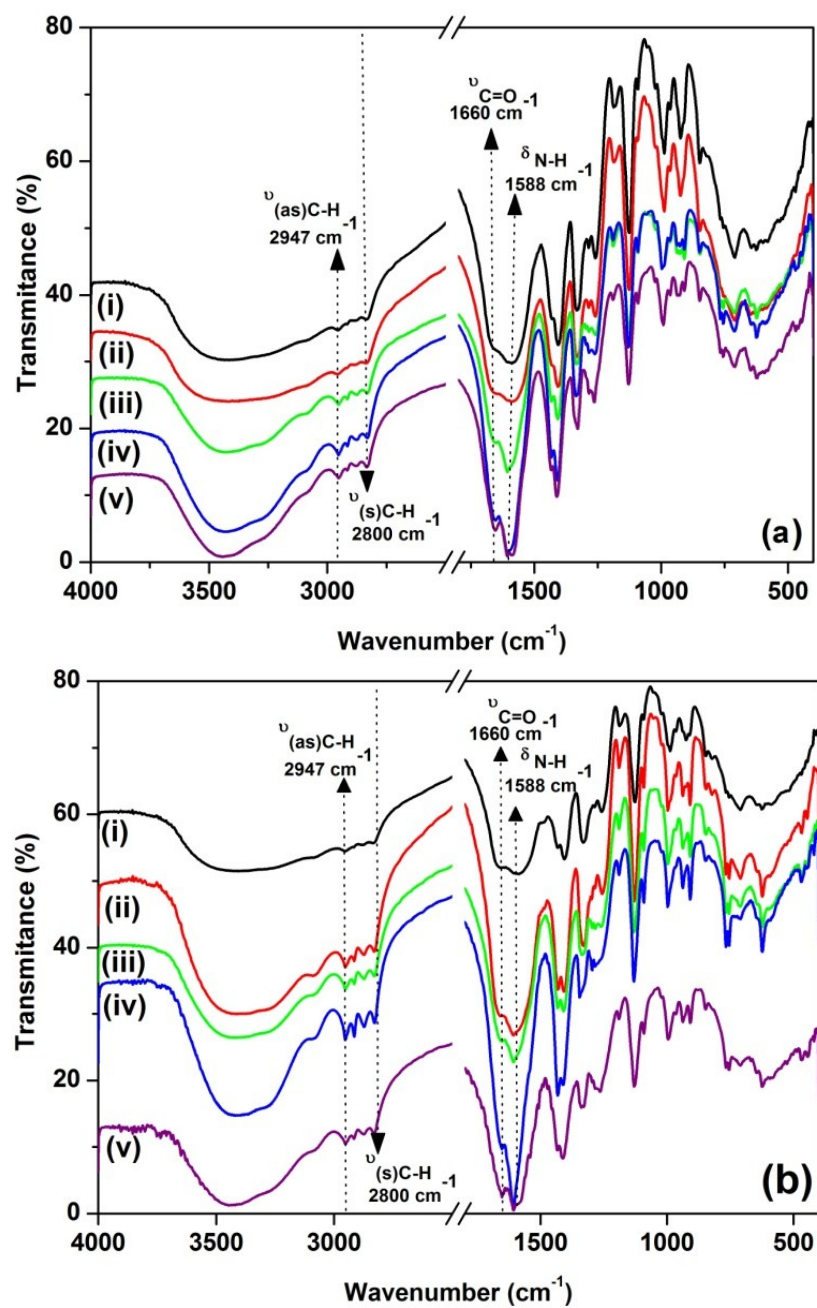


Figure S2. FTIR spectra of the precursor salt (prepared with EDTA:EDA ratio of (a) 1:1.5 and (b) 1:2) after thermal treatment at 140 °C for (i) 2, (ii) 4, (iii) 8, (iv) 12 and (v) 24 hours.

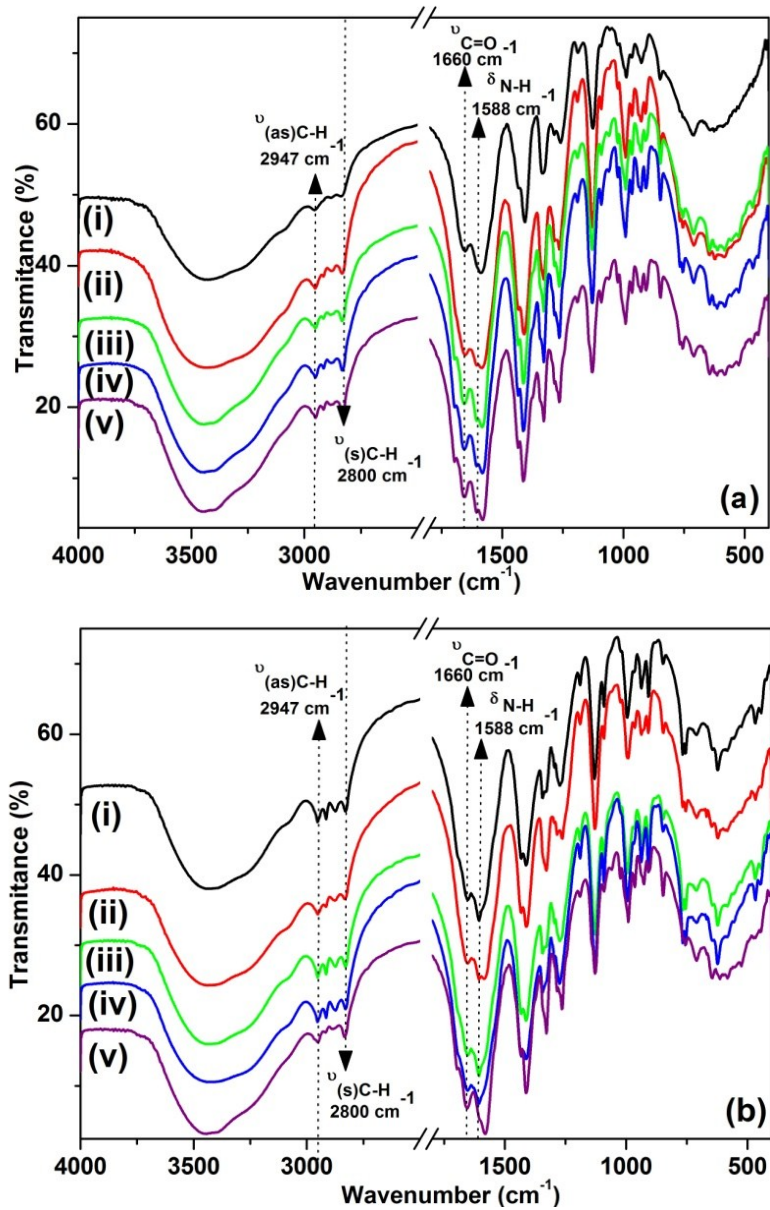


Figure S3. FTIR spectra of the precursor salt (prepared with EDTA:EDA ratio of (a) 1:1.5 and (b) 1:2) after thermal treatment at 160 °C for (i) 2, (ii) 4, (iii) 8, (iv) 12 and (v) 24 hours.

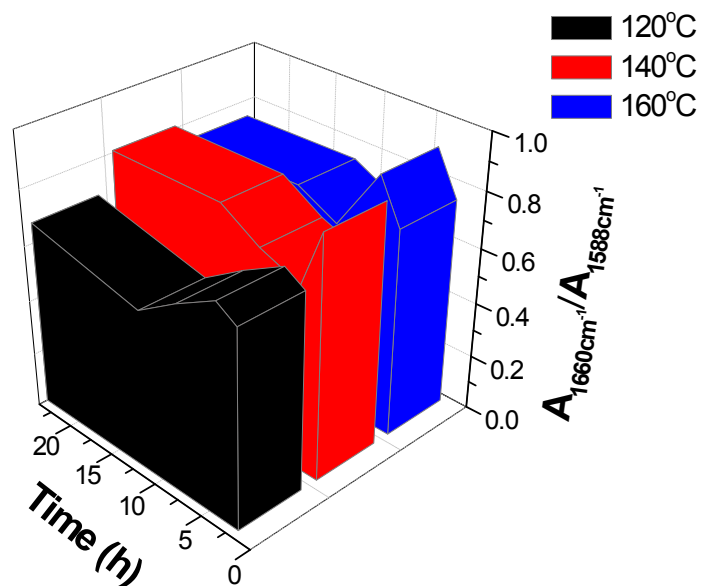


Figure S4. Graphic relating to the conversion of aminium and carboxylate ions in amide groups with EDTA:EDA ratio of 1:1.5 treated at 120, 140 and 160 C for 2, 4, 8, 12 and 24 hours, correlating the relative area of the bands at 1660 cm^{-1} and 1588 cm^{-1} at FTIR spectra.

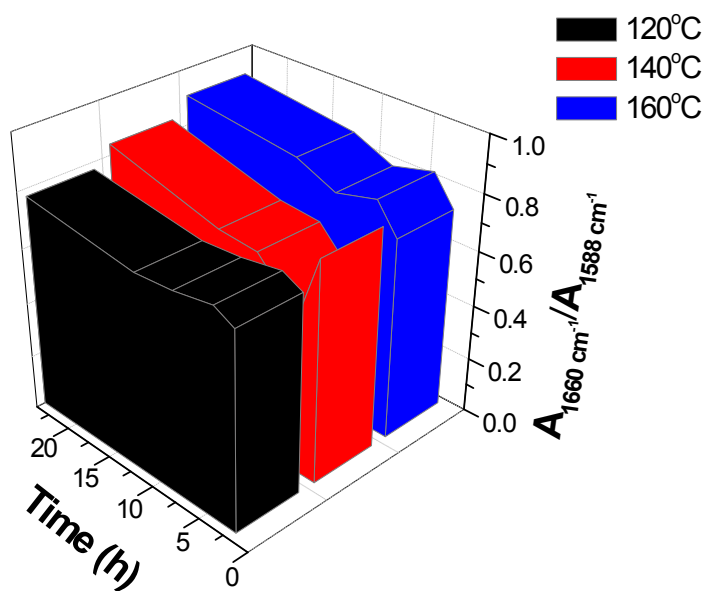


Figure S5. Graphic relating to the conversion of aminium and carboxylate ions in amide groups with EDTA:EDA ratio of 1:2 treated at 120, 140 and 160 C for 2, 4, 8, 12 and 24 hours, correlating the relative area of the bands at 1660 cm^{-1} and 1588 cm^{-1} at FTIR spectra.

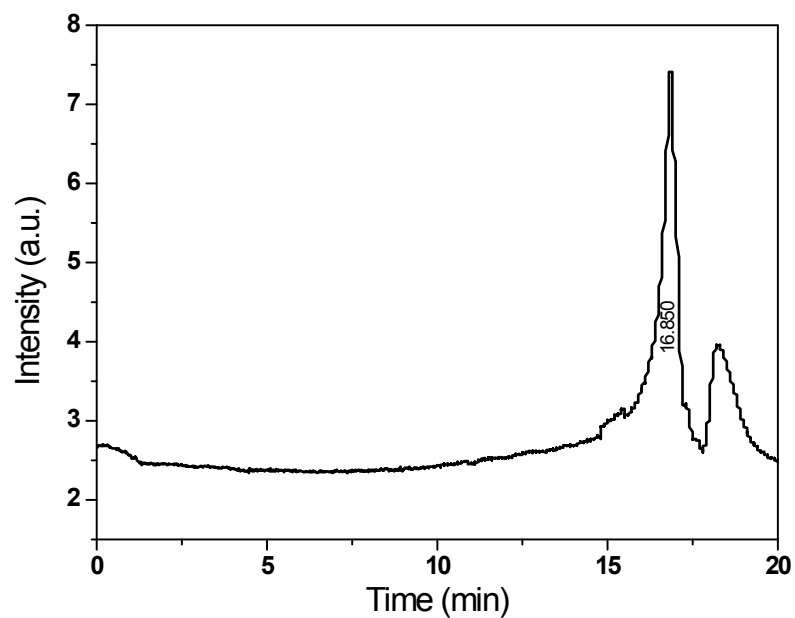


Figure S6. GPC curves of the sample obtained from EDTA: EDA ratio 1:1.5 ($M_n = 7262$ Da; $M_w = 9488$ Da; and $M_w/M_n = PDI = 1.30$).

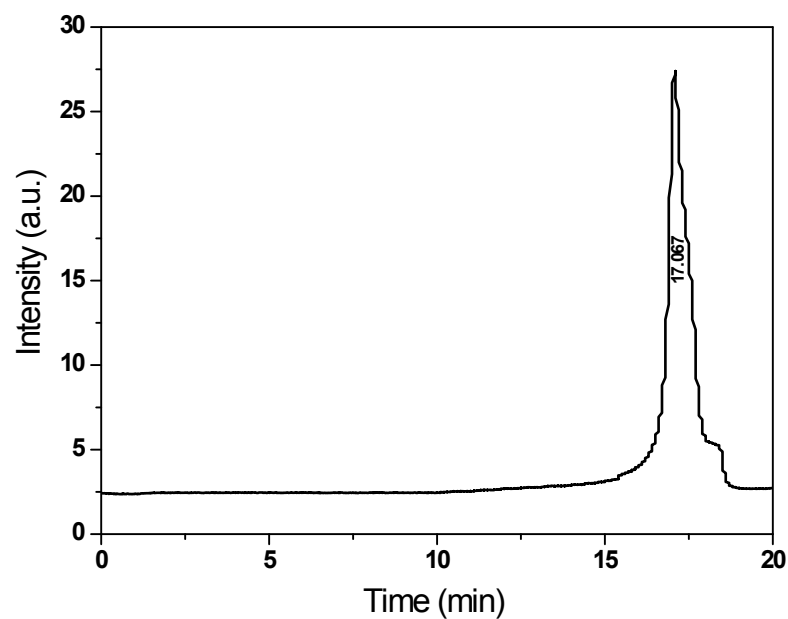


Figure S7. GPC curves of the sample obtained from EDTA: EDA ratio 1:2 ($M_n = 5494$ Da; $M_w = 6161$ Da; and $M_w/M_n = PDI = 1.12$).

Back Titration for the determination of terminal groups

The number of terminal group was determined by back titration. In this experiment, 40 mg of the polymeric material was dissolved in 25 mL of just prepared distilled water, to minimize the effect CO₂ dissolution on the solution pH. 10 mL of a standard 0.1 mol·L⁻¹ HCl solution was added to the polymeric solution. The repaired solution was treated using standard 0.1 mol·L⁻¹ NaOH using a pH meter to monitor the changes in the solution pH in function of the NaOH volume added. The procedure was repeated 3 times for each sample. The titration curves were demonstrated in the Figure S8 and S9. Using this method, it was possible to determine the relative number of terminal R-COOH and R-NH₂ groups, as demonstrated in the Table S1. The relative number of terminal groups were determined through the peaks in the first derivation of the titration curves that demonstrated the equivalence for each acid base specie in the medium.

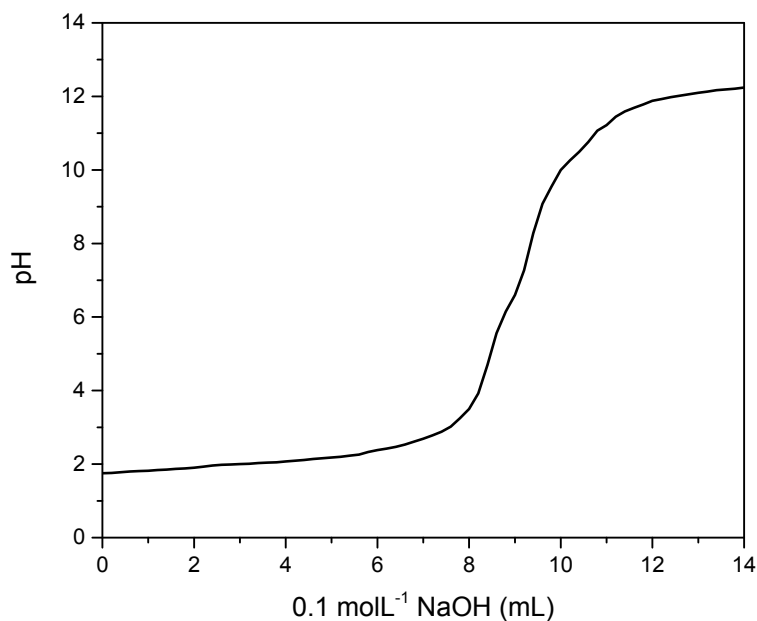


Figure S8. Back titration curves for the hyperbranched polyamides (HBPA) prepared with EDTA to EDA ratio of 1:2.

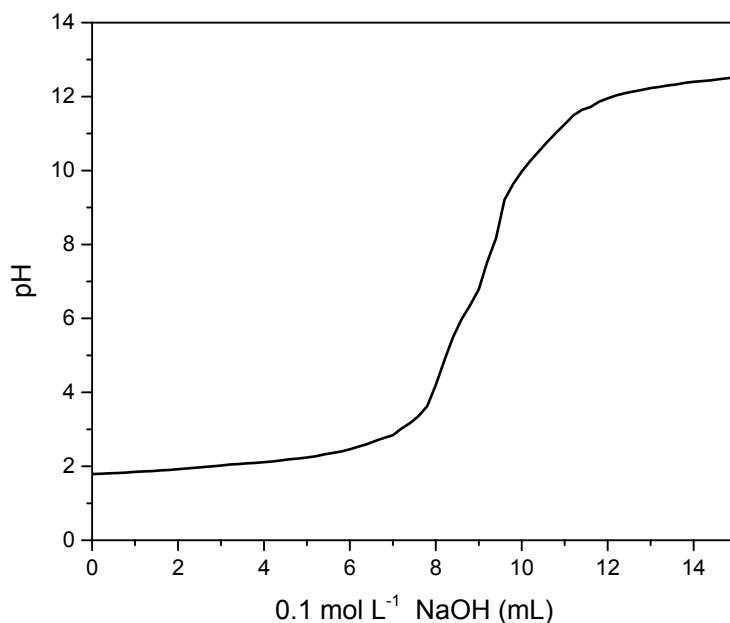


Figure S9. Back titration curves for the hyperbranched polyamides (HBPA) prepared with EDTA to EDA ratio of 1:2.

Table S1. Terminal groups content determined by back titration of the prepared samples.

EDTA:EDA Ratio	Molecular weight M_n (Da)	R-COOH and R-COO ⁻ groups (mmol/g)	R-NH ₂ e R-NH ₃ ⁺ groups (mmol/g)	Total number of terminal groups (mmol/g)
1:1.5	7262	2.42 ± 0.18	2.75 ± 0.25	5.17 ± 0.31
1:2	5494	2.42 ± 0.33	3.54 ± 0.09	5.96 ± 0.34