Poly(vinyl acetate-co-crotonic acid) from bio-based crotonic acid: synthesis, characterization and carbon footprint evaluation

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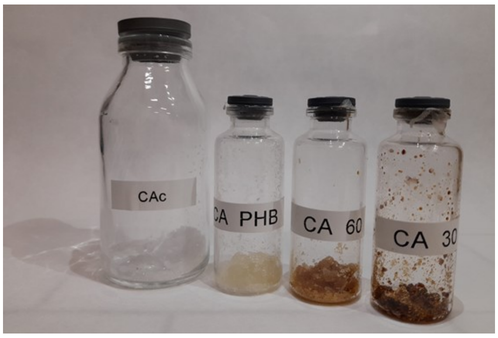

Figure S1. Different samples of crotonic acid (**CA**) used in this work (left to right): commercially available **CA** (**CA$_C$**), **CA** samples obtained through the thermolytic distillation of pure PHB (**CA$_{PHB}$**), and **CA** samples obtained through the thermolytic distillation of bacteria containing 60% and 30% of PHB inclusions (**CA$_{60}$** and **CA$_{30}$**, respectively).

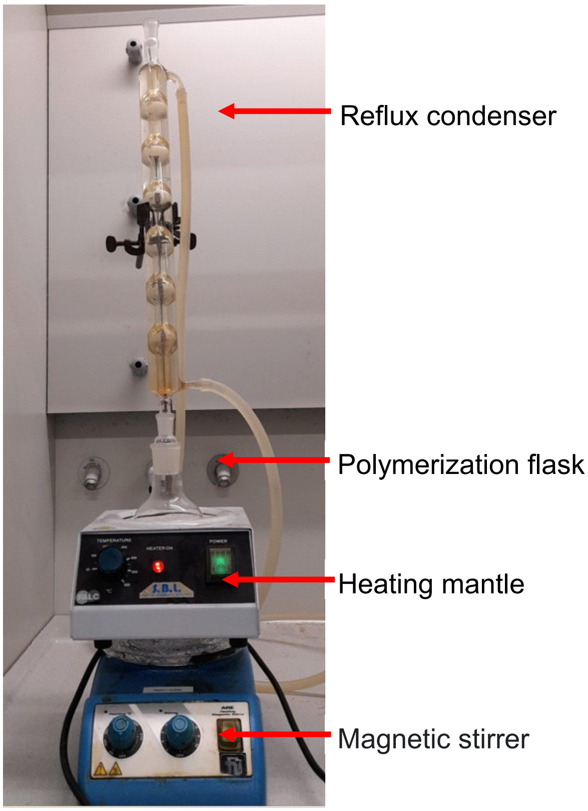

Figure S2. Experimental setup adopted for the synthesis of poly(vinyl acetate-co-crotonic acid) samples.

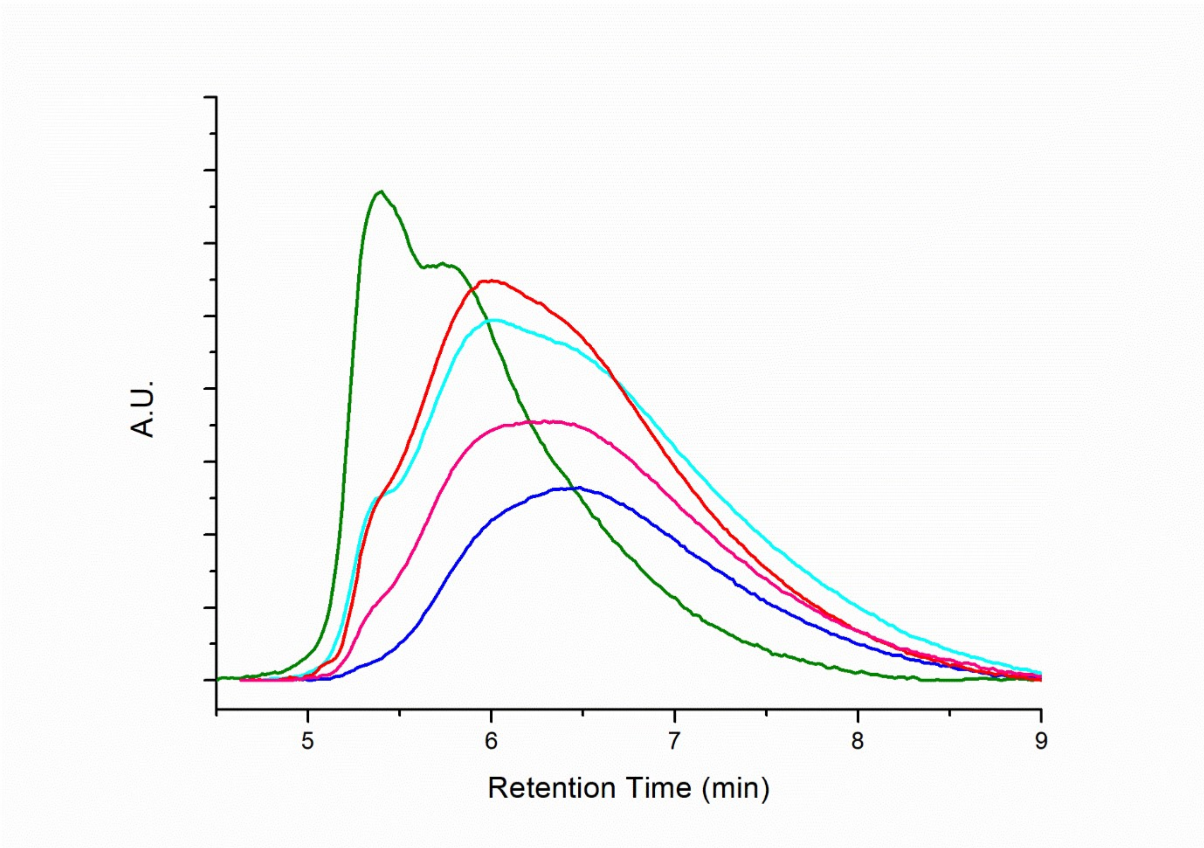

Figure S3. GPC curves of the commercial poly(vinyl acetate-co-crotonic acid) (green line) and the synthesised co-polymers: **VA-CAc** (blue line), **VA-CA$_{\mathbf{PHB}}$** (light blue line), **VA-CA$_{\mathbf{30}}$** (red line), **VA-CA$_{\mathbf{60}}$** (pink line).

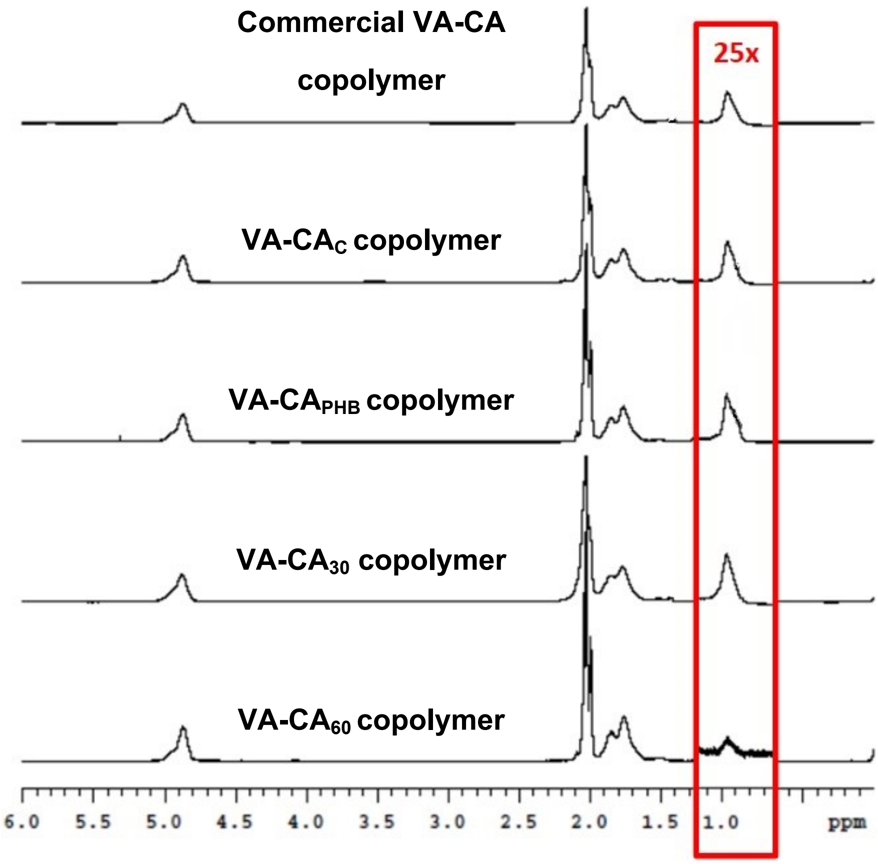

Figure S4. [1]H NMR spectra of the synthesised poly(vinyl acetate-co-crotonic acid) and the reference commercial sample. In the red circled inset a 25x enlargement of the signal in order to make it visible.

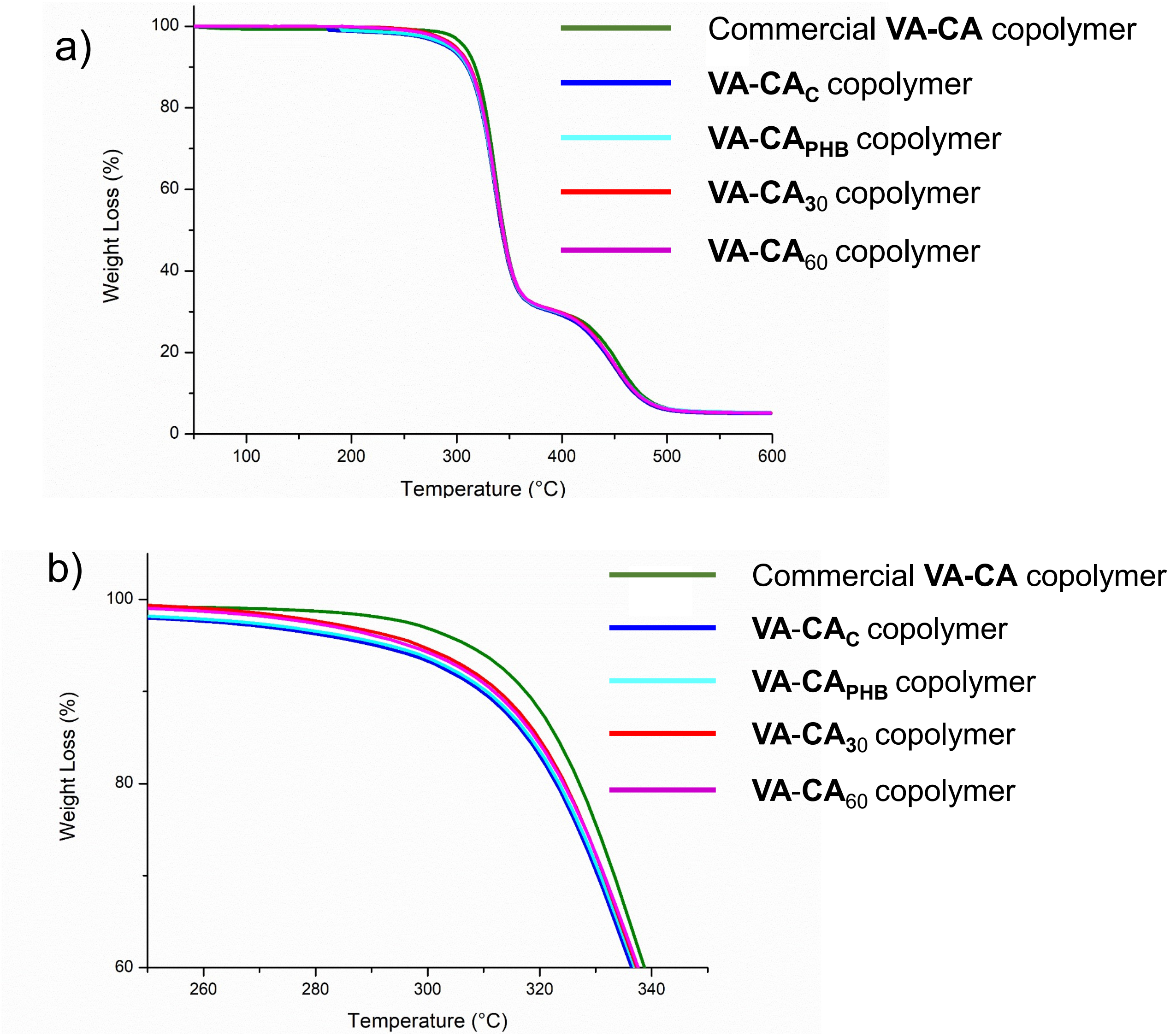

Figure S5. Overlay of TGA curves of the synthesised poly(vinyl acetate-co-crotonic acid) and the reference commercial sample (a), and a zoom on the first weight loss to highlight the differences (b).

Table S1. Reaction conditions for the preparation of the poly(vinyl acetate-co-crotonic acid) polymer beads obtained from different **CA** samples and conditions.

CA source	Temperature (°C)	Time (h)	Emulsifier (wt%)	Radical initiator (wt%)	Poly(vinyl acetate-co-crotonic acid) (mg, mass yield %)
$\mathbf{CA_C}$	60°C	3	-	1.3	-
$\mathbf{CA_C}$	60°C	3	0.050	1.3	-
$\mathbf{CA_C}$	80°C	6	0.050	1.3	-
$\mathbf{CA_C}$	80°C	6	0.050	1.3	<5%
$\mathbf{CA_C}$	80°C	3	0.050	2.5	<5%
$\mathbf{CA_C}$	80°C	6	0.025	1.3	-
$\mathbf{CA_C}$	80°C	6	0.010	1.3	-
$\mathbf{CA_C}$	80°C	16	0.050	1.3	<5%
$\mathbf{CA_C}$	100°C	3	0.050	0.65	<5%
$\mathbf{CA_C}$	100°C	6	0.050	1.3	864 (36%)
$\mathbf{CA_{PHB}}$	100°C	6	0.050	1.3	912 (48%)
$\mathbf{CA_{60}}$	100°C	6	0.050	1.3	741 (39%)
$\mathbf{CA_{30}}$	100°C	6	0.050	1.3	988 (52%)

Poly(vinyl acetate-co-crotonic acid) samples were prepared by heating vinyl acetate (**VA**, 2 mL, ρ = 0.93 g/mL, 1.86 g; 0.01 mol), and the chosen sample of crotonic acid (**CA**, 28 mg, 1.5 wt%) in 4 mL of water at 60–100 °C for 3–16 h, in the presence of benzoyl peroxide as radical initiator and polyvinyl alcohol as the emulsifier.

Table S2. Assumptions adopted for the calculation of the carbon footprint of the production of bio-based **CA** from WWTS. The yields of VFA ($Yield_{VFA}$), PHB ($Yield_{PHB}$), and **CA** ($Yield_{CA}$) here used have been already reported in the literature.[1,2,3] (COD: chemical oxygen demand; DM: dry matter; VFA: volatile fatty acids; TS: total solids; **CA**: crotonic acid; TD: thermolytic distillation).

WWTS input	*HTC-Acidogenic fermentation*	*S/L separation*	*Aerobic fermentation*	*Thermolytic distillation*
WWTS: 1000 t/y COD_{WWTS}: 0.030 gO/g DM_{WWTS}: 4%	$Yield_{VFA}$: 25% on COD_{WWTS} basis $Yield_{others}$: 20% on COD_{WWTS} basis $Yield_{TSS}$: 50% on TS basis	DM_{cake}: 37%	$Yield_{PHB}$: 35% on COD_{VFA} basis $Yield_{PHB\text{-}enriched\ biomass}$: 64% on COD_{VFA} basis $Concentration_{PHB}$: 45% on bacterial biomass basis[a] COD_{PHB}: 1.67 gO/g $COD_{PHB\text{-}enriched\ biomass}$: 1.36 gO/g	$Yield_{CA}$: 68% on PHB basis $Yield_{TDcake}$: 44% on dry bacterial biomass basis

[a] An average concentration of PHB between 30 and 60% on a bacterial biomass basis has been assumed for the calculation.

CA (t) that will be produced from WWTS through the hybrid (thermo)chemical-biological approach can be determined as follows:

$$CA\ (t) = \frac{(WWTS \times CODwwts \times YIELDvfa\ \times YIELDpha \times YIELDca)}{CODpha}$$

According to the assumptions reported in Table S2 and the equation above, the amount of **CA** from 1000 t of WWTS with 4% of dry matter and a COD value of 30 g/L will be:

$$CA\ (t) = \frac{(1000\ t \times 0.03\ gO/g \times 0.25\ \times 0.35 \times 0.68)}{1.67\ gO/g}$$

References

S1 C. Samorì, A. Kiwan, C. Torri, R. Conti, P. Galletti and E. Tagliavini, *ACS Sustain. Chem. Eng*., 2019, **7**, 10266-10273.

S2 B-PLAS DEMO (2018-2021), funded by EIT-Climate KIC, https://site.unibo.it/b-plas/en

S3 A. Parodi, A. Jorea, M. Fagnoni, D. Ravelli, C. Samorì, C. Torri and P. Galletti, *Green Chem*., 2021, **23**, 3420–3427.