Advances in the synthesis of bio-based aromatic polyesters: novel

copolymers derived from vanillic acid and ϵ -caprolactone

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Figure S2: ¹³C-NMR spectrum of poly(caprolactone) (PCL)













Figure S6: ¹³C-NMR spectrum of copolymer poly(ethylene vanillate-*co*-caprolactone) P(EV-*co*-CL)-50/50



Figure S7: ¹H-NMR spectrum of copolymer poly(ethylene vanillate-*co*-caprolactone) P(EV-*co*-CL)-80/20



Figure S8: ¹³C-NMR spectrum of copolymer poly(ethylene vanillate-*co*-caprolactone) P(EV-*co*-CL)-80/20







Figure S10: ¹³C-NMR spectrum of poly(ethylene vanillate) PEV



Equation S1-S4: Quantitative determination of the molar fractions (*F*) of EV-EV, EV-CL, CL-CL and CL-EV sequences by ¹H-NMR signals

$$F_{EV-EV} = \frac{I_f}{I_f + I_{f'}} \qquad S1$$

$$F_{EV-CL} = \frac{I_{f'}}{I_f + I_{f'}} \qquad S2$$

$$F_{CL-CL} = \frac{I_i}{I_i + I_{i'}} \qquad S3$$

$$F_{CL-EV} = \frac{I_{i'}}{I_i + I_{i'}} \qquad S4$$

Equation S5-S8: Quantitative determination of the molar fractions (*F*) of EV-EV, EV-CL, CL-CL and CL-EV sequences by ¹³C-NMR signals

$$F_{EV-EV} = \frac{I_1}{I_1 + I_2} \qquad S5$$

$$F_{EV-CL} = \frac{I_2}{I_1 + I_2} \qquad S6$$

$$F_{CL-CL} = \frac{I_3}{I_3 + I_4} \qquad S7$$

$$F_{CL-EV} = \frac{I_4}{I_3 + I_4} \qquad S8$$

Equation S9-S11: Quantitative determination of the average sequence lengths of EV-EV and CL-CL dyads $(L_{\text{EV-EV}} \text{ and } L_{\text{CL-CL}})$ and the randomness degree (B)

$$L_{EV-EV} = \frac{F_{EV-EV}}{F_{EV-CL}} + 1 \qquad S9$$
$$L_{CL-CL} = \frac{F_{CL-CL}}{F_{CL-EV}} + 1 \qquad S10$$
$$B = \frac{1}{L_{EV-EV}} + \frac{1}{L_{CL-CL}} \qquad S11$$