Poly(carbonate-amide)s derived from bio-based resources: Poly(ferulic acid-co-tyrosine)

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Synthesis of L-serine ethyl ester 1. Freshly distilled EtOH (265 mL) was cooled on ice and SOCl₂ (2 mL, 0.33 mol) was added dropwise. Then L-serine (7 g, 0.66 mol) was added as one portion and the reaction mixture was stirred for 1 h at 0 °C and kept at room temperature overnight. The reaction mixture was concentrated under vacuum to an oil which was triturated with cold Et₂O several times to give the desired product as a white solid (10.3 g, 0.61 mol, 92%). FTIR (ATR) \( \nu_{\text{max}} \) (cm\(^{-1}\)) 3385, 2800-3200, 1734, 1591; \(^{1}\)H NMR spectrum (500 MHz, CD\(_{3}\)OD) \( \delta \) 4.42-4.28 (m, 2 H), 4.15 (dd, \( J = 4.5, 3.5 \) Hz, 1 H), 4.04 (dd, \( J = 11.8, 4.5 \) Hz, 1 H), 3.97 (dd, \( J = 11.8, 3.5 \) Hz, 1 H), 1.36 (t, \( J = 7.1 \) Hz, 3 H) ppm; \(^{13}\)C NMR spectrum (125 MHz, CD\(_{3}\)OD) \( \delta \) 168.9 (C), 63.7 (CH\(_{2}\)), 60.7 (CH\(_{2}\)), 56.1 (CH), 14.3 (CH\(_{3}\)) ppm; MS (ESI\(^{+}\)) m/z (%) 134.1 (100, [M-Cl]); ESIHRMS calcd for C\(_{5}\)H\(_{12}\)NO\(_{3}\) (M-Cl) 134.0812, found 134.0810.

Synthesis of ethyl (E)-O-(tert-butyldimethylsilyl)-N-(3-(4-hydroxy-3-methoxyphenyl)acryloyl)-L-serinate 2. Imidazole (3.61 g, 53.1 mmol) was added at 0 °C to a solution of compound 1 (3 g, 17.7 mmol) and TBDMSCl (5.3 g, 35.4 mmol) in CH\(_{2}\)Cl\(_{2}\) (680 mL), and the reaction was stirred at room temperature overnight. Water was added and the product was extracted with CH\(_{2}\)Cl\(_{2}\). The desired crude product (6.2 g containing 38% of TBDMSOH) was used without purification. The crude, ferulic acid (2.33 g, 12.0 mmol), HOBt (2.44 g, 18.1 mmol) and molecular sieves (3.25 g) in CH\(_{2}\)Cl\(_{2}\) (130 mL) were added, at 0 °C, EDCI (2.8 g, 18.1 mmol) and Et\(_{3}\)N (7.5 mL, 54.0 mmol) were added dropwise. The reaction was stirred at room temperature overnight. 1 M HCl was added and the crude product was extracted with CH\(_{2}\)Cl\(_{2}\). The organic layer was dried over Na\(_{2}\)SO\(_{4}\), filtered and the solvent was removed under vacuum. The desired product was obtained after purification on a silica cartridge (80 g, 0% to 100 % of AcOEt in hexane over 1 h) as a white foam (3.82 g, 9.02 mmol, 51%). FTIR (ATR) \( \nu_{\text{max}} \) (cm\(^{-1}\)) 3400-3200, 17438, 1658; \(^{1}\)H NMR spectrum (500 MHz, CDCl\(_{3}\)) \( \delta \) 7.55 (d, \( J = \)
15.5 Hz, 1 H), 7.04 (dd, J = 8.2, 2.0 Hz, 1 H), 6.99 (d, J = 2.0 Hz, 1 H), 6.89 (d, J = 8.2 Hz, 1 H), 6.48 (d, J = 8.2 Hz, 1 H), 6.33 (d, J = 15.5 Hz, 1 H), 6.27 (brs, 1 H), 4.80 (dt, J = 8.2, 2.8 Hz, 1 H), 4.25-4.17 (m, 2 H), 4.13-4.08 (m, 1 H), 3.91-3.87 (m, 1 H), 3.89 (s, 3 H), 1.28 (t, J = 7.1 Hz, 3 H), 0.86 (s, 9 H), 0.02 (d, J = 0.9 Hz, 6 H) ppm; $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) δ 170.5 (C), 165.8 (C), 147.6 (C), 146.8 (C), 141.8 (CH), 127.1 (C), 122.4 (CH), 117.5 (CH), 114.8 (CH), 109.6 (CH), 63.7 (CH$_2$), 61.6 (CH$_2$), 55.8 (CH), 54.4 (CH$_3$), 25.6 (3 CH$_3$), 18.2 (C), 14.1 (CH$_3$), -5.5 (CH$_3$), -5.7 (CH$_3$) ppm; MS (ESI$^+$) m/z (%) 424.2 (100, [M+H]$^+$), 446.2 (44, [M+Na]$^+$); ESIHRMS caleld for C$_{21}$H$_{34}$NO$_6$Si (M+H)$^+$ 424.2155, found 424.2151, m$_p$ = 53°C.

**Synthesis of ethyl (E)-O-(tert-butyldimethylsilyl)-N-(3-(3-methoxy-4-((4-nitrophenoxy)carbonyl)oxy)phenyl)acryloyl)-L-serinate 3.** A solution of 2 (479 mg, 1.13 mmol) and pyridine (0.18 mL, 1.70 mmol) in CH$_2$Cl$_2$ (3.4 mL) was added dropwise to a solution of p-nitrophenyl chloroformate (462.3 mg, 2.26 mmol) in CH$_2$Cl$_2$ (11.9 mL). The reaction was stirred at room temperature for 6 h. Water was added and the crude was extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$ and filtered. The solvent was removed under vacuum. The residue was purified by flash chromatography on a silica cartridge (12 g, Hexane/AcOEt 0 to 50% over 15 min). The desired product was obtained as a white foam (558.2 mg, 0.95 mmol, 84%). FTIR (ATR) $\nu_{max}$ (cm$^{-1}$) 1784, 1742, 1626, 1184; $^1$H NMR spectrum (500 MHz, CDCl$_3$) δ 8.31 (d, J = 9.2 Hz, 2 H), 7.62 (d, J = 15.6 Hz, 1 H), 7.49 (d, J = 9.2 Hz, 2 H), 7.25-7.21 (m, 1 H), 7.16 (d, J = 7.9 Hz, 2 H), 6.50 (d, J = 8.1 Hz, 1 H), 6.47 (d, J = 15.6 Hz, 1 H), 4.79 (dt, J = 8.1, 2.7 Hz, 1 H), 4.27-4.20 (m, 2 H), 4.13 (dd, J = 10.1, 2.7 Hz, 1 H), 3.94 (s, 3 H), 3.91 (dd, J = 10.1, 2.7 Hz, 1 H), 3.87 (s, 9 H), 0.03 (s, 6 H) ppm; $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) δ 170.4 (C), 164.9 (C), 155.4 (C), 151.0 (C), 150.3 (C), 145.5 (C), 140.56 (C), 140.55 (CH), 134.6 (C), 125.4 (2 CH), 122.4 (CH), 121.6 (2 CH), 121.1 (CH), 120.8 (CH), 111.5 (CH),
63.6 (CH₂), 61.7 (CH₂), 56.1 (CH₃), 54.5 (CH), 25.7 (3 CH₃), 18.2 (C), 14.2 (CH₃), -5.5 (CH₃), -5.6 (CH₃) ppm; MS (ESI⁺) m/z (%) 589.2 (100, [M+H⁺]); ESIHRMS calcd for C₂₈H₃₇N₂O₁₀Si (M+H) 589.2217, found 589.2227.

**Synthesis of ethyl (E)-(3-(3-methoxy-4-(((4-nitrophenoxycarbonyl)oxy)phenyl)acryloyl)-L-serinate 4.** To a solution of 3 (529 mg, 0.90 mmol) in CH₂Cl₂ (4.5 mL) was added dropwise BF₃·OEt₂ (0.23 mL, 1.80 mmol). The reaction was stirred at room temperature for 5 h. Saturated solution of NaHCO₃ was added and the crude was extracted with CH₂Cl₂, dried over Na₂SO₄ and filtered. The solvent was removed under vacuum. The residue was purified by flash chromatography on a silica cartridge (12 g, Hexane/AcOEt 0 to 100% over 15 min). The desired product was obtained as a white foam (375.2 mg, 0.79 mmol, 88%). FTIR (ATR) ν max (cm⁻¹) 3400-3300, 1778, 1731, 1622, 1187; ¹H NMR spectrum (500 MHz, CDCl₃) δ 8.32 (d, J = 9.1 Hz, 2 H), 7.64 (d, J = 15.6 Hz, 1 H), 7.49 (d, J = 9.1 Hz, 2 H), 7.25-7.20 (m, 1 H), 7.20-7.12 (m, 2 H), 6.61 (d, J = 7.0 Hz, 1 H), 6.48 (d, J = 15.6 Hz, 1 H), 4.80 (dt, J = 7.0, 3.6 Hz, 1 H), 4.29 (q, J = 7.1 Hz, 2 H), 4.05 (br t, J = 4.3 Hz, 2 H), 3.95 (s, 3 H), 2.49 (br t, J = 4.3 Hz, 1 H), 1.33 (t, J = 7.1 Hz, 3 H) ppm; ¹³C NMR spectrum (125 MHz, CDCl₃) δ 170.5 (C), 165.8 (C), 155.3 (C), 151.0 (C), 150.3 (C), 145.5 (C), 140.9 (C), 140.6 (CH), 134.4 (C), 125.4 (2 CH), 122.4 (CH), 121.6 (2 CH), 120.76 (CH), 120.73 (CH), 111.6 (CH), 63.6 (CH₂), 62.2 (CH₂), 56.1 (CH₃), 55.1 (CH), 14.3 (CH₃) ppm; MS (ESI⁺) m/z (%) 475.1 (100, [M+H⁺]); ESIHRMS calcd for C₂₂H₂₃N₂O₁₀ (M+H) 475.1353, found 475.1343.

**Confirmation of the structure for the undesired elimination product 5.**

The loss of the p-nitrophenyl carbonate group and the formation of 5 were clearly evidenced by ¹H NMR spectroscopy. The disappearance of the signals at 4.80 ppm (dt) and 2.49 ppm (t) indicated that loss of both the proton at the α position of the ester and that of the alcohol in 4 had
occurred, due to an elimination reaction. The appearance of two downfield singlets at 6.72 ppm and 5.94 ppm in 5 indicated the formation of a terminal alkene in place of the alcohol. This was further confirmed by $^{13}$C NMR spectroscopic analyses where the carbon bearing the hydroxyl group shifted from 63.6 ppm in 4 to 108.6 ppm in 5, characteristic of a double bond. Moreover, the C=O stretching band at 1778 cm$^{-1}$ disappeared in FTIR spectroscopy, confirming the loss of the $p$-nitrophenyl carbonate group, and the presence of a band at 1622 cm$^{-1}$ corroborated the formation of the alkene. High resolution mass spectrometry supported both the loss of $p$-nitrophenyl carbonate and the elimination of the alcohol group, confirming the formation of compound 5.

**Synthesis of ethyl (E)-2-(3-(4-hydroxy-3-methoxyphenyl)acrylamido)acrylate 5.** To a solution of 4 (50 mg, 0.10 mmol) in CH$_2$Cl$_2$ (0.21 mL) was added Et$_3$N (29 μL, 0.21 mmol). The reaction was stirred at room temperature overnight. The solvent was removed. The residue was purified by flash chromatography on a silica cartridge (4 g, Hexane/AcOEt 0 to 50% over 15 min). The desired product was obtained as a white foam (16.2 mg, 0.06 mmol, 60%). FTIR (ATR) $\nu_{\text{max}}$ (cm$^{-1}$) 3400-3200, 1713, 1667, 1622, 1510; $^1$H NMR spectrum (500 MHz, CDCl$_3$) δ 7.90 (s, 1 H), 7.60 (d, J = 15.5 Hz, 1 H), 7.08 (dd, J = 8.2, 1.9 Hz, 1 H), 7.02 (d, J = 1.9 Hz, 1 H), 6.92 (d, J = 8.2 Hz, 1 H), 6.72 (s, 1 H), 6.35 (d, J = 15.5 Hz, 1 H), 5.94 (d, J = 1.4 Hz, 1 H), 4.32 (q, J = 7.1 Hz, 2 H), 3.93 (s, 3 H), 1.36 (t, J = 7.1 Hz, 3 H) ppm; $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) δ 164.7 (C), 164.3 (C), 147.8 (C), 146.7 (C), 142.6 (CH), 131.2 (C), 127.0 (C), 122.8 (CH), 118.0 (CH), 114.8 (CH), 109.4 (CH), 108.6 (CH$_2$), 62.3 (CH$_2$), 56.0 (CH$_3$), 14.1 (CH$_3$) ppm; MS (ESI$^+$) m/z (%) 292.1 (100, [M+H]$^+$).

**Methods to monitor the polymerizations.**
Size exclusion chromatography (SEC) (DMF, 0.05 M LiBr) was used to evaluate the outcome of the polymerizations. Since our experimental setup allowed for the resolution of the oligomeric fractions in the crude polymerization mixtures, a calibration curve was built from the analysis of the oligomers, assuming a first-order evolution of the elution time with log($M_n$), using toluene as flow marker (Figure S2). We found a good correlation between the $M_n$ values obtained from the PEO calibration and those based on the oligomer-based calibration. The validity of those results was further supported by chain-end functionalization experiments performed on the final polymers, subsequently analyzed by $^1$H NMR spectroscopy assuming quantitative functionalization.

**Figure S2.** (a) SEC profile of 16, 8 and a crude mixture; (b) calibration curve obtained from that crude mixture.

The functionalization was first performed on the AA’ monomer 8 as a model compound. Highly reactive allylchloroformate and furfuryl isocyanate were selected due to their compatibility with polymerization conditions and the ease of characterization of the resulting...
products by $^1$H NMR spectroscopy (Scheme S1). Moreover, the byproducts formed are water soluble.\textsuperscript{1}

\textbf{Scheme S1.} Monomer AA’ 8 and model compounds obtained after reaction with allychloroformate (17) or furfuryl isocyanate (18).

The same functionalization protocols as for the model compound 8 were then applied to the polymers synthesized with the exception that the crude reaction mixtures were first treated by a saturated solution of NaHCO$_3$ to obtain the free phenol group as chain-ends. A summary of the results is presented in Table S1.

\textsuperscript{1} Stephenson, R. M. J. Chem. Eng. Data \textbf{1993}, \textit{38}, 634-637.
Table S1. Comparison of the DP_n as determined by 1H NMR spectroscopy and SEC.

| Entry | Polymer          | Polymer chain end | (DP_n)_NMR^a | M_n (kg.mol⁻¹) | (DP_n)_SEC^b | D  |
|-------|------------------|-------------------|---------------|---------------|--------------|----|
| 1     | AA’AA’ from 13   | OH                | /             | 5.8           | 14           | 1.43|
| 2     | Allyl-AA’AA’ 19  | Allyl             | 19            | 5.7           | 14           | 1.45|
| 3     | Furfuryl-AA’AA’ 20| Furfuryl          | 17            | 5.9           | 14           | 1.34|

^a Determined by 1H NMR spectroscopy; ^b Determined by SEC (DMF, 0.05 M LiBr) using the oligomer-based calibration curve.

Both samples were fully characterized (Table S2, Entries 2-3). SEC curves shape remained unaffected by chain end-capping (Figure S2). These experiments display the consistency of the results from both 1H NMR spectroscopy and SEC in determining the molecular weights. This analysis also reveals that the primary component of the system is most likely an acyclic polymer, and provides information about the limit of solubility of this polymer in CH₂Cl₂. For batches with average degrees of polymerization (DP_n) of 20 or above, addition of either Et₃N, fufuryl isocyanate or allyl chloroformate induced precipitation.

Table S2. Full characterization of chain-ends capped polymers and the non-capped precursor.

| Entry | Polymer          | Polymer chain end | T_g^a (°C) | T_p^b (°C) | Yield (%) | Proportion AA’A’A:A’AAA’:AA’AA’^c |
|-------|------------------|-------------------|------------|------------|-----------|----------------------------------|
| 1     | AA’AA’ from 13   | OH                | 134        | 350        | 74        | 22:15:63                         |
| 2     | Allyl-AA’AA’ 19  | Allyl             | 132        | 134        | 95        | 22:15:63                         |
| 3     | Furfuryl-AA’AA’ 20| Furfuryl          | 134        | 225        | 95        | 22:15:63                         |

^a Determined by DSC. ^b Determined by TGA. ^c Determined by 13C NMR spectroscopy.
Figure S3. SEC traces of AA’AA’ polymer from 13 and the corresponding end-capped polymers 19 and 20.

Synthesis of model compound ethyl (S,E)-2-(3-(4-(((allyloxy)carbonyl)oxy)-3-methoxyphenyl)acrylamido)-3-(4-(((allyloxy)carbonyl)oxy)phenyl)propanoate 17. To a solution of 8 (51.1 mg, 0.13 mmol) in CH₂Cl₂ (0.26 mL) were added Et₃N (54 μL, 0.39 mmol) and allylchloroformate (35 μL, 0.33 mmol). The reaction was stirred at room temperature for 1 h. A saturated solution of NaHCO₃ was added and the crude was extracted with CH₂Cl₂, dried over Na₂SO₄ and filtered. The solvent was removed under vacuum. The desired product was obtained after purification on a silica cartridge (4 g, 0% to 100% of AcOEt in hexane over 15 min) as a yellow foam (56.8 mg, 0.10 mmol, 77%). ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, J = 15.6 Hz, 1 H), 7.16-7.04 (m, 7 H), 6.36 (d, J = 15.6 Hz, 1 H), 6.30 (d, J = 7.7 Hz, 1 H), 6.02-5.93 (m, 2 H), 5.44-5.38 (m, 2 H), 5.35-5.27 (m, 2 H), 5.03-4.95 (m, 1 H), 4.74-4.70 (m, 4 H), 4.19 (qd, J = 7.2, 2.3 Hz, 2 H), 3.86 (s, 3 H), 3.25-3.13 (m, 2 H), 1.25 (t, J = 7.2 Hz, 2 H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 171.4 (C), 165.0 (C), 153.4 (C), 152.8 (C), 151.3 (C),150.1 (C), 141.1 (C), 140.9 (CH), 133.76 (C), 133.75 (C), 131.01 (CH), 130.98 (CH), 130.4 (2 CH), 122.6 (CH), 121.0 (2 CH), 120.8 (CH), 120.3 (CH), 119.5 (CH₂), 119.2 (CH₂), 111.3 (CH), 69.3 (CH₂), 69.1 (CH₂), 61.8 (CH₂), 55.9 (CH₃), 53.2 (CH), 37.1 (CH₂), 14.6 (CH₃) ppm; FTIR (ATR) υ_max (cm⁻¹) 1759,
1661, 1625, 1508; MS (ESI+) m/z (%) 554.2 (100, [M+H]+); ESIHRMS calcd for C_{29}H_{32}NO_{10}(M+H) 554.2026, found 554.2019.

**Synthesis of model compound ethyl ((S,E)-2-(3-(((furan-2-ylmethyl)carbamoil)oxy)-3-methoxyphenyl)acrylamido)-3-(((furan-2-ylmethyl)carbamoil)oxy)phenyl)propanoate 18.** To a solution of 8 (51.1 mg, 0.13 mmol) in CH$_2$Cl$_2$ (0.26 mL) were added Et$_3$N (54 μL, 0.39 mmol) and furfuryl isocyanate (36 μL, 0.33 mmol). The reaction was stirred at room temperature for 2 h. A saturated solution of NaHCO$_3$ was added and the crude was extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$ and filtered. The solvent was removed under vacuum. The desired product was obtained after purification on a silica cartridge (4 g, 0% to 100% of AcOEt in hexane over 15 min) as a yellow foam (48.8 mg, 0.08 mmol, 62%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.55 (d, $J$ = 15.6 Hz, 1 H), 7.37 (dd, $J$ = 1.9, 0.9 Hz, 2 H), 7.11-7.00 (m, 7 H), 6.41-6.14 (m, 6 H), 5.60 (t, $J$ = 5.9 Hz, 1 H), 5.52 (t, $J$ = 5.9 Hz, 1 H), 4.98 (dt, $J$ = 7.7, 5.7 Hz, 1 H), 4.41 (t, $J$ = 5.9 Hz, 4 H), 4.18 (q, $J$ = 7.1 Hz, 2 H), 3.81 (s, 3 H), 3.17 (dd, $J$ = 5.7, 3.5 Hz, 2 H), 1.26 (t, $J$ = 7.1 Hz, 3 H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.5 (C), 165.2 (C), 154.3 (C), 153.9 (C), 151.7 (C), 151.0 (C), 150.0 (C), 142.32 (C), 142.26 (CH), 141.12 (C), 141.06 (CH), 133.2 (C), 133.0 (C), 130.2 (2 CH), 123.4 (CH), 121.6 (2 CH), 121.0 (CH), 120.0 (2 CH), 111.1 (CH), 110.44 (CH), 110.42 (CH), 107.6 (CH), 107.53 (CH), 61.7 (CH$_2$), 55.9 (CH$_3$), 53.2 (CH), 38.3 (CH$_2$), 38.2 (CH$_2$), 37.1 (CH$_2$), 14.1 (CH$_3$) ppm; FTIR (ATR) $\nu_{\text{max}}$ (cm$^{-1}$) 3400-3200, 1726, 1663, 1624, 1503; MS (ESI+) m/z (%) 632.3 (100, [M+H]+); ESIHRMS calcd for C$_{33}$H$_{34}$N$_3$O$_{10}$(M+H) 632.2244, found 632.2254.

**Synthesis of AA’AA’ polymer 19.** To a solution of polymer AA’AA’ from 13 (113.4 mg, 0.21 mmol) in CH$_2$Cl$_2$ (0.42 mL) were added triethylamine (86 μL, 0.62 mmol) and allyl chloroformate (56 μL, 0.53 mmol). The mixture was stirred at room temperature for 3 h and was
quenched with a saturated solution of NaHCO₃. The product was extracted with CH₂Cl₂, dried over Na₂SO₄ and the solvent was removed. The mixture was solubilized in CH₂Cl₂, precipitated into MeOH three times and dried under vacuum to give the desired product as a yellowish solid which follows A’AA’, AA’A, AA’AA’ patterns in 22/15/63 proportions (82.2 mg, 0.20 mmol, 95%). DMF SEC: \( M_n = 5.7 \text{ kg.mol}^{-1}, \bar{D} = 1.45 \); FTIR (ATR) \( \nu_{\text{max}} (\text{cm}^{-1}) \) 3400-3200, 1776, 1738, 1661, 1624, 1603, 1505; \(^1\)H NMR (500 MHz, CDCl₃) \( \delta \) 7.61-7.47 (m, 19 H), 7.22-6.97 (m, 133 H), 6.47-6.29 (m, 38 H), 5.97 (ddt, \( J = 17.2, 10.4, 5.6 \) Hz, 2 H), 5.41 (d, \( J = 17.2 \) Hz, 2 H), 5.31 (d, \( J = 10.4 \) Hz, 2 H), 5.08-4.88 (m, 19 H), 4.72 (d, \( J = 5.6 \) Hz, 4 H), 4.29-4.08 (m, 39 H), 4.00-3.82 (m, 57 H), 3.26-3.12 (m, 38 H), 1.28-1.21 (m, 57 H) ppm; \(^{13}\)C NMR (125 MHz, CDCl₃) \( \delta \) 171.5 (19 C), 165.1 (19 C), 152.8 (2 C), 152.0 (4.2 C(O)AA’AA’), 151.3 (12.0 CAA’AA’), 151.2 (7.0 CAA’AA’), 151.1 (12.0 C(O)AA’AA’), 150.7 (2.8 C(O)AA’A), 150.1 (12.0 CAA’AA’), 149.9 (7.0 CAAA’A’), 141.1, 140.9, 140.8 (19 CH + 19 C), 134.2, 134.1, 134.0 (38 C), 130.5 (38 CH), 130.4 (2 CH), 122.5 (12.0 CHAA’AA’), 122.4 (7.0 CHAA’A’), 120.89, 120.85, 120.8 (38 CH), 120.6 (19 CH), 119.2 (2 CH₂), 111.5 (7.0 CHAA’AA’), 111.4 (12.0 CHAA’AA’), 69.3 (2 CH₂), 61.7 (19 CH₂), 56.0 (19 CH₃), 53.3 (19 CH), 37.2 (19 CH₂), 14.1 (19 CH₃) ppm; \( T_g = 132 ^\circ \text{C}, T_p = 351 ^\circ \text{C}. \)

**Synthesis of AA’AA’ polymer 20.** To a solution of polymer AA’AA’ from 13 (120.2 mg, 0.22 mmol) in CH₂Cl₂ (0.424 mL) were added triethylamine (91 \( \mu \text{L}, 0.66 \) mmol) and furfuyl isocyanate (59 \( \mu \text{L}, 0.55 \) mmol). The mixture was stirred at room temperature for 3 h and was quenched with a saturated solution of NaHCO₃. The product was extracted with CH₂Cl₂, dried over Na₂SO₄ and the solvent was removed. The mixture was solubilized in CH₂Cl₂, precipitated into MeOH three times and dried under vacuum to give the desired product as a yellowish solid which follows A’AAA’, AA’A, AA’AA’ patterns in 22/15/63 proportions (87.8 mg, 0.21
mmol, 95%). DMF SEC: $M_n = 5.9$ kg.mol$^{-1}$, $D = 1.34$; FTIR (ATR) $\nu_{\text{max}}$ (cm$^{-1}$) 3400-3200, 1778, 1732, 1661, 1626, 16.03, 1508; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.55 (br d, $J = 16.5$, 17 H), 7.36 (s, 2 H), 7.23-6.98 (m, 119 H), 6.43-6.22 (m, 38 H), 5.55-5.47 (br m, 2 H), 5.04-4.92 (m, 17 H), 4.41 (br d, $J = 5.6$ Hz, 4 H), 4.25-4.11 (m, 34 H), 3.95-3.82 (m, 51 H), 3.26-3.07 (m, 36 H), 1.31-1.14 (m, 51 H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.5 (17 C), 165.1 (17 C), 153.9 (2 C), 152.0 (3.7 C(O)$_{\text{A'AA'}}$), 151.3 (10.7 C$_{\text{AA'AA'}}$), (6.3 C$_{\text{AA'AA'}}$, 151.1 (10.7 C(O)$_{\text{AA'AA'}}$), 151.0 (2 C), 150.7 (2.6 C(O)$_{\text{AA'AA'}}$), 150.2 (10.7 C$_{\text{AA'AA'}}$), 150.0 (6.3 C$_{\text{AA'AA'}}$), 142.4 (2 CH), 142.3 (2 CH), 141.1, 141.0, 140.8 (17 CH + 17 C), 134.2, 134.1 (34 C), 130.50 (34 CH), 122.54 (10.7 CH$_{\text{AA'AA'}}$), 122.47 (6.3 CH$_{\text{AAA'AA'}}$), 120.92, 120.87 (34 CH), 120.6 (17 CH), 111.5 (6.3 CH$_{\text{AAA'AA'}}$), 111.4 (10.7 CH$_{\text{AA'AA'}}$), 111.2 (17 CH), 110.4 (2 CH), 107.6 (2 CH), 61.8 (17 CH$_2$), 56.0 (17 CH$_3$), 53.3 (17 CH), 38.5 (2 CH$_2$), 37.2 (CH$_2$), 14.1 (17 CH$_3$) ppm; $T_g = 134$ °C; $T_p^1 = 135$ °C, $T_p^2 = 225$ °C, $T_p^3 = 339$ °C.

**Table S3.** Optimization of the polymerization conditions for 14.

| Entry | Concentration (M) | Time (h) | $M_n$ ($\text{kg.mol}^{-1}$) ($D$) | Yield (%) |
|-------|------------------|----------|-----------------------------------|-----------|
| 1     | 0.1              |          | 4 units                           | /         |
| 2     | 0.26             | 5        | 17 (5.05), bimodal                 | /         |
| 3     | 0.5              |          | Insoluble                         | /         |
| 4     | 0.75             |          | Insoluble + SM/dimer               | /         |
| 5     | 0.5              | 1.5      | 11.1 (1.92)                       | 14        |
| 6     | 0.5              | 0.5      | Multimodal                        | 47        |
| 7     | 0.5              | 0.25     | 8.3 (2.08)                        | 56        |
| 8     | 0.5              | 0.1      | 8.4 (1.97)                        | 36        |

*Experimental conditions:* 14, AgF (2 eq), CH$_3$CN/Pyridine (1:4), r.t. $^a$ Determined by SEC using the oligomer-based calibration curve.
Table S4. Optimization of polymerization conditions from 16.

| Entry | Diphosgene (eq) | Concentration (M) | Time (h) | $M_n$ a (kg.mol$^{-1}$) (D) | Yield (%) |
|-------|-----------------|------------------|----------|----------------------------|-----------|
| 1     | 0.55            | 0.53             |          | 8.1 (3.29)                 | 40        |
| 2     | 0.55            | 0.1              |          | 5.2 (3.26)                 | 36        |
| 3     | 1.0             | 15               |          | 6.4 (2.95)                 | 88        |
| 4     | 2.0             | 0.26             |          | 12.3 (2.22)                | 87        |
| 5     | 2.0             |                  |          | b                          | /         |
| 6     | 1.1             | 2                |          | 18 (2.06)                  | 74        |

Experimental conditions: 16, pyridine, r.t. a Determined by SEC using the oligomer-based calibration curve. b No precipitation occurred in MeOH.

Table S5. Optimization of polymerization conditions from 8.

| Entry | Diphosgene (eq) | Concentration (M) | T (°C) | Time (h) | $M_n$ a (kg.mol$^{-1}$) (D) | Yield (%) |
|-------|-----------------|------------------|--------|----------|----------------------------|-----------|
| 1     | 0.55            | 0.53             | 60     | Insoluble|                           | /         |
| 2     | 1.35            |                  |        |          | 3.9 (2.90)                 | 60        |
| 3     | 0.26            |                  |        |          | b                          | /         |
| 4     | 0.55            | 0.53             |        |          | 14 (2.57)                  | 48        |
| 5     | 0.53            |                  |        |          | 8.8 (2.01)                 | 86        |
| 6     |                  | r.t.             |        | 6.0      | (1.98)                    | 40        |
| 7     | 1.0             |                  | 2      |          | 4.1 (4.04)                 | 67        |
| 8     | 1.1             | 0.26             | 2      |          | 4.8 (3.25)                 | 86        |
| 9     | 2.0             |                  |        |          | b                          | /         |
| 10    | 0.5             |                  |        |          | Insoluble                  | /         |

Experimental conditions: 8, pyridine. a Determined by SEC using the oligomer-based calibration curve. b No precipitation occurred in MeOH.

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**Figure S4.** SEC profile for each polymer synthesized.

**Figure S5.** Absorbance, excitation and emission spectra of l-tyrosine ethyl ester.

**Figure S6.** Absorbance, excitation and emission spectra of FA.
Figure S7. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 1 in CD$_3$OD
Figure S8. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 2 in CDCl$_3$
Figure S9. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 3 in CDCl$_3$. 

![NMR Spectra Image]
Figure S10. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 4 in CDCl$_3$
Figure S11. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 5 in CDCl$_3$
Figure S12. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 8 in CDCl$_3$
Figure S13. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 10 in CDCl$_3$. 

Artifact from the RMN
Figure S14. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 11 in CDCl$_3$
Figure S15. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 12 in CDCl$_3$
Figure S16. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 13 in CDCl$_3$
Figure S17. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for AA’AA’ polymer from 13 in CDCl$_3$. 
Figure S18. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for AA’AA’ polymer 19 in CDCl$_3$. 
Figure S19. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for AA’AA’ polymer 20 in CDCl$_3$
Figure S20. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 14 in CDCl$_3$
Figure S21. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for AA’AA’ polymer from 14 in $d_6$-DMSO
Figure S22. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 15 in CDCl$_3$
Figure S23. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 16 in $d_8$-THF
Figure S24. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 16 in $d_6$-DMSO/THF-Water.
Figure S25. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for A'AAA'A'AAA' polymer from 16 in $d_6$-DMSO
**Figure S26.** $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for the random polymer from 8 in CDCl$_3$
Figure S27. \(^1\)H (500 MHz), \(^{13}\)C (125 MHz) NMR spectra for the random polymer from 8 in \(d_6\)-DMSO.

Water
Figure S28. $^1$H (500 MHz), $^{13}$C (125 MHz), HMQC NMR spectra for compound 17 in CDCl$_3$
Figure S29. $^1$H (500 MHz), $^{13}$C (125 MHz) NMR spectra for compound 18 in CDCl$_3$
Stephenson, R. M. J. Chem. Eng. Data 1993, 38, 634-637.