Supplementary Information (SI) for Polymer Chemistry. This journal is © The Royal Society of Chemistry 2025

Supporting information

Sustainably One-pot Synthesis of Imide-containing Polyesters with Programable Structures and High Performance

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Material and Methods

Purchased Materials

All the chemistries were used as-received without any further purification. 2-Aminoethanol (99%), DL-alaninol (98%), DL-1-amino-2-propanol (>99%), Succinic acid (99.5%), Glutaric acid (99%), Adipic acid (99%), Triphenyl phosphite (98%) and antimony(III) oxide (Sb₂O₃, 99.5%) were purchased from Shanghai Macklin Biochemical Co., Ltd. 3-Amino-1,2-propanediol (95%), 2-Aminopropane-1,3-diol (98%), 2-Amino-2-methyl-1,3-propanediol (98%), 2-Aminobutane-1,3-diol (98%), 1,4-Butanediol (99%), 2-Methylsuccinic acid (95%), 2,2-Dimethylsuccinic acid (95%), 2-Phenylsuccinic acid (98%), Phthalic acid ((98%), Cyclohexane-1,2-dicarboxylic acid (≥95%), 1,1-Cyclohexanediaceticacid (97%), Glutaric acid (95%), Adipic acid (95%), Titanium(IV) butoxide(TBT, 99%), Scandium(III) trifluoromethanesulfonate $(Sc(CF_3SO_4)_3,$ 99%), Cerium(III) trifluoromethanesulfonate (Ce(CF₃SO₄)₃, 99%) and stannous chloride (SnCl₂, 98%) were purchased from Bide Pharmatech Co., Ltd. CHCl₃ (HPLC) was purchased from Honeywell International Inc. Dimethyl sulfoxide-d₆ (DMSO-d₆) and deuterated chloroform (CDCl₃) were purchased from Anhui Senrise Technologies Co., Ltd.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE NEO 500 (RT Probe or Cryo Probe) (¹H at 500 MHz; ¹³C at 126 MHz), Bruker AVANCE NEO 600 (RT Probe or Cryo Probe) (¹H at 600 MHz; ¹³C at 151 MHz) or Bruker AVANCE NEO 500 (MAS Probe) (¹³C at 126 MHz).

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were measured on a Horiba Bruker FTIR spectrometer, and the spectra ranged from 4000 to 500 cm⁻¹.

High-resolution mass spectra (HRMS) of small molecules were recorded on a Waters Mass spectrometer using ESI-TOF (electrospray ionization-time of flight) and HRMS data was processed by Masslynx V 4.2.

Gel permeation chromatography (GPC) measurements were performed on a Waters Breeze QS system with a 1515 isocratic HPLC pump, a 2414 refractive index detector, and a 2707 autosampler. Separations were performed using serially connected columns (Shodex K805, KF-804L and K-803) at 40 °C using CHCl₃ as the mobile phase at a flow rate of 0.8 mL/min. The resulted M_n , M_w and \tilde{D} were determined basing on polystyrene (PS) standards instead.

Thermogravimetric Analysis (TGA) analysis was carried out using a TGA/DSC 3+/1600 HT instrument (Mettler Toledo). Samples were heated under nitrogen from 30 to 800 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C/min.

Differential Scanning Calorimetry (DSC) analysis was carried out using a DSC 3+/700 instrument (Mettler Toledo), in nitrogen, with a heating and cooling rate of 10 °C/min. Melting-transition temperature (T_m) and glass-transition Temperature (T_g) were obtained from the second heating scan (from -60 to 200 °C) after the thermal history was removed (from RT to 200 °C and hold at 200 °C for 5 min). Crystalline-transition temperature (T_c) was obtained from the second cooling scan from (from 200 to -60 °C).

Degree of crystallinity (X_c) was calculated by the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} * 100\%$$

Where Melting enthalpy (ΔH_m) was calculated by integrating the melting peak for semicrystalline polymer on the second heating scan. ΔH_m^0 is the theoretical melting enthalpy of 100% crystalline polymer. For poly(butylene succinate), $\Delta H_m^0 = 110.3 \text{ J/g.}^1$

Powder angle X-ray scattering (PXRD) measurements were performed on a Bruker D8 Advance instrument with a Cu K α X-ray source, a wavenumber λ of 0.1542 nm, and a scattering angle of 20.

The tensile test of different materials was acquired on a single-column electronic universal testing machine (SUST, China) with a 1KN load cell at a speed of 10 mm min⁻¹ at room temperature. Each mechanical test was repeated at least five splines.

Compost degradation experiments were conducted in cooperation with Shanghai WEIPU Testing Technology Group Co., Ltd., following the standard GB/T 19277.1-2011.

Model Reaction

From the outset, we intended to select 2-aminoethanol and succinic acid (**2a**) as substrates to research the possibility of synthesizing performance-advantage poly(ester-amide) (Figure S1). Surprisingly, we discovered that using an excess molar ratio of succinic acid to react with 2-aminoethanol at 150 °C with nitrogen flow primarily yielded disuccinimidyl succinate compound and succinic anhydride (Fig. S1). Due to the involvement of thermal esterification and imidization, this reaction was considered a model for synthesizing di(ester-imide) compounds. Further, we investigated additional dicarboxylic acids, including 2-methylsuccinic acid (**2b**), 2,2-dimethylsuccinic acid (**2c**), 2-phenylsuccinic acid (**2d**), phthalic acid (**2e**), cyclohexane-1,2-dicarboxylic acids such as glutaric acid, adipic acid and 1,1-cyclohexanediaceticacid (**2g**) for this model reaction.

General synthesized procedure:



Amino alcohols (50mmol, 1.0 eq.) and dicarboxylic acids (100 mmol, 2.2 eq.) were weighted into a 100ml, three-neck, round-bottom flasks equipped with a top stirrer. The reactor was heated to 150 °C under a constant nitrogen flow to remove the water (10–16 h). The reaction mixture was then heated to 180–260 °C and over 30 min, the pressure in the reaction vessel was reduced to below 50 Pa. The reaction was allowed to proceed for 6–14 h, after which the final mixture was poured into the cold water. The precipitates were vacuum dried at 60 °C for 6 h prior to subsequent characterization.



¹H NMR (500 MHz, DMSO-d₆) δ 4.13 (t, J = 5.6 Hz, 4H), 3.60 (t,

J = 5.5 Hz, 4H), 2.62 (s, 8H), 2.46 (s, 4H) ppm. ¹³**C NMR** (126 MHz, None) δ 181.19, 180.44, 173.20, 58.68, 38.61, 29.84, 28.62, 28.26 ppm. **HRMS** (ESI): m/z calculated for C₁₆H₂₀N₂O₈ [H]⁺ 369.1298, found 369.1296.



DI-2

¹H NMR (600 MHz, DMSO-d₆) δ 4.41 - 4.34 (m, 2H), 4.31 - 4.24

(m, 2H), 4.17 - 4.11 (m, 2H), 2.59 (s, 8H), 2.46 (s, 4H), 1.27 (d, J = 7.1 Hz, 6H) ppm. ¹³C NMR (151 MHz, DMSO-d₆) δ 177.72, 171.54, 63.38, 45.52, 28.41, 27.83, 13.76 ppm. HRMS (ESI): m/z calculated for C₁₈H₂₄N₂O₈ [H]⁺ 397.1611, found 397.1601.



¹H NMR (500 MHz, DMSO-d₆) δ 5.07 – 4.94 (m, 2H), 3.55 (dd, *J*

= 13.9, 7.8 Hz, 2H), 3.44 (dd, J = 13.9, 4.0 Hz, 2H), 2.61 (s, 8H), 2.46 - 2.34 (m, 4H), 1.15 (d, J = 6.5 Hz, 6H) ppm. ¹³**C NMR** (126 MHz, DMSO-d₆) δ 177.64, 171.57, 67.49, 41.93, 28.58, 27.91, 17.43 ppm. **HRMS** (ESI): m/z calculated for C₁₈H₂₄N₂O₈ [H]⁺ 397.1611, found 397.1605.



DI-4

¹H NMR (500 MHz, CDCl₃) δ 4.26 (dt, *J* = 10.5, 5.1 Hz, 4H),

3.82 - 3.68 (m, 4H), 2.97 - 2.78 (m, 5H), 2.68 - 2.61 (m, 1H), 2.38 - 2.27 (m, 3H), 1.37 - 1.31 (m, 6H), 1.17 (d, J = 7.2 Hz, 3H) ppm. ¹³**C NMR** (126 MHz, CDCl₃) δ 180.60, 180.57, 176.49, 176.47, 175.03, 171.76, 38.02, 37.98, 37.22, 36.46, 36.42, 35.60, 35.58, 34.74, 16.89, 16.88, 16.68 ppm. **HRMS** (ESI): m/z calculated for C₁₉H₂₆N₂O₈ [H]⁺ 411.1767, found 411.1775.



¹H NMR (500 MHz, CDCl₃) δ 4.23 (dt, *J* = 14.0, 5.2 Hz, 4H),

3.73 (dt, J = 16.3, 5.2 Hz, 4H), 2.53 (s, 4H), 2.49 (s, 2H), 1.29 (s, 12H), 1.19 (s, 6H) ppm. ¹³**C NMR** (126 MHz, CDCl₃) δ 183.13, 183.02, 176.42, 175.78, 175.71, 171.10, 61.38, 60.77, 43.78, 43.57, 43.55, 40.44, 40.05, 39.99, 38.00, 37.94, 25.52, 25.49, 25.22 ppm. **HRMS** (ESI): m/z calculated for C₂₂H₃₂N₂O₈ [H]⁺ 453.2237, found 453.2249.



DI-6

¹H NMR (500 MHz, DMSO-d₆) δ 7.37 - 7.17 (m,

15H), 4.31 - 4.08 (m, 5H), 4.07 - 3.87 (m, 2H), 3.75 - 3.60 (s, 4H), 3.23 - 2.92 (m, 5H), 2.77 - 2.52 (m, 1H). ¹³**C NMR** (126 MHz, DMSO-d₆) δ 177.89, 177.75, 176.14, 175.87, 173.76, 172.38, 138.35, 138.06, 137.93, 128.72, 128.68, 128.64, 127.94, 127.77, 127.76, 127.69, 127.34, 60.81, 60.47, 46.69, 46.55, 46.33, 45.44, 45.31, 37.33, 37.23, 36.76 ppm. **HRMS** (ESI): m/z calculated for C₃₄H₃₂N₂O₈ [H]⁺ 597.2237, found 597.2233.



DI-7

¹H NMR (500 MHz, DMSO-d₆) δ 7.88 - 7.78 (m, 8H), 7.63 (s, 4H), 4.31 (t, *J* = 5.4 Hz, 4H), 3.87 (t, *J* = 5.4 Hz, 4H) ppm. ¹³C NMR (126 MHz, DMSO-d₆) δ 167.70, 166.47, 134.44, 131.65, 131.54, 131.05, 128.68, 123.10, 62.45, 36.55 ppm. HRMS (ESI): m/z calculated for C₂₈H₂₀N₂O₈ [H]⁺ 513.1298, found 513.1296.



¹H NMR (500 MHz, CDCl₃) δ 4.39 - 4.12 (m, 4H), 3.83 -

3.62 (m, 4H), 2.89 - 2.70 (m, 5H), 2.59 - 2.48 (m, 1H), 1.99 - 1.69 (m, 12H), 1.51 - 1.28 (m, 12H) ppm. ¹³**C NMR** (126 MHz, CDCl₃) δ 180.00, 179.69, 179.64, 178.87, 174.55, 173.38, 61.09, 60.87, 44.48, 44.46, 42.43, 42.27, 39.72, 37.60, 28.85, 28.51, 25.12, 23.73, 21.69 ppm. **HRMS** (ESI): m/z

calculated for C₂₈H₃₈N₂O₈ [H]⁺ 531.2706, found 531.2701.



¹H NMR (500 MHz, DMSO-d₆) δ 4.07 (t, *J* = 5.6 Hz,

4H), 3.88 (t, J = 5.6 Hz, 4H), 2.57 (s, 8H), 2.36 (s, 4H), 1.49 – 1.28 (m, 30H) ppm. ¹³**C** NMR (126 MHz, DMSO-d₆) δ 171.73, 170.91, 60.47, 42.99, 40.40, 37.34, 35.11, 34.75, 34.42, 31.30, 25.36, 20.94 ppm. HRMS (ESI): m/z calculated for C₃₄H₅₀N₂O₈ [H]+ 615.3646, found 615.3651.

General polymerization experiments of two-component system



Amino diols (100 mmol, 1.0 eq.) and dicarboxylic acids (210 mmol, 2.1 eq.) were weighted into a 150 ml, three-neck, round-bottom flasks equipped with a top stirrer. The reactor was heated to 150–200 °C under a constant nitrogen flow to remove the water. The reaction was monitored by ¹H-NMR and once the complete conversion from amino groups to imide groups was confirmed (~10-18 h), the nitrogen flow was turned off. Subsequently, the polycondensation catalyst was added or the polycondensation reaction was conducted without a catalyst. The reactor was then evacuated to a pressure of less than 50 Pa, and heated to 180-260 °C for 18–48 h. Under high temperature and high vacuum, the polycondensation reaction was driven by the removal of carboxyl-terminated prepolymers and the reaction by-products (water and corresponding anhydrides). The final reaction mixtures were poured into cold water, and the precipitates were vacuum dried at 80 °C for 6 h before subsequent characterization.



P(2a3a)

¹H NMR (500 MHz, CDCl₃) δ 5.29 (s, 1H), 4.29 - 4.06 (m, 2H), 3.87 - 3.76

(m, 1H), 3.70 - 3.57 (m, 1H), 2.77 - 2.50 (m, 8H). ¹³**C NMR** (126 MHz, CDCl₃) δ 177.70, 177.44, 171.94, 171.78, 68.84, 63.27, 38.90, 28.92, 28.75, 28.55, 28.14.



P(**2a3b**) ¹H NMR (500 MHz, CDCl₃) δ 4.65 - 4.47 (m, 3H), 4.39 - 4.30 (m, 2H), 2.70 (s, 4H), 2.54 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 177.47, 171.67, 60.62, 50.17, 28.73, 28.08. ¹³C NMR (126 MHz, CDCl₃) δ 177.47, 171.67, 60.62, 50.17, 28.73, 28.08.



P(2a3c)
 ¹H NMR (500 MHz, CDCl₃) δ 5.61 - 5.44 (m, 1H), 4.72 - 4.49 (m, 1H), 4.32 (s, 2H), 2.81 - 2.66 (m, 4H), 2.62 - 2.37 (m, 4H), 1.28 (s, 2H), 1.13 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 178.06, 177.61, 171.84, 171.49, 67.54, 60.46, 54.83, 28.92, 28.79, 28.64, 28.43, 17.92.



P(2a3d) ¹H NMR (500 MHz, CDCl₃) δ 4.69 - 4.44 (m, 4H), 2.63 (s, 4H), 2.56 (s, 2H),
 1.60 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 178.34, 171.63, 64.82, 61.66, 28.86, 28.52.



P(**2b3b**) ¹**H NMR** (500 MHz, CDCl₃) δ 4.62 - 4.42 (m, 3H), 4.32 (s, 2H), 3.01 - 2.72 (m, 3H), 2.69 - 2.56 (m, 1H), 2.42 - 2.24 (m, 2H), 1.31 (d, J = 7.2 Hz, 3H), 1.14 (d, J = 7.2 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 180.66, 176.51, 174.49, 171.12, 60.66, 60.57, 50.19, 37.06, 36.24, 35.49, 34.49, 16.90, 16.61.



 $\label{eq:product} \begin{array}{l} \mbox{P(2c3b)} & \mbox{$^{P(2c3b)}$} & \mbox{$^{P(2c3b)}$} & \mbox{1H NMR$ (600 MHz, CDCl_3) δ 4.55 - 4.27 (m, 4H), 4.02 - 3.77 (m, 1H), 2.63 \\ - 2.39 (m, 4H), 1.28 (s, 6H), 1.16 (s, 6H). \mbox{1^{3}$C NMR$ (126 MHz, CDCl_3) δ 183.91, 183.14, 175.85, 170.48, 60.86, 60.41, 50.18, 43.79, 43.35, 40.49, 39.74, 25.51, 25.31, 25.15, 24.94. \end{array}$



P(2d3b)
 ¹H NMR (500 MHz, CDCl₃) δ 7.40 - 6.90 (m, 10H), 4.56 (s, 3H), 4.25 (s, 2H), 3.95 (s, 2H), 3.07 (s, 2H), 2.56 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 175.91, 172.16, 172.03, 171.01, 170.82, 137.24, 136.98, 129.11, 129.06, 128.98, 127.77, 127.57, 127.50, 60.78, 60.55, 50.08, 46.74, 45.60, 45.49, 36.81.



 $\label{eq:product} \begin{array}{c} \mathsf{P}(\textbf{2e3b}) & \ensuremath{^1\text{H}}\ \mathsf{NMR}\ (500\ \mathsf{MHz},\ \mathsf{CDCI}_3)\ \delta\ 8.01\ -\ 7.33\ (\mathsf{m},\ 8\mathsf{H}),\ 5.03\ -\ 4.89\ (\mathsf{m},\ 1\mathsf{H}),\ 4.82\\ -\ 4.60\ (\mathsf{m},\ 4\mathsf{H}),\ 4.17\ -\ 4.01\ (\mathsf{m},\ 1\mathsf{H}).\ ^{13} \mbox{C}\ \mathsf{NMR}\ (126\ \mathsf{MHz},\ \mathsf{CDCI}_3)\ \delta\ 168.58,\ 167.97,\ 166.79,\ 166.61,\ 134.15,\ 131.66,\ 131.32,\ 129.04,\ 123.46,\ 77.11,\ 62.23,\ 60.79,\ 52.41,\ 49.12. \end{array}$



 $\begin{array}{l} \mbox{P(2f3b)} & \mbox{$^{P(2f3b)}$} \\ \mbox{$^{P(2f3b)}$} & \mbox{HNMR$} (600 \mbox{$MHz$, CDCl}_3) \ \delta \ 4.58 \ - \ 4.39 \ (m, \ 3H), \ 4.38 \ - \ 4.21 \ (m, \ 2H), \ 2.85 \\ \mbox{$(s, 2H), 2.73$} (s, \ 1H), \ 2.55 \ - \ 2.43 \ (m, \ 1H), \ 2.00 \ - \ 1.66 \ (m, \ 8H), \ 1.47 \ - \ 1.19 \ (m, \ 8H). \ {}^{13}\mbox{C} \ NMR \ (126 \ MHz, \ CDCl}_3) \ \delta \ 179.63, \ 179.54, \ 174.28, \ 172.86, \ 60.60, \ 60.53, \ 49.83, \ 44.39, \ 42.44, \ 39.66, \ 39.64, \ 28.76, \ 25.09, \ 23.82, \ 21.84. \end{array}$



P(**2g3b**) ¹H NMR (500 MHz, CDCl3) δ 5.16 - 5.11 (m, 1H), 4.50 - 4.28 (m, 4H), 2.64 - 2.40 (m, 8H), 1.53 - 1.35 (m, 20H). ¹³C NMR (126 MHz, CDCl₃) δ 172.31, 171.33, 61.26, 50.21, 36.00, 35.96, 35.59, 35.15, 31.83, 25.77, 25.71, 21.49, 21.38.

General copolymerization experiments of three-component system



General procedures, such as the synthesis of P(2a3a4a)_x, are outlined in the following steps:

3-Amino-1,2-propanediol (**3a**), 1,4-butanediol (**4a**) and succinic acid (**2a**) were weighted into a 500ml, three-neck, round-bottom flasks equipped with a top stirrer, using a molar ratio of x/(1-x)/(1.1+x). The reactor was heated to 150 °C under a constant nitrogen flow to remove water. After 20 h of imidization and prepolymerization, the polycondensation catalyst, SnCl₂ (300 ppm), was added to the mixture. The reactor was then evacuated to a pressure of less than 50 Pa over 30 min and heated to 220 °C for 24 h. Under high temperature and high vacuum, the polycondensation reaction proceeded by removing the carboxyl-terminated prepolymer reaction by-products (water and succinic anhydride). The final reaction mixtures were poured into cold water and the precipitates were vacuum dried at 80 °C for 6 h before subsequent characterization. The structures were confirmed by FTIR spectra, ¹H, and ¹³C NMR spectra.

DFT study

All DFT calculations were performed using the Gaussian 16 suite of programs.² The Pope 6-31G(d, p) basis set was applied for C, H, O and N atoms. The Gibbs free energy was calculated using the B3LYP/6-311G (d) method at 453.15K. The transition state (TS) energy was calculated via the m062x/6-31g(d,p) method.

Supplementary data



Figure S1. Schematic feasibility study for the reaction of 2-aminoethanol and excess. Reaction condition: 2-aminoethanol (40 mmol, 2.468 g), succinic acid (fellow the feed ratio), catalyst-free and solvent-free, one-pot two-step procedure (first, 150 °C, N₂ flow, 10 h; second, 180 °C, < 50 Pa, 6 h). Yield determined by separation product.



Figure S2. ¹H NMR analysis of the di(ester imide) DI-1 preparation process.



Figure S3. ¹H NMR spectrum of removed by-product succinic anhydride of the di(ester imide) **DI-1** preparation process.



Figure S4. Full UPLC-HRMS spectra of the mixture when di(ester imide) **DI-I** preparation process was proceeded to 120 min.

	Monomers	m/z [H]+			Monomers	m/z [H]⁺	
		Calculated	Found		-	Calculated	Found
1	0~0~0~0	101.0239	101.0240	7	о N N O O O O O O O H	244.0821	244.0829
2	° L N = 0	126.0555	126.0561	8	HO T HO H H O O O O O O O O O O O O O O	262.0927	262.0930
3	O N O O O O O H	144.0661	144.0665	9	Chool	287.1243	287.1248
4	HO C N N N N N N N N N N N N N N N N N N	162.0766	162.0771	10	но∽∽йд~~ди~~од~~Сон	305.1349	305.1357
5	Со NН ОН	187.1083	187.1089	(11)		369.1298	369.1299
6	HO N N N N OH	205.1188	205.1191	(12)		387.1404	387.1412

 Table S1. The corresponding compounds in Figure S2.



Figure S5. (a) Catalyst- and solvent-free synthesis of di(ester imide) **DI-1**. (b) The proposed reaction pathway, including the corresponding intermediates, is illustrated in Table S1.



Figure S6. ¹H NMR spectrum of di(ester imide) DI-1.



Figure S7. ¹³C NMR spectrum of di(ester imide) DI-1.



Figure S8. ¹H NMR spectrum of di(ester imide) DI-2.



Figure S9. ¹³C NMR spectrum of di(ester imide) DI-2.



Figure S10. ¹H NMR spectrum of di(ester imide) DI-3.



Figure S11. ¹³C NMR spectrum of di(ester imide) DI-3.



Figure S12. ¹H NMR spectrum of di(ester imide) DI-4.



Figure S13. ¹³C NMR spectrum of di(ester imide) DI-4.



Figure S14. ¹H NMR spectrum of di(ester imide) DI-5.



Figure S15. ¹³C NMR spectrum of di(ester imide) DI-5.



Figure S16. ¹H NMR spectrum of di(ester imide) DI-6.



Figure S17. ¹³C NMR spectrum of di(ester imide) DI-6.



Figure S18. ¹H NMR spectrum of di(ester imide) DI-7.



Figure S19. ¹³C NMR spectrum of di(ester imide) DI-7.



Figure S20. ¹H NMR spectrum of di(ester imide) DI-8.



Figure S21. ¹³C NMR spectrum of di(ester imide) DI-8.



Figure S22. ¹H NMR spectrum of di(ester imide) DI-9.



Figure S23. ¹³C NMR spectrum of di(ester imide) DI-9.



Figure S24. DFT calculated energy profiles for the thermal imidization of amic acids A_{2b-1} and A_{2b-2}.



Figure S25. DFT calculated energy profiles for the thermal imidization of amic acids A2c-1 and A2c-2.



Figure S26. DFT calculated energy profiles for the thermal imidization of amic acids A_{2d-1} and A_{2d-2} .



Figure S27. FTIR spectrum of imide-containing polyester P(2a3a).



Figure S28. ¹H NMR spectrum of P(2a3a).



Figure S29. ¹H, ¹H-COSY NMR spectrum of P(2a3a).



Figure S30. ¹³C NMR spectrum of P(2a3a).



Figure S31. ¹H, ¹H-COSY NMR spectrum of P(2a3a).



Figure S32. Properties of P(2a3a). (a) GPC curve. (b) WAXS profile. (c) TGA profiles. (d) Second heating DSC scan curve.

				01	5		
Entry	P(23)s	Time ^b	M _n c	M _w ^c	Ð ¢	Tg ^d	Td5 ^e
		(h)	(Da)	(Da)		(°C)	(°C)
1	P(2a3a)	18	9857	17377	1.76	77.7	352
2	P(2a3b)	18	9042	13991	1.55	60.8	358
3	P(2a3b)	26	11846	19414	1.64	59.4	361
4	P(2a3c)	18	4751	8610	1.81	75.7	324
5	P(2a3d)	18	5083	9454	1.86	57.5	263
6	P(2b3b)	18	9983	19555	1.96	46.1	363
7	P(2c3b)	18	2641	3425	1.30	33.5	319
8	P(2d3b)	18	11354	23747	2.09	94.9	356
9	P(2e3b)	18	4535	7242	1.60	115.4	356
10	P(2f3b)	18	30617	51861	1.69	88.3	379
11	P(2g3b)	18	15949	28182	1.77	57.3	335

Table S2. Model-inspired one-pot synthesis of imide-containing polyester^a

^a Reactions were carried out in two-step polymerization process. In the first step, imidization and prepolymerization (~20 h) occurred at 150 °C under a nitrogen flow. In the second step, the temperature was increased to 180 °C, and high vacuum (< 50 Pa) was applied. The polycondensation catalyst, SnCl₂ (300 ppm), was added at the beginning of the second stage. ^b Reaction time in the second stage. ^c Determined by GPC using PS standards. ^d Determined by DSC at 10 °C min⁻¹. ^e Determined by TGA at 10 °C min⁻¹.



Figure S33. Properties of P(**2a3a**) polymerized at different conditions. (a) GPC curves. (b) TGA curves. (c) Second heating DSC scan curves. (d) Photographs of P(**2a3a**) as bulk solids.



Figure S34. ¹H NMR spectrum of P(2a3b).



Figure S35. ¹³C NMR spectrum of P(2a3b).



Figure S36. ¹H NMR spectrum of P(2a3c).





Figure S37. ¹³C NMR spectrum of P(2a3c).



Figure S38. ¹H NMR spectrum of P(2a3d).



Figure S39. ¹³C NMR spectrum of P(2a3d).



Figure S40. Properties of P(**2a3a**), P(**2a3b**), P(**2a3c**) and P(**2a3d**). (a) GPC curves. (b) TGA curves. (c) Second heating DSC scan curves. (d) The corresponding structures of imide-containing polyesters. (e) The corresponding photographs of imide-containing polyesters.






Figure S42. ¹³C NMR spectrum of P(2b3b).



Figure S43. ¹H NMR spectrum of P(2c3b).





Figure S44. ¹³C NMR spectrum of P(2c3b).



Figure S45. ¹H NMR spectrum of P(2d3b).







Figure S47. ¹H NMR spectrum of P(2e3b).



Figure S48. ¹³C NMR spectrum of P(2e3b).



Figure S49. ¹H NMR spectrum of P(2f3b).



Figure S50. ¹³C NMR spectrum of P(2f3b).



Figure S51. ¹H NMR spectrum of P(2g3b).



Figure S52. ¹³C NMR spectrum of P(2g3b).



Figure S53. Properties of P(**2a3b**), P(**2b3b**), P(**2c3b**) and P(**2d3b**). (a) GPC curves. (b) TGA curves. (c) Second heating DSC scan curves. (d) The corresponding structures of imide-containing polyesters. (e) The corresponding photographs of imide-containing polyesters.





Figure S54. Properties of P(**2e3b**), P(**2f3b**) and P(**2g3b**). (a) GPC curves. (b) TGA curves. (c) Second heating DSC scan curves. (d) The corresponding structures of imide-containing polyesters. (e) The corresponding photographs of imide-containing polyesters.



Figure S55. Overlay of FTIR spectra of P(**2a3a4a**)_x, x = 2.5, 30 and 70.



Figure S56. Overlay of FTIR spectra of P(2a3a4a)_x, x = 5, 10, 20, 50 and 90.



Figure S57. Overlay of FTIR spectra of P(2a3a4a)₁₅, P(2a3b4a)₁₅, P(2a3c4a)₁₅ and P(2a3d4a)₁₅.



Figure S58. Overlay of FTIR spectra of P(2d3b4a)₃₀, P(2e3b4a)₃₀, P(2f3b4a)₃₀ and P(2g3b4a)₃₀.



Figure S59. Overlay of ¹H NMR spectra of P(2a3a4a)_x, x = 2.5, 10, 30, 50, 70 and 90.



Figure S60. ¹H NMR spectrum of P(2a3a4a)₅.



Figure S61. ¹H NMR spectrum of P(2a3a4a)₁₅.



Figure S62. ¹H NMR spectrum of P(2a3a4a)₂₀.



Figure S63. ¹H NMR spectrum of P(2a3a4a)₃₀.



Figure S64. ¹H NMR spectrum of P(2a3a4a)₅₀.











Figure S69. ¹³C NMR spectrum of P(2a3a4a)₇₀.



Figure S70. ¹³C NMR spectrum of P(2a3a4a)₉₀.



Figure S71. ¹H NMR spectrum of P(2a3b4a)₁₅.



1.15 A 2.98 A 36.27 v 48.25-5.5 5.0 4.5 Chemical Shift (ppm) 10.0 9.5 9.0 3.5 3.0 2.5 1.0 0.5 0.0 8.5 8.0 7.5 7.0 6.5 6.0 4.0 2.0 1.5

de

с

٣ 8

36

g 0 а

b

Ŧ

8

Figure S73. ¹H NMR spectrum of P(2a3c4a)₁₅.



5.5 5.0 4.5 Chemical Shift (ppm) 10.0 9.5 9.0 6.0 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 8.5 8.0 7.5 7.0 6.5

Figure S75. ¹H NMR spectrum of P(2a3d4a)₁₅.



Figure S76. ¹³C NMR spectrum of P(2a3d4a)₁₅.







Figure S78. ¹³C NMR spectrum of P(2d3b4a)₃₀.



Figure S79. ¹H NMR spectrum of P(2e3b4a)₃₀.



Figure S81. ¹H NMR spectrum of P(2f3b4a)₃₀.



Figure S83. ¹H NMR spectrum of P(2g3b4a)₃₀.



Figure S84. ¹³C NMR spectrum of P(2g3b4a)₃₀.



Figure S85. GPC curves of P(2a3a4a)_x, x = 2.5, 5, 10, 20, 30, 50, 70 and 90.



Figure S86. GPC curves of P(2a3a4a)15, P(2a3b4a)15, P(2a3c4a)15 and P(2a3d4a)15.



Figure S87. GPC curves of P(2d3b4a)₃₀, P(2e3b4a)₃₀, P(2f3b4a)₃₀ and P(2g3b4a)₃₀.



Figure S88. Thermal properties of P(**2a3a4a**)_x, x = 2.5, 5, 10, 15, 20, 30, 50, 70 and 90. (a) and (b) TGA profiles. (c) and (d) DSC profiles.



Figure S89. Variation storage modulus, Tan δ and Loss modulus of P(2a3a4a)₁₀.



Figure S90. Variation storage modulus, Tan δ and Loss modulus of P(2a3a4a)₁₅.



Figure S91. Variation storage modulus, $Tan\delta$ and Loss modulus of P(2a3a4a)₂₀.



Figure S92. XRD profiles of P(**2a3a4a**)_x, x = 2.5, 5, 10, 20, 30, 50, 70 and 90.



Figure S93. TGA profiles of P(2a3a4a)15, P(2a3b4a)15, P(2a3c4a)15 and P(2a3d4a)15.



Figure S94. XRD profiles of $P(2a3a4a)_{15}$, $P(2a3b4a)_{15}$, $P(2a3c4a)_{15}$ and $P(2a3d4a)_{15}$.



Figure S95. TGA and DSC profiles of P(2d3b4a)₃₀, P(2e3b4a)₃₀, P(2f3b4a)₃₀ and P(2g3b4a)₃₀.



Figure S96. XRD profiles of P(2d3b4a)₃₀, P(2e3b4a)₃₀, P(2f3b4a)₃₀ and P(2g3b4a)₃₀.



Figure S97. Tensile stress-strain curves of P(2a3a4a)_{2.5}.



Figure S98. Tensile stress-strain curves of P(2a3a4a)5.



Figure S99. Tensile stress-strain curves of P(2a3a4a)₁₀.



Figure S100. Tensile stress-strain curves of P(2a3a4a)15.



Figure S101. Tensile stress-strain curves of P(2a3a4a)₂₀.



Figure S102. Tensile stress-strain curves of $P(2a3a4a)_{30}$.



Figure S103. Tensile stress-strain curves of P(2a3b4a)₁₅.



Figure S104. Tensile stress-strain curves of P(2a3c4a)15.



Figure S105. Tensile stress-strain curves of P(2a3d4a)₁₅.

Table S3. Synthesis of copolymers P(2a3a4a)_x





 $P(2a3a4b)_x$ x: mole ratio of ester imide block

Feed Ratio	X%	P(2a3a4a) _x	<i>M</i> _n	M _w	Ð	X _c	T_{g}	$T_{\rm c}$	$\Delta H_{\rm m}$	T _m	$T_{\rm d5}$
(3a/4a/2a)			(Da)	(Da)		(%)	(°C)	(°C)	(J/g)	(°C)	(°C)
0.025/0.975/1.125	2.5	P(2a3a4a) _{2.5}	45038	65878	1.46	70.1	-24.6	69.6	77.3	117.9	364
0.05/0.95/1.15	5	P(2a3a4a) ₅	38834	57364	1.48	64.5	-19.4	53.6	71.1	114.9	366
0.10/0.90/1.20	10	P(2a3a4a) ₁₀	38895	59846	1.54	48.9	-8.5	51.8	53.9	102.5	345
0.15/0.85/1.25	15	P(2a3a4a) ₁₅	24670	53781	2.18	26.9	-21.1	54.3	29.7	97.5	360
0.20/0.80/1.30	20	P(2a3a4a) ₂₀	27103	45090	1.66	12.6	-14.2	/	13.9	89.4	356
0.30/0.70/1.40	30	P(2a3a4a) ₃₀	21931	40744	1.86	1	-2.6	/	/	/	359
0.50/0.50/1.60	50	P(2a3a4a) ₅₀	19313	37571	1.94	1	13.3	1	/	/	342
0.70/0.30/1.80	70	P(2a3a4a) ₇₀	11812	19859	1.68	1	43.8	1	/	/	362
0.90/0.10/2.00	90	P(2a3a4a) ₉₀	10483	21716	2.07	/	56.2	/	1	1	351
Table S4. Properties of copolymers

Polymer	<i>M</i> _n (Da)	M _w (Da)	Ð	X _c (%)	<i>Т</i> _g (°С)	<i>Т</i> _с (°С)	$\Delta H_{\rm m}$ (J/g)	<i>T</i> _m (°C)	<i>Т</i> _{d5} (°С)
P(2a3a4a) ₁₅	24670	53781	2.18	26.9	-21.1	54.3	29.7	97.5	360
P(2a3b4a) ₁₅	25658	47412	1.85	51.1	-24.6	30.2	56.4	95.4	359
P(2a3c4a) ₁₅	35155	78209	2.22	35.2	-22.5	49.3	38.8	96.5	343
P(2a3d4a) ₁₅	39558	110822	2.80	38.4	-26.0	42.2	42.4	93.3	354
P(2d3b4a) ₃₀	19313	37571	1.95	/	34.0	/	/	1	342
P(2e3b4a) ₃₀	11059	20063	1.81	/	37.4	/	/	1	303
P(2f3b4a) ₃₀	34325	55831	1.63	/	19.7	/	/	1	263
P(2g3b4a) ₃₀	17308	34605	2.00	/	-3.9	/	/	1	284

Table S5. Mechanical properties of P(2a3a4a)_x

Sample	<i>E</i> (MPa)	συτs (MPa)	ε (%)	ε _{max} (%)
P(2a3a4a) _{2.5}	290 ± 9	34.5 ± 1.2	15 ± 2	17
P(2a3a4a) ₅	229 ± 3	22.0 ± 1.3	107 ± 5	117
P(2a3a4a) ₁₀	200 ± 33	21.0 ± 0.6	325 ± 71	410
P(2a3a4a) ₂₀	202 ± 7	14.3 ± 0.4	25 ± 3	29
P(2a3a4a) ₃₀	86 ± 8	8.0 ± 0.4	23 ± 5	35

Table S6. Mechanical properties of P(2a3a4a)₁₅, P(2a3b4a)₁₅, P(2a3c4a)₁₅ and P(2a3d4a)₁₅

Sample	E	συτε	3	εmax
	(MPa)	(MPa)	(%)	(%)
P(2a3a4a)15	116 ± 11	15.3 ± 2.3	164 ± 40	238
P(2a3b4a) ₁₅	108 ± 11	18.9 ± 0.3	285 ± 8	297
P(2a3c4a)15	125 ± 8	23.7 ± 0.8	407 ± 38	454
P(2a3d4a)15	108 ± 7	23.3 ± 0.3	431 ± 27	472

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