Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Indole as a new sustainable aromatic unit for high quality biopolyesters

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Materials and Methods

Methyl 2-bromoacetate (>97%), methyl indole-3-carboxylate (>99%), mesitylene, dibutyltin oxide (DBTO) (>98%), 1,6-hexanediol (>99%), 1,5-pentanediol (>97%), 1,4-butanediol (>99%), 1,3-propaneodiol (>98%), 2,2-dimethylpropane-1,3-diol (NPG) (>96%) and sodium hydride (60 % dispersion in mineral oil) were purchased from Sigma-Aldrich. $MgSO_4$, dimethylformamide (DMF) (ACS, Reag. Ph. Eur.) and ethyl acetate (EtOAc) (ACS, Reag. Ph. Eur.) were purchased from VWR Chemicals. Methanol was purchased from Honeywell. Chloroform (Analytical grade, stabilized with ethanol) and xylene (Analytical grade, ACS) were purchased from Scharlau. All chemicals and reagents were used as received. PET (Ramapet N180) was purchased from Indorama Ventures PCL. PETG (Genius 80M) was purchased from IMG Selenis. Akestra 100 was provided through the courtesy of Perstorp AB.

Nuclear magnetic resonance (NMR) measurements were carried out on a Bruker DRX400 spectrometer at the proton frequency of 400.13 MHz and a carbon frequency of 100.61 MHz. Fourier transform infrared (FTIR) spectra were obtained with an attenuated total reflection (ATR) setup using a Bruker Alpha FT-IR spectrometer. Twenty-four scans were co-added using a resolution of 4 cm^{-1}. Gel permeation chromatography (GPC) was carried out with three Shodex columns in series (KF-805, 2804, and 2802.5) and a refractive index (RI) detector (Viscotek Model 250). All measurements were carried out at 35 °C at a concentration of 10 mg mL^{-1} using chloroform as the eluent, and at an elution rate of 1 mL min^{-1}. Calibration was performed with four polystyrene standard samples (M_n = 650 kg mol^{-1} from Water Associates, 96 and 30 kg mol^{-1} from Polymer Laboratories, and 3180 g mol^{-1} from Agilent Technologies). Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments DSC Q2000. The samples were studied with a heating rate of 10 °C min^{-1} under nitrogen with a purge rate of 50 mL min^{-1}. The sequence consisted of a heating ramp from 0 °C to 200 °C, followed by a cooling ramp to 0 °C and finally a heating ramp to 200 °C, which was employed to determine the glass transition temperature (T_g). Thermogravimetric analysis (TGA) was performed with a thermogravimetric analyser TA Instruments Q500 at a heating rate of 10 °C min^{-1} under nitrogen with a purge rate of 50 mL min^{-1}. Isothermogravimetric analysis was performed with a thermogravimetric analyser TA Instruments Q500 under nitrogen with a purge rate of 50 mL min^{-1}. The isothermal temperature used were 250, 275, 300, 325, 350, 375 and 400 °C. High resolution mass spectrometry (HRMS) was performed by direct infusion on a Water Xero-G2 QTOF mass spectrometer using electrospray ionization. The water contact angle of the polyester films was measured using the sessile drop method. A drop of water was formed by the addition of water to the polymer film surface with a syringe driven by a motor. The water drop was monitored by a camera, and the water contact angles were evaluated from the photos taken.

Synthesis of monomer and polymers

1-(2-methoxy-2-oxoethyl) indole-3-carboxylate (monomer 3)

To a suspension of NaH (60% dispersion in mineral oil, 1.2 g, 30 mmol) was added dropwise a solution of methyl indole-3-carboxylate (4.375 g, 25.00 mmol) in DMF (50 mL) at 0 °C for 15 minute. After the addition, the reaction mixture was stirred at room temperature for 45 min. Then, methyl 2-bromoacetate (2.375 mL, 25.00 mmol) was added dropwise at 0 °C and stirred overnight. Afterward, the reaction mixture was poured into EtOAc (500 mL) and then water (50 mL) was added. The aqueous phase was separated, and then extracted with EtOAc (3 X 50 mL). The organic phases were combined, and washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by recrystallization from methanol to afford white crystals in 71% yield. ^{1}H-NMR (400.13 MHz, $CDCl_3$). δ, ppm: 8.24-8.20 (br, 1H), 7.85 (s, 1H), 7.35–7.28 (br, 3H), 4.92 (s, 1H), 3.94 (s, 1H), 3.79 (s, 1H). ^{13}C-NMR (100.61 MHz, $CDCl_3$). δ, ppm: 167.89, 166.13, 136.75, 134.83, 126.43, 123.22, 122.16, 121.82, 109.33, 108.36, 52,73, 50.99, and 47.89. FT-IR ν(cm^{-1}): 3055 (Ar C-H str.), 2952 (CH_2 C-H str.), 2851 (CH_3 + CH_2 + CH_1 C-H str.), 1748 (ester C=O str.), 1694 (ester C=O str.), 1615 (C=C str. + Ar C–C str.), 1537 (Ar C=C str.), 1486 (Ar C=C str.), 1467(CH_2 C-H str.), 1437(Ar C=C str.), 1385 (CH_3 C-H str.), 1337 (ester C-O str.), 1273 (CH_3 C-H str.), 1240 (C-N str.), 1214 (ether C-O str.), 1177 (C-N str.), 1097 (ester C–O str.), 1036 (C-N str.), 749 (Ar C–H out-of plane bend.). HRMS (ESI+) calcd for $C_{13}H_{13}NO_4$ 247.0825, found 247.0825.

Polyester 5a

Monomer **3** (0.50 g, 2.0 mmol), 1,6-hexanediol (0.72 g, 6.1 mmol), DBTO (5 mg) were dissolved in xylene (1 mL), and then stirred at 180 °C for 3 h. Afterward, mesitylene (5 mL) was added to the reaction mixture, which was heated at 200 °C overnight under N_2. After the polymerization, the reaction mixture was dissolved in chloroform (5 mL), precipitated into methanol (200 mL) and dried under vacuum, to yield polyester **5a** as a white powder (0.45 g, 74%). GPC M_n = 33,400 g mol^{-1}, M_w = 67,600 g mol^{-1}, PDI = 2.3. ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ ppm: 8.20–8.17 (br, 1H), 7.84–7.80 (t, 1H), 7.30-7.24 (br, 3H), 4.85-4.81 (t, 2H), 4.36-4.29 (m, 2H), 4.17-4.14 (t, 1H), 4.10-4.07 (t, 1H), and 1.83-1.12 (m, 8H). ^{13}C-NMR (100.61 MHz, $CDCl_3$). δ ppm: 167.64, 167.59, 164.92, 136.87, 135.06, 136.00, 126.56, 123.22, 123.17, 122.19, 121.86, 109.53, 108.52, 65.88, 65,68, 63.78, 63.61, 48.17, 48.10, 28.82, 28.75, 28.30, 28.18, 25.89, 25.65, 25.41 and 25.10. FT-IR ν (cm^{-1}): 2936, 1745, 1693, 1614, 1536, 1467, 1393, 1272, 1239, 1175, 1096, 1015 and 749.

Polyester 5b

Monomer **3** (0.50 g, 2.0 mmol), 1,5-pentanediol (0.63 g, 6.1 mmol), DBTO (5 mg) were dissolved in xylene (1 mL), and then stirred at 180 °C for 3 h. Afterward, mesitylene (5 mL) was added to the reaction mixture, which was heated at 200 °C overnight under N_2. After the polymerization, the reaction mixture was dissolved in chloroform (5 mL), precipitated into methanol (200 mL) and dried under vacuum, to yield polyester **5b** as a white powder (0.41 g, 71%). GPC M_n = 35,100 g mol^{-1}, M_w = 80,900 g mol^{-1}, PDI = 2.3. ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ ppm: 8.19–8.15 (br, 1H), 7.84–7.78 (t, 1H), 7.29-7.21 (br, 3H), 4.83-4.77 (m, 2H), 4.38-4.34 (t, 1H), 4.30-4.26 (m, 1H), 4.21-4.14 (t, 1H), 4.05-4.01 (t, 1H), and 1.92-1.09 (m, 6H). ^{13}C-NMR (100.61 MHz, $CDCl_3$) δ, ppm: 167.61, 167.55, 136.89, 135.86, 135.06, 126.48, 123.25, 123.17, 122.22, 121.83, 109.55, 108.46, 65.79, 65,58, 63.67, 63.41, 48.12, 48.03, 28.63, 28.41, 28.05, 27.80, 22.88, 22.42, and 22.04. FT-IR ν (cm^{-1}): 2946, 1745, 1691, 1614, 1536, 1467, 1393, 1272, 1239, 1175, 1096, 1018 and 749.

Polyester 5c

Monomer **3** (0.50 g, 2.0 mmol), 1,4-butanediol (0. 55 g, 6.1 mmol), DBTO (5 mg) were dissolved in xylene (1 mL), and then stirred at 180 °C for 3 h. Afterward, mesitylene (5 mL) was added to the reaction mixture, which was heated at 200 °C overnight under N_2. After the polymerization, the reaction mixture was dissolved in chloroform (5 mL), precipitated into methanol (200 mL) and dried under vacuum, to yield polyester **5c** as a white powder (0.44 g, 80%). GPC M_n = 43,900 g mol^{-1}, M_w = 91,100 g mol^{-1}, PDI = 2.1. ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ ppm: 8.17–8.16 (br, 1H), 7.79 (s. 1H), 7.27-7.25 (br, 3H), 4.84-4.78 (t, 2H), 4.40 (s, 1H), 4.27-4.21 (d, 2H), 4.02 (t, 1H), and 1.97-1.46 (m, 4H). ^{13}C-NMR (100.61 MHz, $CDCl_3$) δ ppm: 167.62, 164.79, 136.87, 135.11, 126.47, 123.30, 123.21, 122.26, 121.77, 109.54, 108.25, 65.57, 65,03, 63.47, 62.99, 48.02, 25.88, 25.31 and 24.77. FT-IR ν (cm^{-1}): 2952, 1745, 1691, 1614, 1536, 1467, 1393, 1269, 1239, 1175, 1096, 1028 and 749.

Polyester 5d

Monomer **3** (0.50 g, 2.0 mmol), 2,2-dimethylpropane-1,3-diol (0.63 g, 6.1 mmol), DBTO (5 mg) were dissolved in xylene (1 mL), and then stirred at 180 °C for 3 h. Afterward, mesitylene (5 mL) was added to the reaction mixture, which was heated at 200 °C overnight under N_2. After the polymerization, the reaction mixture was dissolved in chloroform (5 mL), precipitated into methanol (200 mL) and dried under vacuum, to yield polyester **5d** as pale yellow powder (0.42 g, 80%). GPC M_n = 35,800 g mol^{-1}, M_w = 71,700 g mol^{-1}, PDI = 2.0. ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ ppm: 8.19–8.11 (br. 1H), 7.74–7.69 (t. 1H), 7.27-7.14 (m. 3H), 4.75-4.64 (d. 2H), 4.50 (s. 1H), 4.31-4.26 (s. 2H), 4.00-3.98 (s. 1H), and 2.25-2.04 (m. 2H).^{13}C-NMR (100.61 MHz, $CDCl_3$) δ ppm: 167.41, 164.64, 136.77, 135.25, 126.35, 123.28, 122.30, 121.77, 109.59, 108.07, 62.92, 61.76, 60.99, 60.00, 47.78, 28.03 and 27.40. FT-IR ν (cm^{-1}): 2952, 1745, 1691, 1614, 1536, 1467, 1393, 1269, 1237, 1173, 1096, 1040 and 749.

Polyester 5e

Monomer **3** (0.50 g, 2.0 mmol), 2,2-dimethylpropane-1,3-diol (0.63 g, 6.1 mmol), DBTO (5 mg) were dissolved in xylene (1 mL), and then stirred at 180 °C for 3 h. Afterward, mesitylene (5 mL) was added to the reaction mixture, which was heated at 200 °C overnight under N_2. After the polymerization, the reaction mixture was dissolved in chloroform (5 mL), precipitated into methanol (200 mL) and dried under vacuum, to yield polyester **5e** as pale yellow powder (0.40 g, 69%). GPC M_n = 41,100 g mol^{-1}, M_w = 112,300 g mol^{-1}, PDI = 2.7. ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ ppm: 8.20–8.12 (m, 1H), 7.81–7.78 (m, 1H), 7.30-7.19 (m, 3H), 4.80-4.73 (m, 2H), 4.31-4.29 (s, 1H), 4.06-4.04 (t, 2H), 3.61 (s, 1H), and 1.20-0.57 (m, 6H). ^{13}C-NMR (100.61 MHz, $CDCl_3$). δ ppm: 167.44, 167.10, 164.32, 136.81, 135.16, 126.36, 123.23, 122.26, 121.63, 109.50, 107.92, 70.57, 69.37, 68.96, 67.88, 47.89, 35.26, 34.92, 34.35, 22.22, 21.78 and 21.14. FT-IR ν (cm^{-1}): 2966, 1746, 1695, 1615, 1536, 1466, 1389, 1268, 1240, 1174, 1095, 1028 and 773.

Preparation of biopolyester films

Polyester powder (200 mg) was dissolved in chloroform (1 mL) at room temperature with constant stirring for 1 h to yield a clear and viscous polymer solution. This solution was cast onto a Petri dish with a diameter of 35 mm and dried at room temperature for 3 days to yield a film for further characterization.

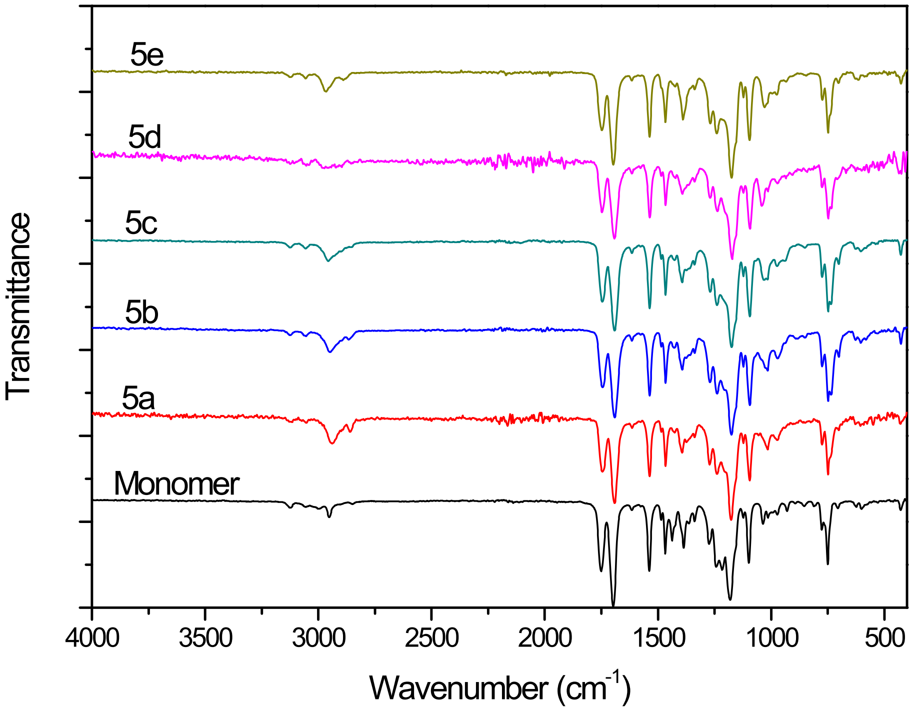

Figure S1. FTIR spectrum of monomer **3** and polyesters **5a-e.**

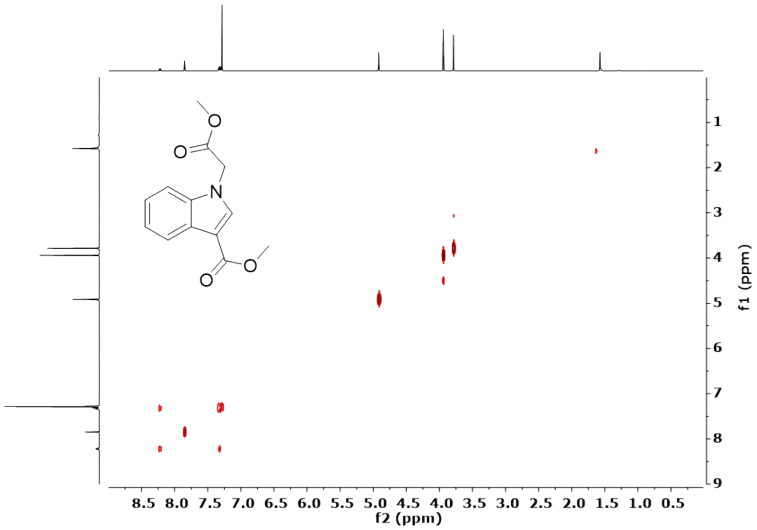

Figure S2. COSY-NMR spectrum of monomer **3**.

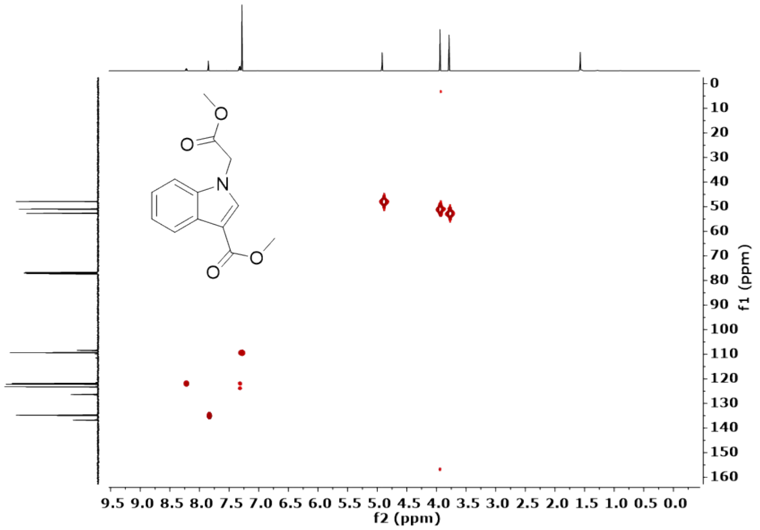

Figure S3. HMQC-NMR spectrum of monomer **3**.

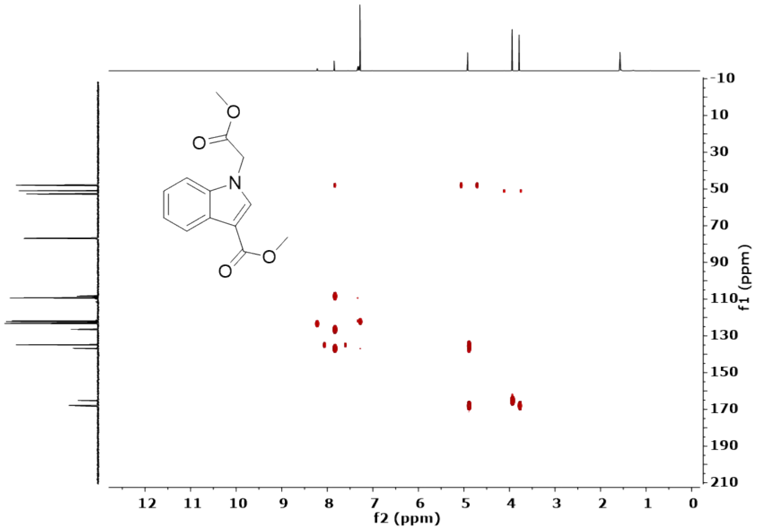

Figure S4. HMBC-NMR spectrum of monomer **3**.

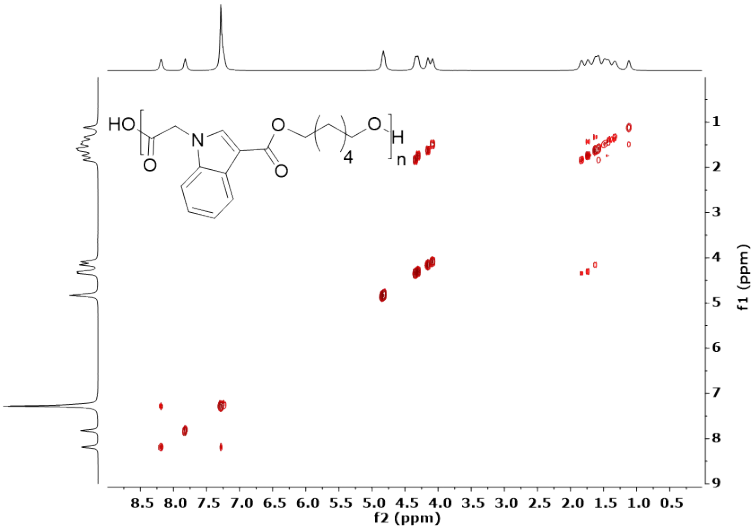

Figure S5. COSY-NMR spectrum of **5a**.

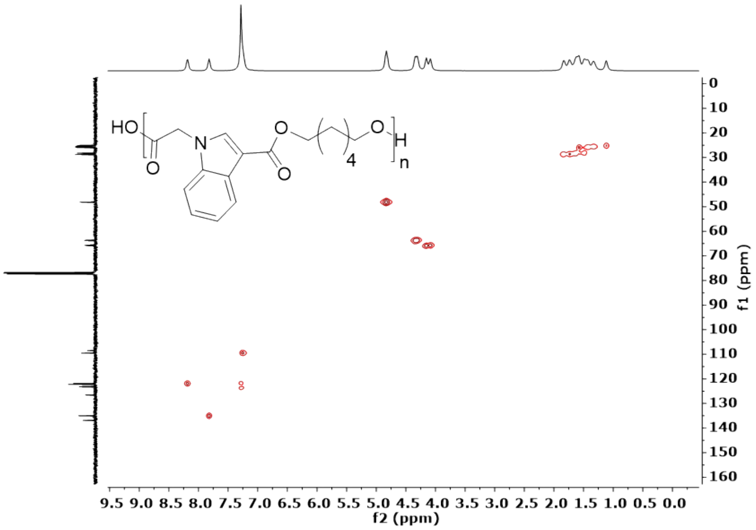

Figure S6. HMQC NMR spectrum of **5a**.

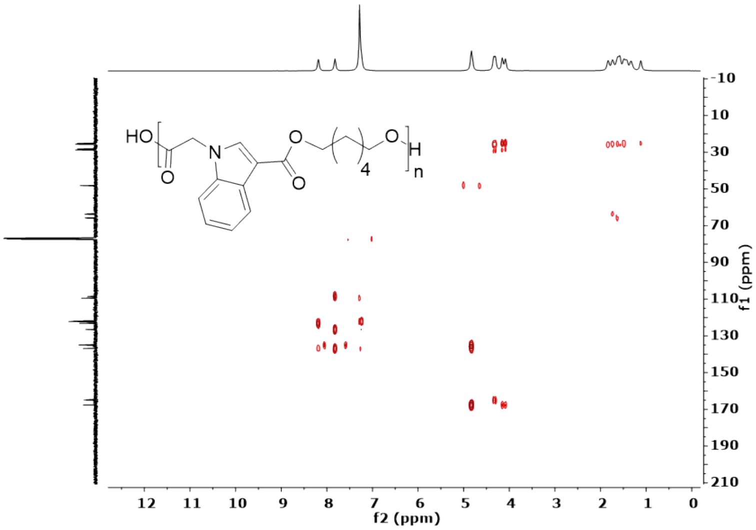

Figure S7. HMBC NMR spectrum of **5a**.

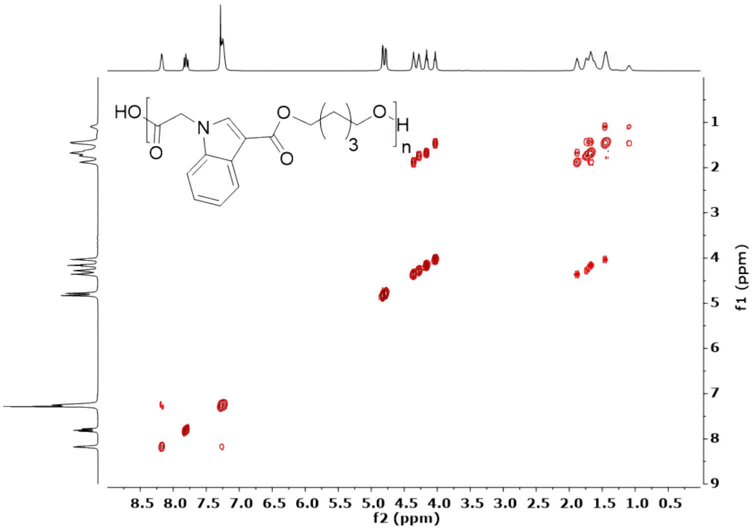

Figure S8. COSY-NMR spectrum of **5b**.

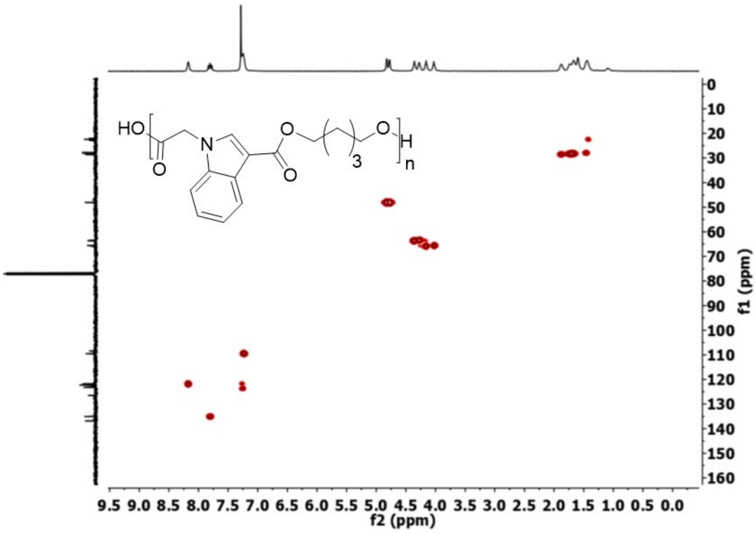

Figure S9. HMQC NMR spectrum of **5b**.

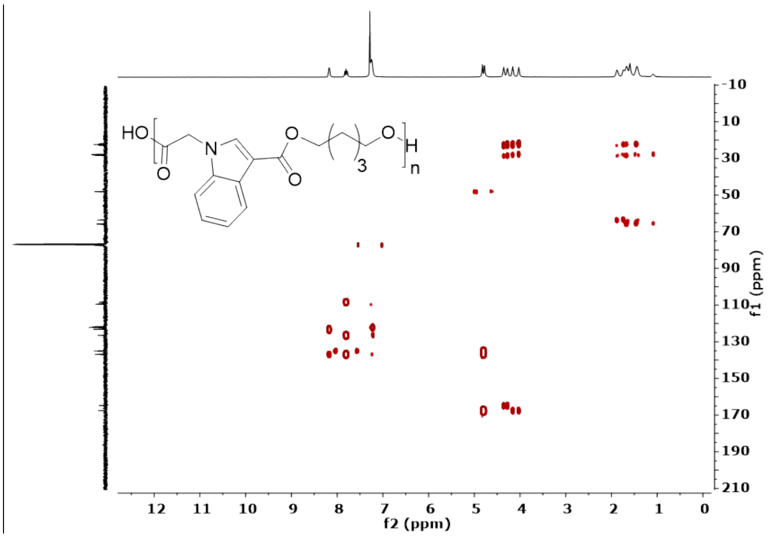

Figure S10. HMBC NMR spectrum of **5b**.

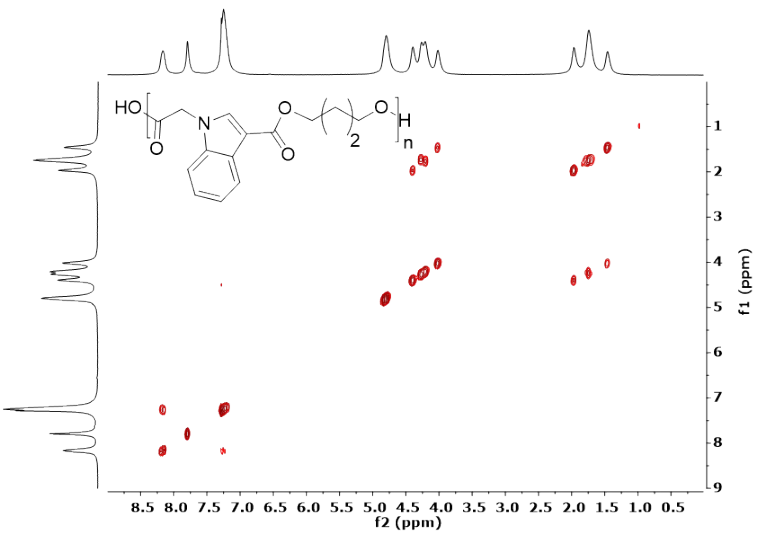

Figure S11. COSY-NMR spectrum of **5c**.

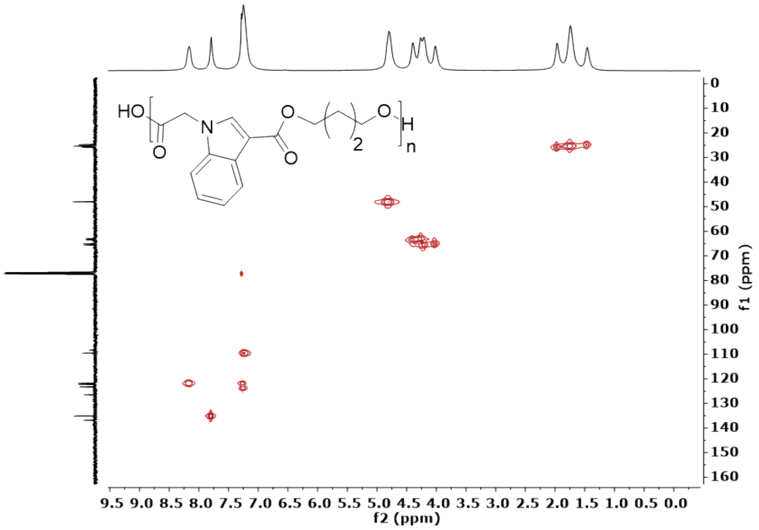

Figure S12. HMQC NMR spectrum of **5c**.

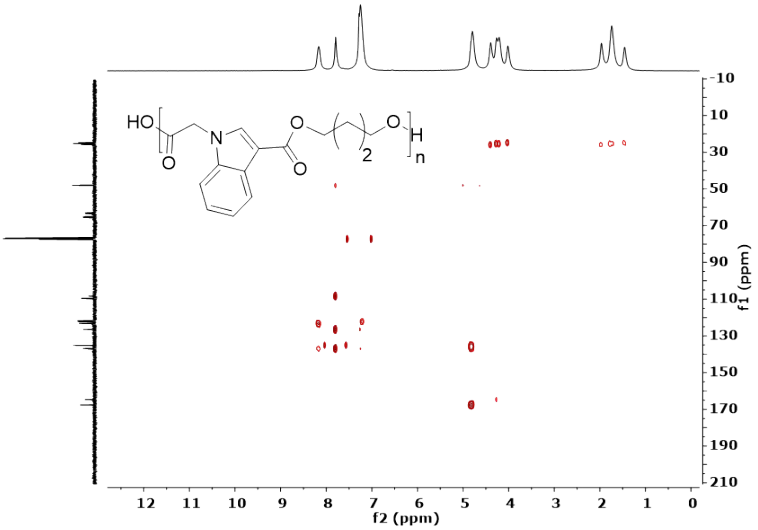

Figure S13. HMBC NMR spectrum of **5c**.

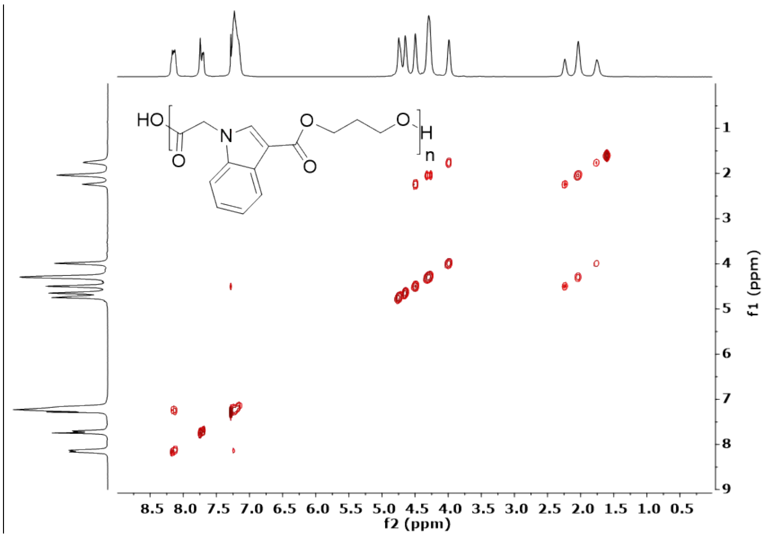

Figure S14. COSY-NMR spectrum of **5d**.

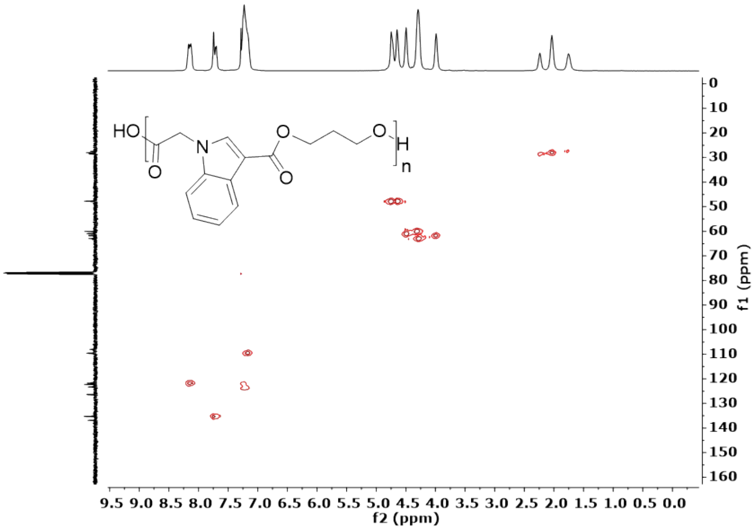

Figure S15. HMQC NMR spectrum of **5d**.

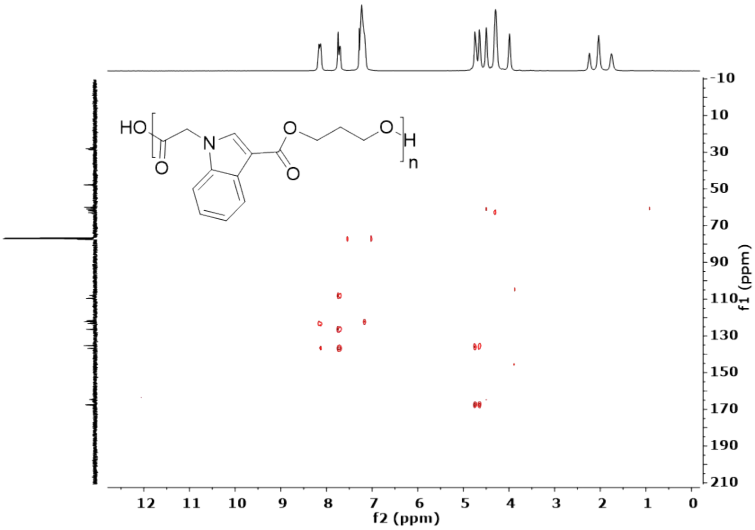

Figure S16. HMBC NMR spectrum of **5d**.

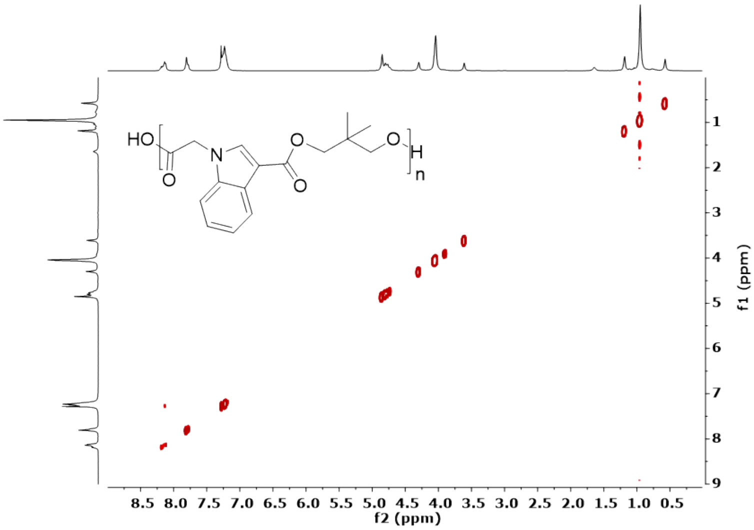

Figure S17. COSY NMR spectrum of **5e**.

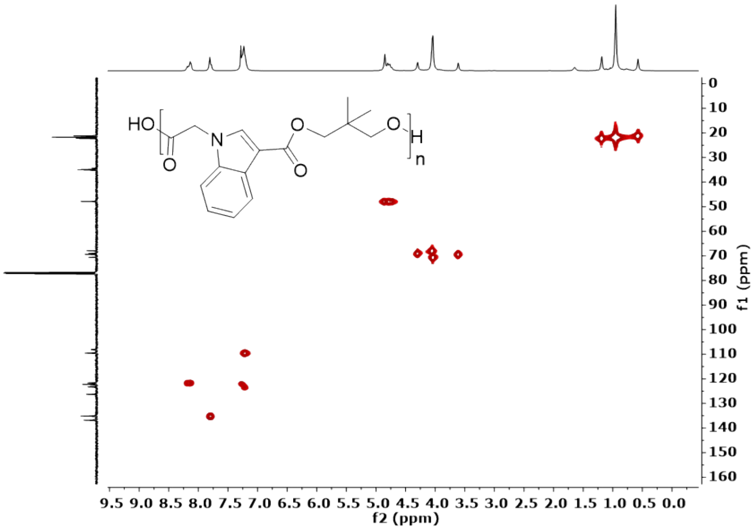

Figure S18. HMQC NMR spectrum of **5e**.

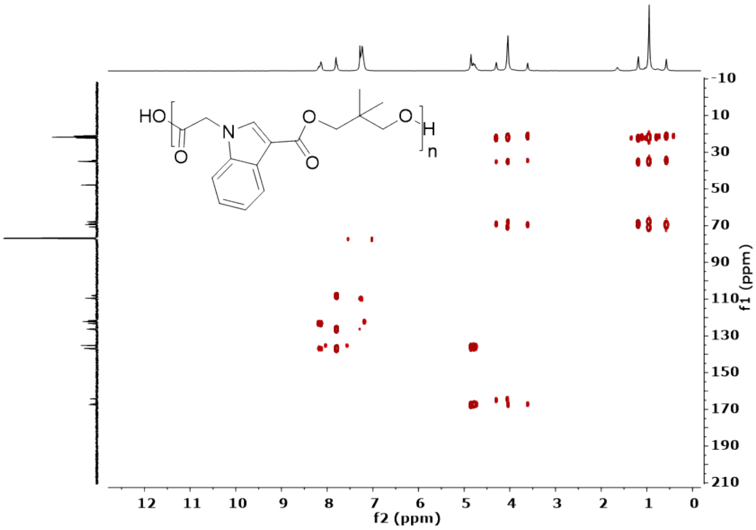

Figure S19. HMBC NMR spectrum of **5e**.

Figure S20. Films made from **5b** that was synthesized under different polymerization temperatures (a: 200 °C, b: 220 °C).

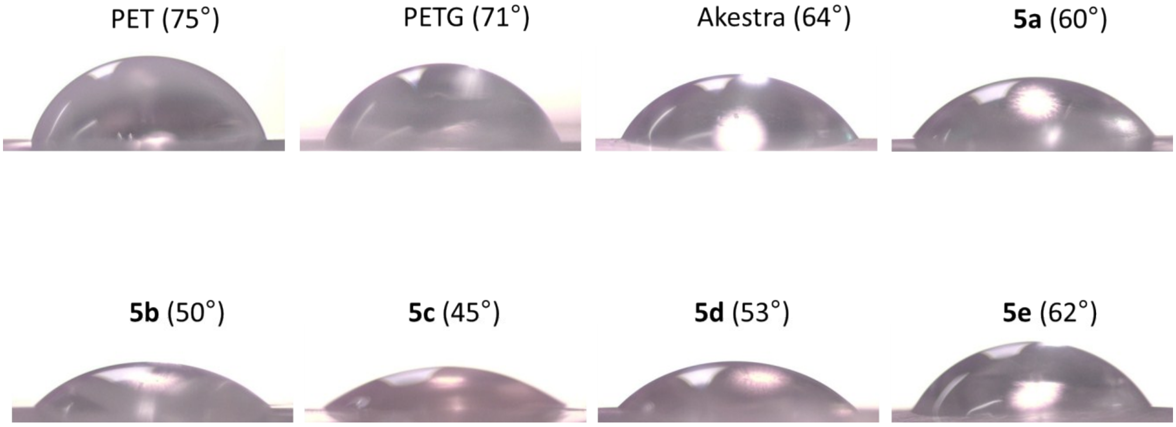

Figure S21. Images of the water droplets on flat polyester samples, including three commercial polyesters PET, PETG and Akestra, and five synthesized new indole-based polyesters **5a-e**. The water contact angle value for each sample was given in parenthesis.

Long term thermal stability analysis

Long-term thermal stability of an indole-based polyester **5a** and PET was evaluated by isothermal TGA studies at different temperatures. As shown in Figure S22, at all the tested temperatures, **5a** decomposed faster than PET. The times for 10%, 20% and 50% weight loss for both polymers were tabulated in Tables S1-3.

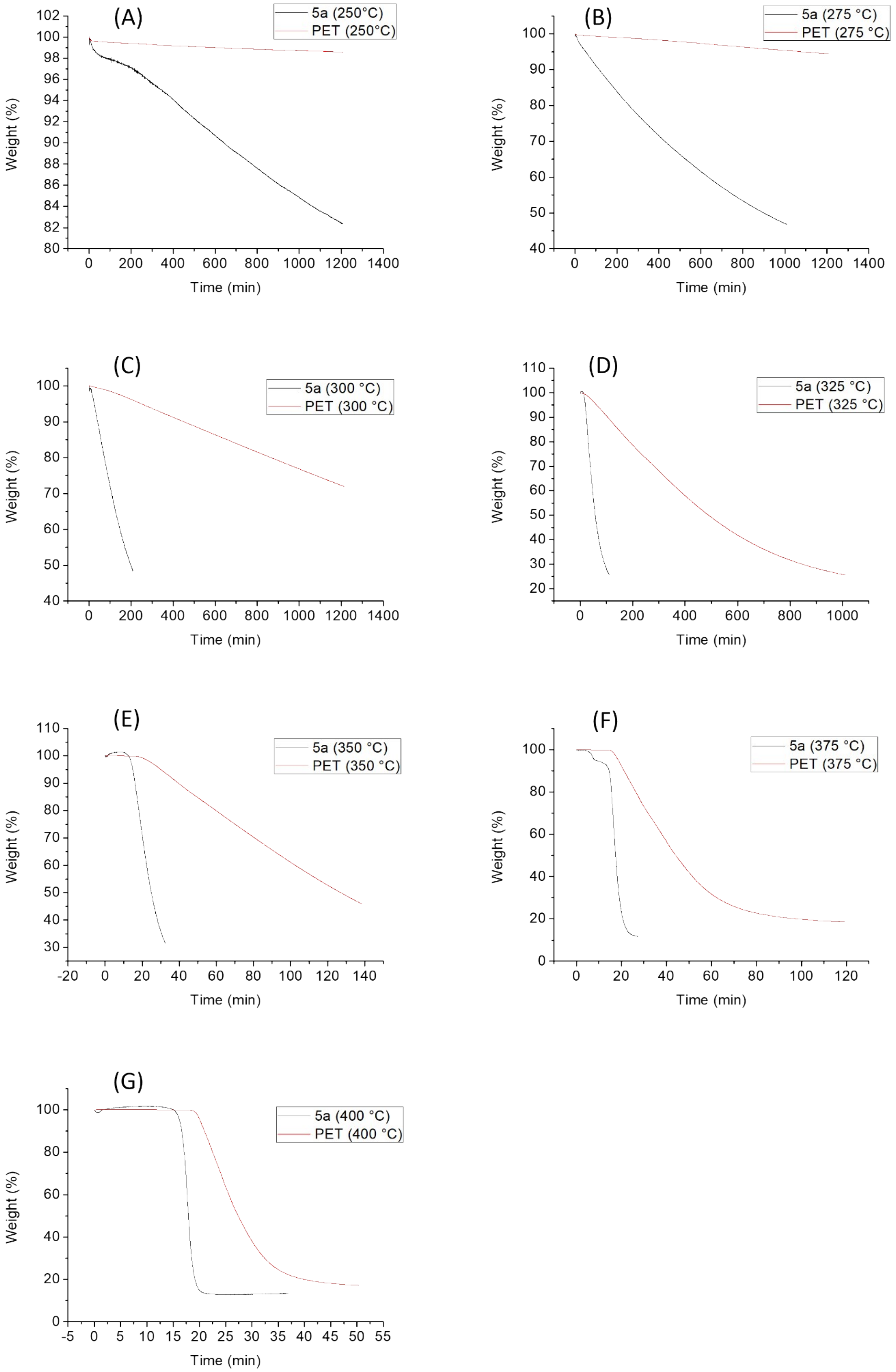
(A)
5a (250°C)
PET (250°C)
Weight (%)
102
100
98
96
94
92
90
88
86
84
82
80
Time (min)
0
200
400
600
800
1000
1200
1400
(B)
5a (275 °C)
PET (275 °C)
Weight (%)
100
90
80
70
60
50
40
Time (min)
0
200
400
600
800
1000
1200
1400
(C)
5a (300 °C)
PET (300 °C)
Weight (%)
100
90
80
70
60
50
40
Time (min)
0
200
400
600
800
1000
1200
1400
(D)
5a (325 °C)
PET (325 °C)
Weight (%)
110
100
90
80
70
60
50
40
30
20
Time (min)
0
200
400
600
800
1000
(E)
5a (350 °C)
PET (350 °C)
Weight (%)
110
100
90
80
70
60
50
40
30
Time (min)
-20
0
20
40
60
80
100
120
140
(F)
5a (375 °C)
PET (375 °C)
Weight (%)
100
80
60
40
20
0
Time (min)
0
20
40
60
80
100
120
(G)
5a (400 °C)
PET (400 °C)
Weight (%)
100
80
60
40
20
0
Time (min)
-5
0
5
10
15
20
25
30
35
40
45
50
55

Figure S22 Weight-loss curves of **5a** and PET degraded under nitrogen by isothermal heating at the different temperatures. (A) 250 °C, (B) 275 °C, (C) 300 °C, (D) 325 °C, (E) 350 °C, (F) 375 °C, (G) 400 °C.

Table S1 Time of 10% weight loss for **5a** and PET (min) at different temperatures.

Polymer	250 (°C)	275 (°C)	300 (°C)	325 (°C)	350 (°C)	375 (°C)	400 (°C)
5a	642	115	41	24	16	16	16
PET	>1200	>1200	453	105	40	21	21

Table S2 Time of 20% weight loss for **5a** and PET (min) at different temperatures.

Polymer	250 (°C)	275 (°C)	300 (°C)	325 (°C)	350 (°C)	375 (°C)	400 (°C)
5a	>1200	257	73	31	18	17	17
PET	>1200	>1200	867	188	60	26	22

Table S3 Time of 50% weight loss for **5a** and PET (min) at different temperatures.

Polymer	250 (°C)	275 (°C)	300 (°C)	325 (°C)	350 (°C)	375 (°C)	400 (°C)
5a	>1200	900	199	57	25	18	18
PET	>1200	>1200	>1200	490	127	44	27

Microstructure analysis based on NMR investigations

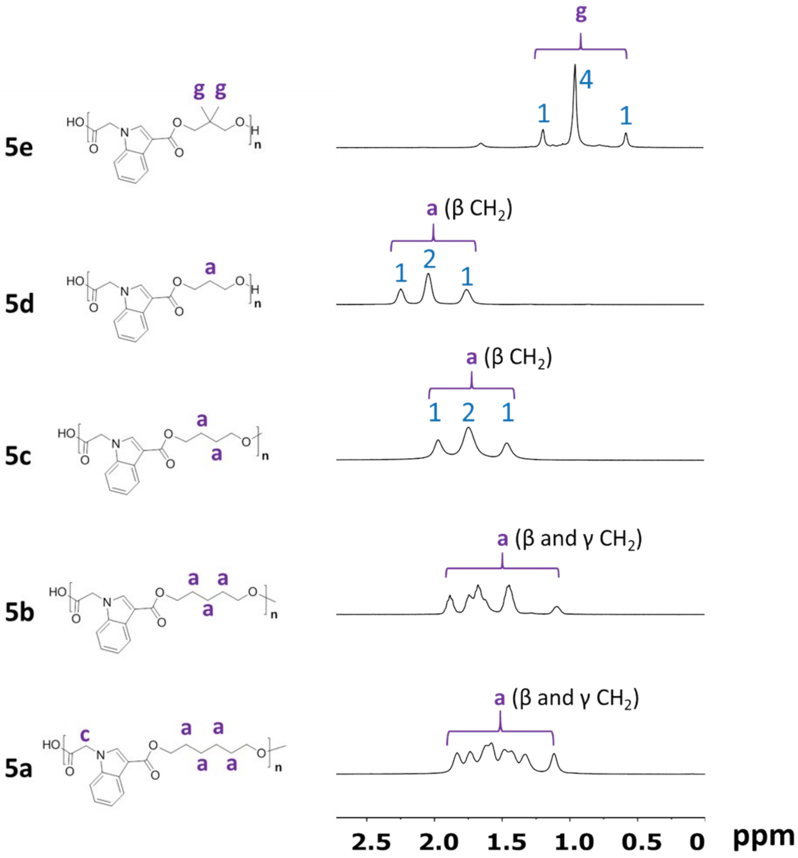

Figure S23 Expanded ^{1}H NMR spectra of indole-based polyesters **5a-e**.

The percentage of the head to tail (*h-t*) microstructure in the obtained polymers was estimated based on the integral of the NMR signals (Figure S23). For **5e**, the CH_3 proton signals (g) showed 1: 4 :1 pattern (corresponding to the *h-h*, *h-t*, and *t-t* microstructures), which suggested ~67% *h-t* microstructure. This suggested similar reactivity of the two kinds of carboxylates with small diols **4c** and **4d**. However, the reactivity of the two kinds of carboxylates with sterically hindered diol 4e was different, which caused the higher microstructural regularity for polymer **5e** (higher *h-t* ratio). Unfortunately, for **5a** and **5b**, the patterns of “a” signals were undiscernible, due to the overlapping of β and γ CH_2 protons.

End group analysis based on NMR investigations

The end groups of the resulting polyesters were evaluated based on ^{1}H NMR analyses (Figure S24). First, no signal corresponded to $COOCH_3$ or COOH groups was observed in any spectrum, which indicated that all the end groups were CH_2OH groups. In the spectra of **5a** and **5b**, two small signals at 3.63 and 3.56 *ppm* were observed, which corresponded to the two different kinds of CH_2 protons (α to OH) at the chain ends. The integrals of two signals (x : y) were roughly the same, indicating an equal distribution of the two kind of end groups. Unfortunately, the end groups of the other polyesters (**5c-e)**, no end group signal was observed.

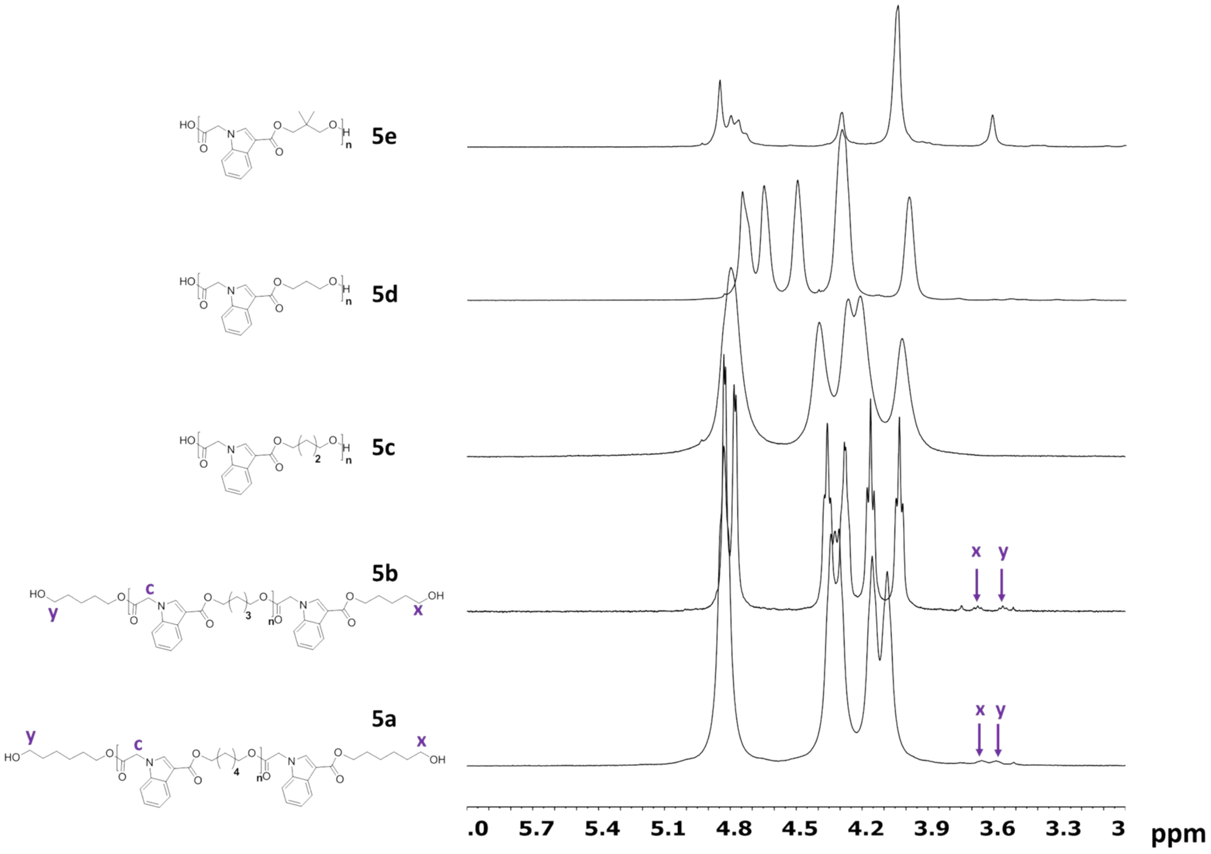

Figure S24 Expanded ^{1}H NMR spectra of indole-based polyesters **5a-e**. The signals corresponded to the end groups were marked with x and y.