

Supramolecular complexation between chain-folding poly(ester-imide)s and polycyclic aromatics: a fractal-based pattern of NMR ring-current shielding

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ELECTRONIC SUPPORTING INFORMATION

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Polymer synthesis and characterisation

HFDI-based poly(ester imide)s

Anhydrous solvent (1-chloronaphthalene or 1,2-dichlorobenzene), *N,N'*-bis-(2-hydroxyethyl)-hexafluoroisopropylidene-biphthalimide (dried at 120 °C for 24 h) and a diacyl chloride were combined at room temperature. The mixture was stirred and heated to 120 °C for 4 h under a slow dinitrogen purge. After cooling to room temperature the reaction mixture was dissolved in chloroform (20 mL) and the solution was added dropwise into an excess of methanol (400 mL). The precipitate was filtered off and dried at 80 °C for 24 h. The reprecipitation was repeated three times to afford pure polymer.

Homopolymer 4

Synthesised in 1,2-dichlorobenzene (7 mL). Monomers used: *N,N'*-bis-(2-hydroxyethyl)-hexafluoroisopropylidene diphthalimide (8.66 g, 16.34 mmol); pentanedioyl dichloride (2.78 g, 16.44 mmol), yield: 8.99 g, 87%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.83 dL g⁻¹. GPC: M_n = 30,100 g/mol ; M_w = 62,300 g/mol; D = 2.07. T_g (DSC): 109 °C.

FTIR ν_{max} ATR (cm⁻¹): 2961 (aromatic ν C-H), 1779 (imide -CO-N-CO-), 1708 (ester ν C=O), 1387 (imide C-N stretch), 1188 (vs, C-F), 1163 (ester C-O-C), 1139 (imide ring deformation), 745 (imide ring deformation).

Homopolymer 5

Synthesised in 1-chloronaphthalene (1.5 mL). Monomers used: *N,N'*-bis-(2-hydroxyethyl)-hexafluoroisopropylidene diphthalimide (1.25 g, 2.35 mmol); heptanedioyl dichloride (0.46 g, 2.36 mmol). Yield: 1.29 g, 84%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.56 dL g⁻¹. GPC: M_n = 20,400 g/mol ; M_w = 39,200 g/mol; D = 1.92. T_g (DSC): 72 °C.

¹H NMR (400 MHz, CDCl₃) δ ppm 7.93 (d, J = 8.0 Hz, 2H), 7.85 (s, 2H), 7.77 (d, J = 8.0 Hz, 2H), 4.31 (t, J = 5.2 Hz, 4H), 3.96 (t, J = 5.1 Hz, 4H), 2.26 (t, J = 7.5 Hz, 4H), 1.65 – 1.50 (m, 8H), 1.37 – 1.25 (m, 2H). ¹³C NMR (100 MHz, CDCl₃/TFE 9:1, v:v) δ ppm 174.49, 167.43, 139.15, 136.13, 132.84, 132.48, 125.07, 123.98, 61.23, 37.47, 33.85, 28.45, 24.29.

FTIR ν_{max} ATR (cm⁻¹): 2958 (aromatic ν C-H), 1779 (imide -CO-N-CO-), 1709 (ester ν C=O), 1387 (imide C-N stretch), 1188 (vs, C-F), 1164 (ester C-O-C), 1136 (imide ring deformation), 708 (imide ring deformation).

PMDI-based poly(ester imide)s

1,2-Dichlorobenzene (4.5 mL, distilled from CaH₂), *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (dried at 100 °C for 24 h) and a diacid chloride were combined and heated at 170 °C for 24 h under a slow dinitrogen purge. After cooling to room temperature, the reaction mixture was dissolved in 25 mL of chloroform/1,1,1,3,3,3-hexafluoroisopropanol (4:1 v/v) and the solution was added dropwise into an excess of methanol (400 mL). The precipitate was filtered off and dried at 80 °C for 24 h. The reprecipitation was repeated three times to afford pure polymer.

Homopolymer 6

Monomers used: *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (2.020 g, 6.64 mmol); propanedioyl chloride (0.985 g, 6.991 mmol). Yield: 1.700 g, 68%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.48 dL g⁻¹. T_m (DSC): 194 °C.

^1H NMR (400 MHz, CDCl_3/TFA 9:1, v:v) δ ppm 8.34 (s, 2H), 4.36–4.15 (m, 4H), 3.82 (t, 4H), 3.58 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3/TFE 10:1, v:v) δ ppm 172.56, 166.44, 137.16, 118.30, 65.01, 38.11, 25.67.

FTIR ν_{max} ATR (cm^{-1}): 2949 (aromatic $\nu\text{C-H}$), 1696 (imide $-\text{CO-N-CO}-$, ester $\nu\text{C=O}$), 1397 (imide C-N stretch), 1154 (ester C-O-C), 1048 (imide ring deformation), 728 (imide ring deformation).

Homopolymer 7

Monomers used: *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (2.099 g, 6.90 mmol), butanedioyl chloride (1.080 g, 6.97 mmol). Yield: 2.246 g, 84%.

Inherent viscosity (η_{inh} , CHCl_3/TFE 6:1, v:v): 0.36 dL g^{-1} . T_{m} (DSC): 233 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3/TFA 9:1, v:v) δ ppm 8.34 (s, 2H), 4.21 (t, 4H), 3.88–3.74 (m, 4H), 2.74 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3/TFE 9:1, v:v) δ ppm 173.05, 166.45, 137.16, 118.29, 61.85, 38.17, 28.94.

FTIR ν_{max} ATR (cm^{-1}): 2948 (aromatic $\nu\text{C-H}$), 1698 (imide $-\text{CO-N-CO}-$, ester $\nu\text{C=O}$), 1397 (imide C-N stretch), 1155 (ester C-O-C), 1050 (imide ring deformation), 727 (imide ring deformation).

Homopolymer 8

Monomers used: *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (1.991 g, 6.54 mmol); pentanedioyl chloride (1.119 g, 6.621 mmol). Yield: 2.331 g, 88%.

Inherent viscosity (η_{inh} , CHCl_3/TFE 6:1, v:v): 0.60 dL g^{-1} . T_{m} (DSC): 223 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3/TFA 9:1, v:v) δ ppm 8.35 (s, 2H), 4.41 (t, 4H), 4.08 (t, 4H), 2.45–2.31 (m, 4H), 1.87 (m, 2H). ^{13}C NMR (100 MHz, $\text{CD}_2\text{Cl}_2/\text{TFE}$ 6:1, v:v) δ ppm 174.03, 166.74, 137.52, 118.74, 61.87, 37.86, 33.12, 19.75.

FTIR ν_{max} ATR (cm^{-1}): 2953 (aromatic $\nu\text{C-H}$), 1702 (imide $-\text{CO-N-CO}-$, ester $\nu\text{C=O}$), 1388 (imide C-N stretch), 1155 (ester C-O-C), 1032 (imide ring deformation), 723.48 (imide ring deformation).

Homopolymer 9

Monomers used: *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (2.061 g, 6.77 mmol); hexanedioyl chloride (1.240 g, 6.77 mmol). Yield: 2.7503 g, 96%.

Inherent viscosity (η_{inh} , CHCl_3/TFE 6:1, v:v): 0.55 dL g^{-1} . T_g (DSC): 77°C; T_m : 253 °C.

^1H NMR (400 MHz, CDCl_3/TFA 9:1, v:v) δ ppm 8.36 (s, 2H), 4.43 (t, $J = 4.8$ Hz, 4H), 4.09 (t, $J = 4.9$ Hz, 4H), 2.37 (m, 4H), 1.67–1.49 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3/TFE 6:1 v:v) δ ppm 176.55, 166.60, 137.07, 119.11, 62.55, 37.71, 33.58, 23.65.

FTIR ν_{max} ATR (cm^{-1}): 2951 (aromatic $\nu\text{C-H}$), 1699 (imide $-\text{CO-N-CO}-$, ester $\nu\text{C=O}$), 1387 (imide C-N stretch), 1155 (ester C-O-C), 1252 (imide ring deformation), 759 (imide ring deformation).

Homopolymer 10

Monomers: *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (2.101 g, 6.91 mmol); heptanedioyl chloride (1.374 g, 6.97 mmol). Yield: 2.442 g, 82%.

Inherent viscosity (η_{inh} , CHCl_3/TFE 6:1, v:v): 0.59 dL g^{-1} . T_m (DSC): 190 °C.

^1H NMR (400 MHz, CDCl_3/TFA 9:1, v:v) δ ppm 8.38 (s, 2H), 4.45 (t, $J = 5.1$ Hz, 4H), 4.10 (t, $J = 5.1$ Hz, 4H), 2.36 (t, $J = 7.6$ Hz, 4H), 1.58 (p, $J = 7.7$ Hz, 4H), 1.40–1.20 (m, 2H). ^{13}C

NMR (100 MHz, CDCl₃/TFE 6:1, v:v) δ ppm 177.17, 166.64, 137.07, 119.14, 62.53, 37.72, 33.81, 28.03, 23.93.

FTIR ν_{\max} ATR (cm⁻¹): 2944 (aromatic ν C-H), 1698 (imide -CO-N-CO-, ester ν C=O), 1397 (imide C-N stretch), 1155 (ester C-O-C), 1051 (imide ring deformation), 727 (imide ring deformation).

Homopolymer 11

Monomers: *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (2.065 g, 6.79 mmol); octanedioyl chloride (1.447 g, 6.856 mmol). Yield: 2.640 g, 88%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.62 dL g⁻¹. T_m (DSC): 217 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.37 (s, 2H), 4.43 (t, 4H), 4.09 (t, 4H), 2.34 (t, 4H), 1.63–1.46 (m, 4H), 1.27 (m, 4H). ¹³C NMR (100 MHz, CDCl₃/TFE 6:1, v:v) δ ppm 174.39, 166.13, 137.12, 118.56, 61.43, 37.69, 33.80, 28.49, 24.28.

FTIR ν_{\max} ATR (cm⁻¹): 2938 (aromatic C-H), 1712 (imide -CO-N-CO-, ester C=O), 1386 (imide C-N stretch), 1153 (ester C-O-C), 1030 (imide ring deformation), 723 (imide ring deformation).

Homopolymer 12

Monomers: *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (2.029 g, 6.67 mmol); nonanedioyl chloride (1.516 g, 6.735 mmol). Yield: 3.070 g, 98%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.37 dL g⁻¹. T_m (DSC): 203 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.37 (s, 2H), 4.44 (t, 4H_b), 4.10 (t, 4H), 2.35 (t, 4H), 1.62–1.49 (m, 4H), 1.25 (m, 6H). ¹³C NMR (100 MHz, CDCl₃/TFE 6:1, v:v) δ ppm 173.50, 165.91, 137.17, 118.49, 61.06, 37.88, 33.85, 28.78, 24.51.

FTIR ν_{\max} ATR (cm^{-1}): 2931 (aromatic $\nu\text{C-H}$), 1712 (imide $-\text{CO-N-CO}-$, ester $\nu\text{C=O}$), 1386 (imide C-N stretch), 1155 (ester C-O-C), 1032 (imide ring deformation), 724 (imide ring deformation).

Monomers: *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide (2.148 g, 7.06 mmol); decanedioyl chloride (1.705 g, 7.13 mmol). Yield: 3.231 g, 97%.

Inherent viscosity (η_{inh} , CHCl_3/TFE 6:1, v:v): 0.59 dL g^{-1} . T_m (DSC): 207 °C.

^1H NMR (400 MHz, CDCl_3/TFA 9:1, v:v) δ ppm 8.37 (s, 2H), 4.44 (t, 4H), 4.10 (t, 4H), 2.35 (t, 4H), 1.66–1.45 (m, 4H), 1.24 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3/TFE 6:1, v:v) δ ppm 174.58, 166.12, 137.12, 118.56, 61.23, 37.70, 33.92, 28.86, 24.50.

FTIR ν_{\max} ATR (cm^{-1}): 2929 (aromatic $\nu\text{C-H}$), 1709 (imide $-\text{CO-N-CO}-$, ester $\nu\text{C=O}$), 1386 (imide C-N stretch), 1155 (ester C-O-C), 1032 (imide ring deformation), 723 (imide ring deformation).

NDI-based poly(ester imide)s

1,2-Dichlorobenzene (4.5 mL, distilled from CaH_2), *N,N'*-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide (dried at 120 °C for 24 h) and a diacyl chloride were combined at room temperature and heated to 170 °C for 24 h under a slow nitrogen purge. After cooling to room temperature the reaction mixture was dissolved in 30 mL of dichloromethane/1,1,1,3,3,3-hexafluoroisopropanol (1:1, v/v) and the solution was added dropwise into an excess of methanol (400 mL). The precipitate was filtered off and dried at 80 °C for 24 h. The reprecipitation was repeated three times to afford pure polymer.

Homopolymer 14

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalenetetracarboxylic diimide (0.702 g, 1.98 mmol); propanedioyl chloride (0.282 g, 2.00 mmol). Yield: 0.32 g, 38%.

Inherent viscosity (η_{inh} , CHCl₃/HFIP 1:1, v:v): 0.17 dL g⁻¹. T_g (DSC): 189 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.81 (s, 4H), 4.65–4.34 (m, 8H), 3.47 (s, 2H). ¹³C NMR (100 MHz, CDCl₃/HFIP, 6:1) δ ppm 168.09, 164.00, 131.65, 126.73, 126.20, 63.05, 60.90, 39.16.

FTIR ν_{max} ATR (cm⁻¹): 2965 (aromatic ν C-H), 1732 (imide -CO-N-CO-), 1704 (ester ν C=O), 1371 (imide C-N stretch), 1188 (ester C-O-C), 1144 (imide ring deformation), 766 (imide ring deformation).

Homopolymer 15

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide (0.876 g, 2.47 mmol); butanedioyl chloride (0.392 g, 2.50 mmol). Yield: 0.67 g, 62%.

Inherent viscosity (η_{inh} , CHCl₃/HFIP 1:1, v:v): 0.56 dL g⁻¹. T_g (DSC): 139 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.82 (s, 4H, C-H), 4.53 (m, 8H, N-CH₂, O-CH₂), 2.64 (m, 4H, CH₂). ¹³C NMR (100 MHz, CD₂Cl₂/HFIP 3:1, v:v) δ ppm 174.57, 164.19, 131.91, 127.17, 126.71, 62.58, 39.69, 28.96.

FTIR ν_{max} ATR (cm⁻¹): 2966 (aromatic ν C-H), 1732 (imide -CO-N-CO-), 1703 (ester ν C=O), 1371 (imide C-N stretch), 1188 (ester C-O-C), 1146 (imide ring deformation), 765 (imide ring deformation).

Homopolymer 16

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide (2.005 g, 5.66 mmol); pentanedioyl chloride (0.967 g, 5.72 mmol). Yield: 1.450 g, 56%.

Inherent viscosity (η_{inh} , CHCl₃/HFIP 1:1, v:v): 1.54 dL g⁻¹. T_g (DSC): 132 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.82 (s, 4H), 4.6–4.48 (m, 8H), 2.39 (t, 4H), 1.86 (m, 2H). ¹³C NMR (100 MHz, CD₂Cl₂/HFIP 6:1, v:v) δ_c 175.37, 163.98, 131.81, 127.17, 126.72, 62.36, 39.77, 33.26, 19.48.

FTIR ν_{max} ATR (cm⁻¹): 2963 (aromatic ν C-H), 1731 (imide -CO-N-CO-), 1703 (ester ν C=O), 1372 (imide C-N stretch), 1189 (ester C-O-C), 1142 (imide ring deformation), 765 (imide ring deformation).

Homopolymer 17

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide (2.090 g, 5.90 mmol); hexanedioyl chloride (1.091 g, 5.96 mmol). Yield: 2.101 g, 76%.

Inherent viscosity (η_{inh} , CHCl₃/HFIP 1:1, v:v): 0.75 dL g⁻¹. T_g (DSC): 116 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.83 (s, 4H), 4.57 (m, 4H), 4.54 (m, 4H), 2.34 (t, 4H), 1.57 (t, 4H). ¹³C NMR (100 MHz, CD₂Cl₂/HFIP 6:1, v:v) δ ppm 175.89, 163.91, 131.77, 127.17, 126.76, 62.23, 39.78, 33.91, 24.10.

FTIR ν_{max} ATR (cm⁻¹): 2959 (aromatic ν C-H), 1731 (imide -CO-N-CO-), 1703 (ester ν C=O), 1372 (imide C-N stretch), 1192 (ester C-O-C), 1138 (imide ring deformation), 766 (imide ring deformation).

Homopolymer 18

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide (2.0052 g, 5.66 mmol); heptanedioyl chloride (1.134 g, 6.80 mmol). Yield: 2.125 g, 78%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.58 dL g⁻¹. T_g (DSC): 90 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.83 (s, 4H), 4.57 (m, 4H), 4.54 (m, 4H), 2.32 (t, 4H), 1.54 (m, 4H), 1.37–1.17 (m, 2H). ¹³C NMR (100 MHz, CD₂Cl₂/HFIP 6:1, v:v) δ ppm 176.46, 163.97, 131.82, 127.17, 126.76, 62.19, 39.78, 34.14, 28.52, 24.38.

FTIR ν_{max} ATR (cm⁻¹): 2950 (aromatic ν C-H), 1731.72 (imide -CO-N-CO-), 1703 (ester ν C=O), 1372 (imide C-N stretch), 1192 (ester C-O-C), 1160 (imide ring deformation), 766 (imide ring deformation).

Homopolymer 19

Monomers used: *N,N'*-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide (2.079 g, 5.87 mmol); octanedioyl chloride (1.252 g, 5.93 mmol). Yield: 2.74 g, 95%.

Inherent viscosity (η_{inh} , CHCl₃/HFIP 1:1, v:v): 0.19 dL g⁻¹. T_g (DSC): 73 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.83 (s, 4H), 4.57 (m, 4H), 4.54 (m, 4H), 2.32 (t, 4H), 1.52 (m, 4H), 1.33–1.10 (m, 4H). ¹³C NMR (100 MHz, CD₂Cl₂/HFIP 6:1, v:v) ¹³C NMR (100 MHz, CDCl₃/HFIP 9:1) δ ppm 176.13, 163.59, 131.69, 127.01, 126.57, 61.96, 39.78, 34.15, 28.61, 24.43.

FTIR ν_{max} ATR (cm⁻¹): 2935 (aromatic ν C-H), 1731 (imide -CO-N-CO-), 1703 (ester ν C=O), 1373 (imide C-N stretch), 1161 (ester C-O-C), 1154 (imide ring deformation), 766 (imide ring deformation).

Homopolymer 20

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide (2.121 g, 5.99 mmol); nonanedioyl chloride (1.362 g, 6.05 mmol). Yield: 3.010 g, 98%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 1.20 dL g⁻¹. T_g (DSC): 76 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.83 (s, 4H), 4.58 (m, 4H), 4.55 (m, 4H), 2.34 (t, 4H), 1.60–1.42 (m, 4H), 1.22 (m, 6H). ¹³C NMR (100 MHz, CD₂Cl₂/HFIP 6:1, v:v) δ ppm 176.70, 163.92, 131.78, 127.17, 126.76, 62.12, 39.79, 34.40, 28.99, 24.77.

FTIR ν_{max} ATR (cm⁻¹): 2933 (aromatic ν C-H), 1732 (imide -CO-N-CO-), 1704 (ester ν C=O), 1373 (imide C-N stretch), 1156 (ester C-O-C), 1154 (imide ring deformation), 766 (imide ring deformation).

Homopolymer 21

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide (2.081 g, 5.88 mmol); decanedioyl chloride (1.420 g, 5.94 mmol). Yield: 3.002 g, 97%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.93 dL g⁻¹. T_g (DSC): 50 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.83 (s, 4H), 4.58 (m, 4H), 4.55 (m, 4H), 2.33 (t, 4H), 1.73–1.40 (m, 4H), 1.22 (m, 8H). ¹³C NMR (100 MHz, CD₂Cl₂/HFIP 6:1, v:v) δ ppm 178.30, 165.43, 133.31, 128.68, 128.28, 63.64, 41.32, 35.98, 30.69, 26.37).

FTIR ν_{max} ATR (cm⁻¹): 2929 (aromatic ν C-H), 1732 (imide -CO-N-CO-), 1704 (ester ν C=O), 1373 (imide C-N stretch), 1156 (ester C-O-C), 1154 (imide ring deformation), 766 (imide ring deformation).

NDI/HFDI co- poly(ester imide)s

1-Chloronaphthalene (2.5 mL, distilled from CaH₂), *N,N'*-bis(2-hydroxyethyl)-naphthalene-tetracarboxylic diimide (dried at 100 °C for 24 h), *N,N'*-bis(2-hydroxyethyl)-hexafluoroisopropylidene-diphthalic diimide (dried at 100 °C for 24 h) and a diacyl chloride were combined at room temperature. The mixture was heated to 160 °C for 24 h under a slow dinitrogen purge. After cooling to room temperature the reaction mixture was dissolved in 30 mL of dichloromethane/1,1,1,3,3,3-hexafluoroisopropanol (4:1, v/v) and the solution was added dropwise into an excess of methanol (400 mL). The precipitate was filtered off and dried at 80 °C for 24 h. The reprecipitation was repeated three times to afford pure polymer.

1:1 Copolymer 22

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalenetetracarboxylic diimide (1.011 g, 2.82 mmol), *N,N'*-bis(2-hydroxyethyl)-hexafluoroisopropylidene-diphthalic diimide (1.513 g, 2.82 mmol), butanedioyl dichloride (0.902 g, 5.82 mmol). Yield: 1.853 g, 60%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.47 dL g⁻¹. *T*_g (DSC): 130 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.83 (s, 4H, -CH-, NDI), 7.98 (d, *J* = 8.0 Hz, 2H, CH, HFDI), 7.92–7.79 (m, 4H, CH, HFDI), 4.83–3.87 (m, 16H, N-CH₂, O-CH₂), 2.64 (m, 8H, CO-CH₂). ¹³C NMR (100 MHz, CDCl₃/TFE 6:1, v:v) δ ppm 172.92, 172.78, 163.32, 163.29, 138.98, 135.97, 132.61, 132.25, 131.24, 126.77, 126.41, 124.88, 61.83, 39.38, 37.09, 28.55.

FTIR ν_{max} ATR (cm⁻¹): 2973 (aromatic ν C-H), 1779 (imide -CO-N-CO-), 1707 (ester ν C=O), 1388 (imide C-N stretch), 1189 (vs, C-F), 1146 (ester C-O-C), 1100 (imide ring deformation), 768 (imide ring deformation).

1:1 Copolymer 23

Monomers: *N,N'*-bis-(2-hydroxyethyl)-naphthalenetetracarboxylic diimide (1.001 g, 2.80 mmol), *N,N'*-bis(2-hydroxyethyl)-hexafluoroisopropylidene-diphthalic diimide (1.517 g, 2.90 mmol), pentanedioyl dichloride (0.980 g, 5.80 mmol). Yield: 1.221 g, 38%.

Inherent viscosity (η_{inh} , CHCl₃/TFE 6:1, v:v): 0.26 dL g⁻¹. T_g (DSC): 99 °C.

¹H NMR (400 MHz, CDCl₃/TFA 9:1, v:v) δ ppm 8.82 (s, 4H, -CH- NDI), 7.98 (d, *J* = 8.0 Hz, 2H, -CH, HFDI), 7.92–7.79 (m, 4H, CH, HFDI), 4.73–3.96 (m, 16H, N-CH₂, O-CH₂), 2.51–2.33 (m, 8H, CO-CH₂), 1.95–1.81 (m, 4H, CO-C-CH₂). ¹³C NMR (100 MHz, CDCl₃/TFE 6:1, v:v) δ ppm 173.81, 173.66, 167.33, 163.15, 139.00, 136.01, 132.59, 132.23, 131.26, 126.38, 124.88, 123.80, 61.65, 39.47, 37.17, 32.84, 19.35.

FTIR ν_{max} ATR (cm⁻¹): 2958 (aromatic ν C-H), 1779 (imide -CO-N-CO-), 1701 (ester ν C=O), 1388 (imide C-N stretch), 1189 (vs, C-F), 1163 (ester C-O-C), 1140 (imide ring deformation), 768 (imide ring deformation).

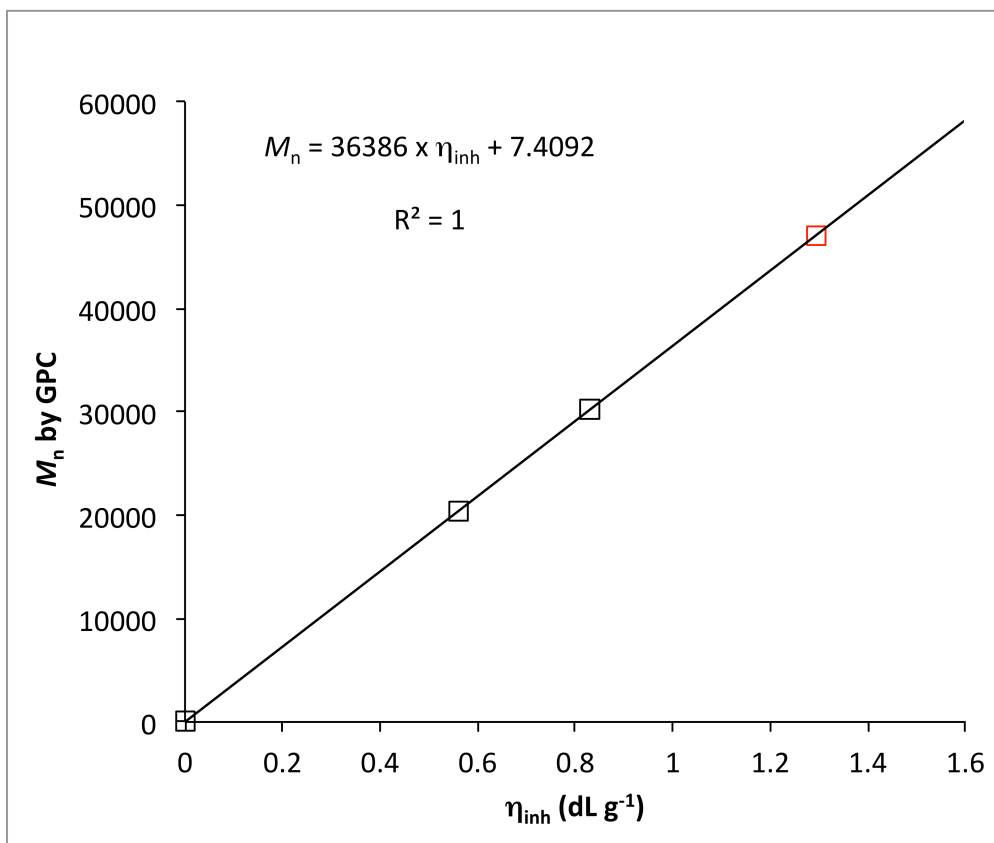


Figure S1. Calibration plot: Inherent viscosity vs M_n (GPC). The straight-line equation of fit is derived from the zero point and the experimental data for HFDI-based poly(ester-imide)s **4** and **5**. The marker point in red is an extrapolation, using the equation of fit for the first three points.

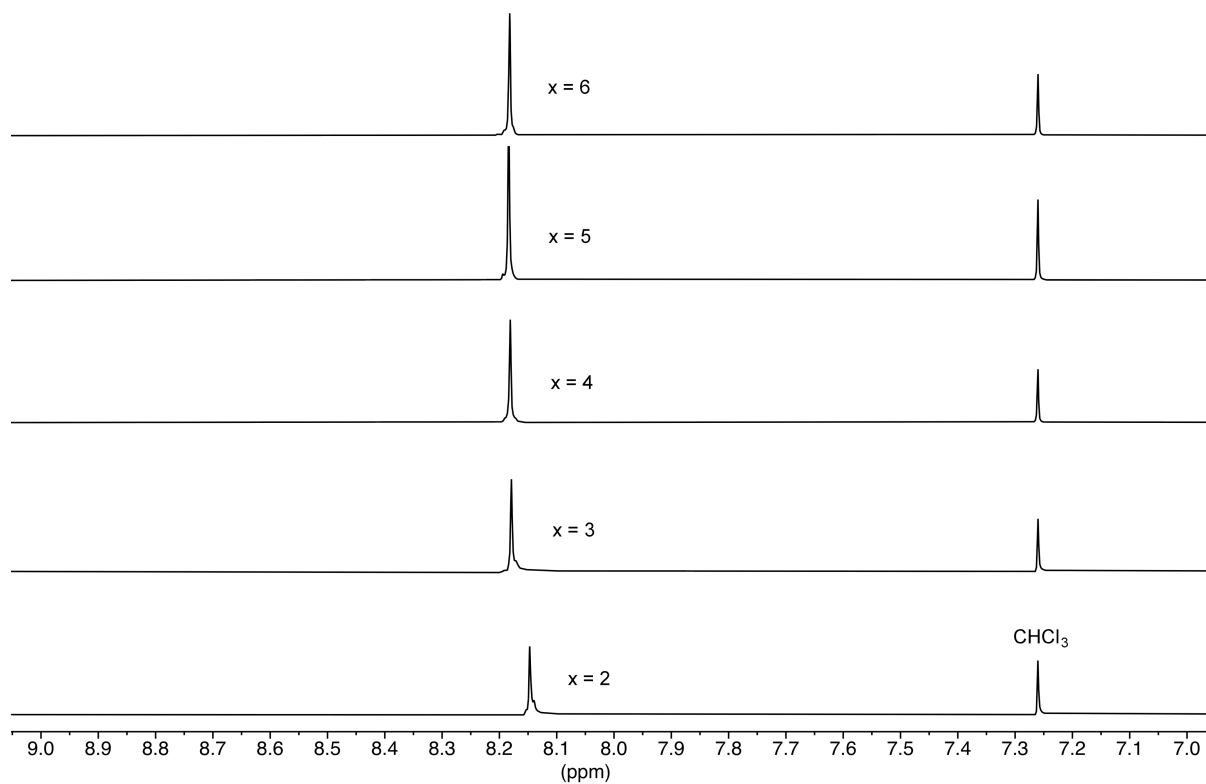


Figure S2. ¹H NMR spectra (CDCl₃/HFIP, 1:1 v/v) in the diimide region for PDI homopolymers **7-12** in the presence of pyrene-*d*₁₀ (2 equiv. per NDI residue).

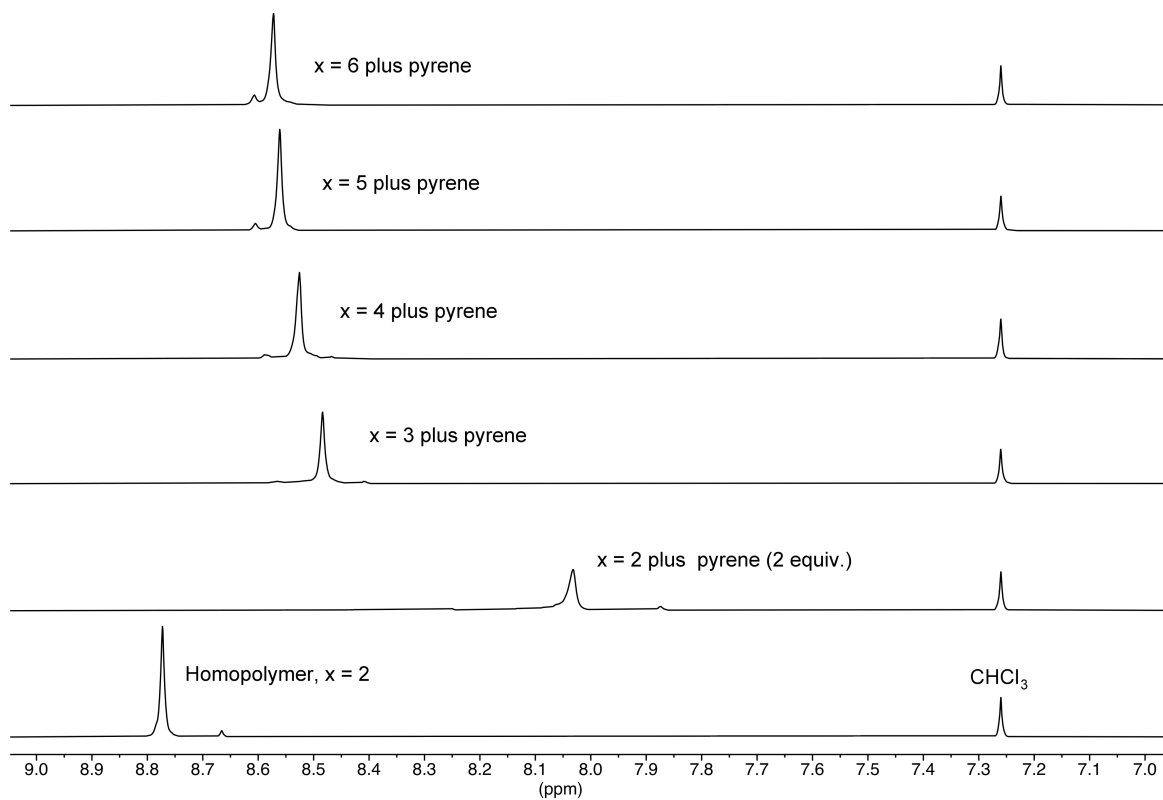


Figure S3. ¹H NMR spectra (CDCl₃/HFIP, 1:1 v/v) in the diimide region for NDI homopolymers **15-19** in the presence of pyrene-*d*₁₀ (2 equiv. per NDI residue). The spectrum of pure homopolymer **15** (*x* = 2) is also shown for reference.

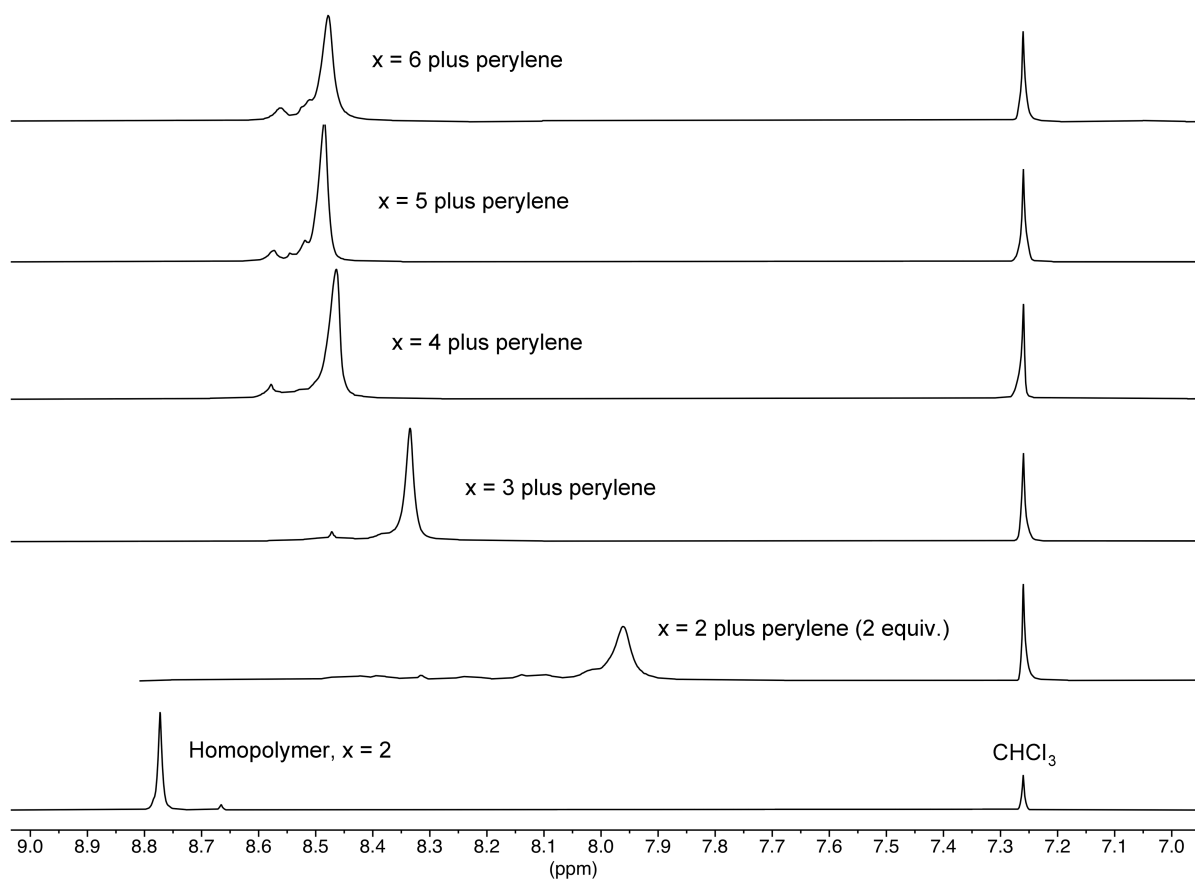


Figure S4. ^1H NMR spectra ($\text{CDCl}_3/\text{HFIP}$, 1:1 v/v) in the diimide region for NDI homopolymers **15-19** in the presence of perylene- d_{12} (2 equiv. per NDI residue). The spectrum of pure homopolymer **15** ($x = 2$) is also shown for reference.

¹H NMR titration method: Copolymer **22** vs pyrene-*d*₁₀

The NMR titration was carried out by adding defined volumes (see below) of pyrene-*d*₁₀ stock-solution (24 mM) into 600 μ L of copolymer **22** solution (4 mM in NDI residues). The resulting molar ratios of NDI:pyrene covered the range from 1:0 to 1:3. A ¹H NMR spectrum was recorded at each ratio using a Bruker AVANCE 500 spectrometer with TCI Cryoprobe system (500 MHz) at 298 K. The solvent was CDCl₃/trifluoroethanol (6:1 v/v).

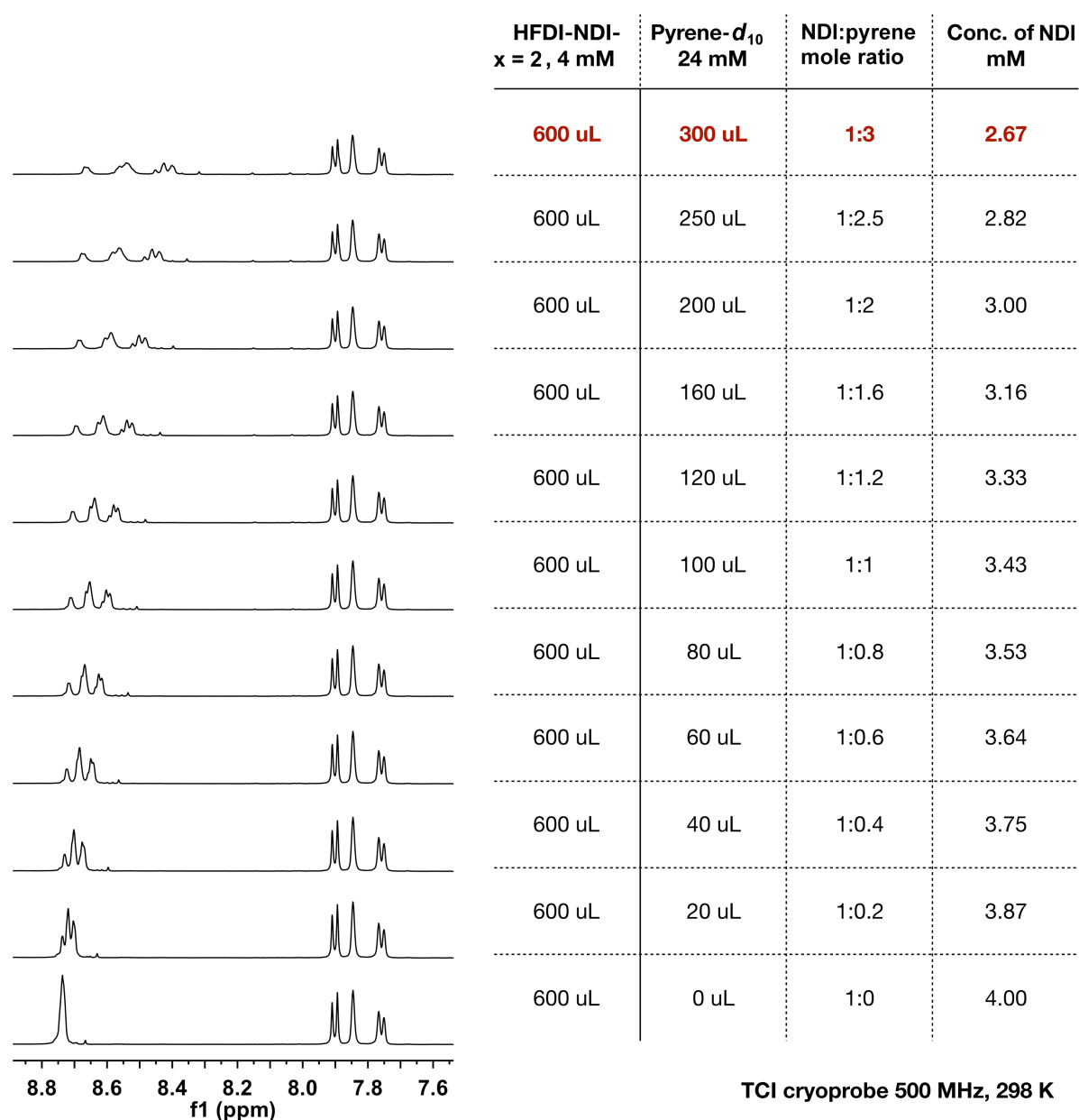


Figure S5. Stacked spectra and ¹H NMR titration data: Copolymer **22** vs pyrene-*d*₁₀ at 298 K. Solvent was CDCl₃/111-trifluoroethanol (6:1 v/v).

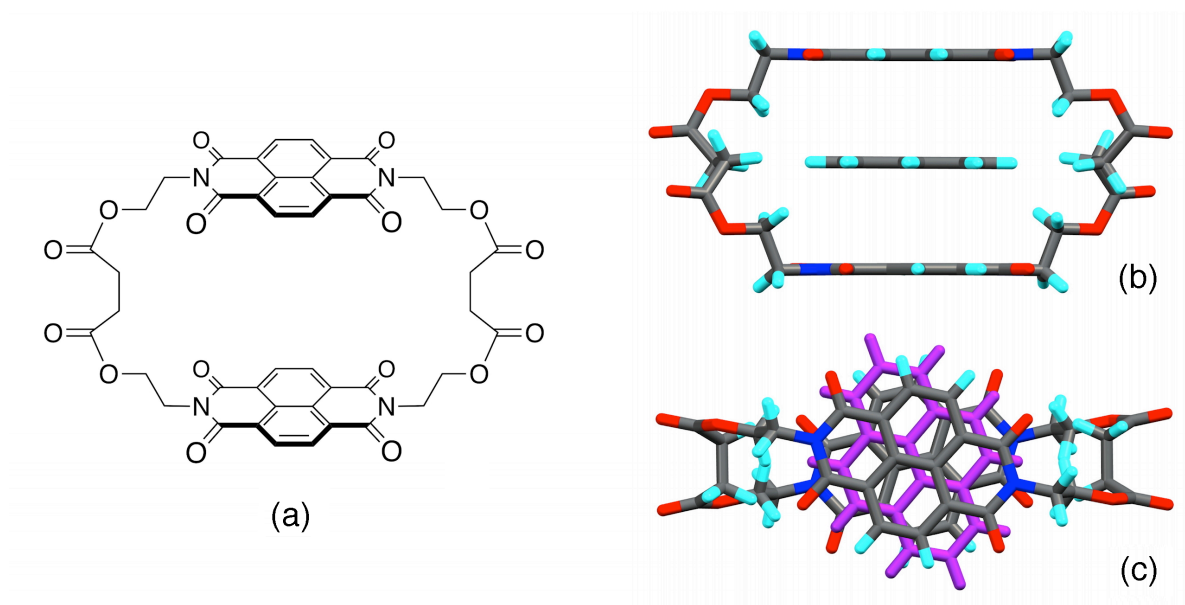


Figure S6. (a) Molecular structure of the proposed cyclic dimer of polymer **15** (NDI, $x = 2$); (b) energy-minimised model of this dimer complexed with pyrene, viewed along the (essentially parallel) NDI and pyrene mean planes; (c) viewed perpendicular to the mean plane of the encapsulated pyrene.

This structure can be regarded as a ring-closed analogue of the tight chain-fold for $x = 2$ described in the main paper (Figure 4).

¹H NMR resonance intensities and the degree of randomness of the copolymer chain

An infinite, 100% random, I/F copolymer chain would contain equal numbers of I-centred sequences and F-centred sequences. As randomness decreases (and blockiness conversely increases) the I-centred sequences become progressively enriched in I residues, and the F-centred sequences become similarly enriched in F residues. By NMR we only observe resonances originating from the I-centred sequences, the intensities being directly proportional to the sequence-probabilities. In such sequences the probability of finding another I increases from 0.5 at 100% randomness to 1 at 0% randomness (Figure S7 below), and the probability of finding an F correspondingly decreases from 0.5 to zero.

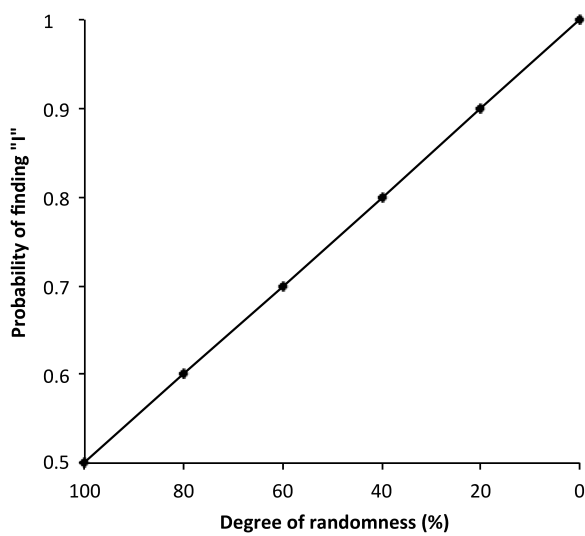


Figure S7. Probability of finding an "I" residue in an I-centred I/F copolymer sequence as a function of the degree of randomness of the copolymer chain.

The probability P of any I-centred sequence is the product of the individual probabilities p_I and p_F for I and F residues respectively. As shown in the graph, for 100% randomness $p_I = 0.5$ and, as the combined probabilities of p_I and p_F must equal 1, p_F is also 0.5. For 80% randomness $p_I = 0.6$ and $p_F = 0.4$, and for 60% randomness $p_I = 0.7$ and $p_F = 0.3$. **Note:** as we only observe I-centred sequences, the probability of the central I in a sequence is, by definition, always equal to 1.

Thus, for example, the probability P of the sequence FIIF at 100% randomness is $0.5 \times 0.5 \times 1 \times 0.5 \times 0.5 = \mathbf{0.0625}$. At 80% randomness the probability of the same sequence is $0.4 \times 0.6 \times 1 \times 0.6 \times 0.4 = \mathbf{0.0576}$, and at 60% randomness the sequence-probability is $0.3 \times 0.7 \times 1 \times 0.7 \times 0.3 = \mathbf{0.0441}$.

This methodology enables sequence-probabilities to be calculated for all sequences at all degrees of randomness. The results for I-centred quintet sequences at 60%, 80% and 100% randomness are given in Table S1 below. Probabilities are grouped by shielding code as shown in Table 2 of the main paper, and the shielding parameters T for each group, from Table 2, are given in the final column.

Plotting sequence probabilities (as intensities) against shielding parameters (as chemical shifts) gives simulated ¹H NMR spectra for comparison with the experimental data (Figure S8). It is clear that, of the three degrees of randomness considered, a value of 80% gives much the best fit to the experimental spectrum (Figure 8, main paper).

Table S1. Calculated sequence-probabilities for all I-centred quintet sequences within an infinite I/F copolymer chain, at varying degrees of chain-randomness.

Quintet sequence	Probability at 60% randomness	Probability at 80% randomness	Probability at 100% randomness	Total shielding parameter T
FFIFF	0.0081	0.0256	0.0625	
FFIFI	0.0189	0.0384	0.0625	
IFIFF	0.0189	0.0384	0.0625	
IFIFI	0.0441	0.0576	0.0625	
Group probability	0.09	0.16	0.25	0
FFIIF	0.0189	0.0384	0.0625	
FIIFF	0.0189	0.0384	0.0625	
FIIFI	0.0441	0.0576	0.0625	
IFIIF	0.0441	0.0576	0.0625	
Group probability	0.126	0.192	0.25	0.25
FFIII	0.0441	0.0576	0.0625	
IIIFF	0.0441	0.0576	0.0625	
IFIII	0.1029	0.0864	0.0625	
IIIFI	0.1029	0.0864	0.0625	
Group probability	0.294	0.288	0.25	0.3125
FIIIF	0.0441	0.0576		
Group probability	0.0441	0.0576	0.0625	0.5
FIIII	0.1029	0.0864		
IIIIF	0.1029	0.0864		
Group probability	0.2058	0.1728	0.125	0.5625
IIIII	0.2401	0.1296		
Group probability	0.2401	0.1296	0.0625	0.625
Total probability	1	1	1	

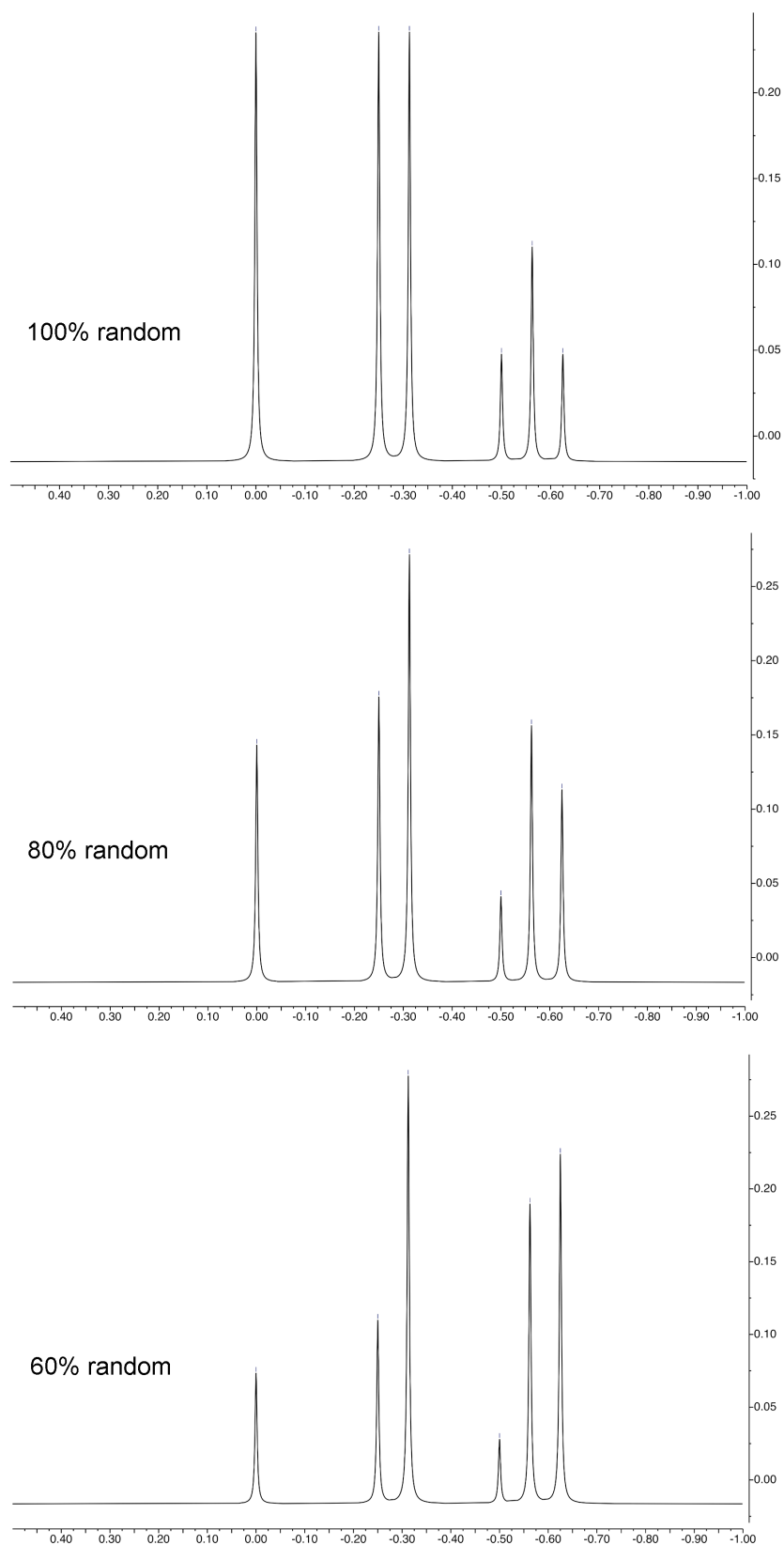


Figure S8. Simulated ^1H NMR spectra in the diimide region for the pyrene complex of copolymer **22**, assuming three different degrees of randomness in the copolymer chain, plotted from the data in Table S1. Of the above simulations, the best match with the experimental data is at 80% randomness, as shown in Figure 8 of the main paper. A more exact match might be achievable by further simulations, over a narrower randomness range around 80%, but would provide no further insight into the system.