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

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SUPPORTING INFORMATION

Atomic coordinates in .mol2 format for modelled polymer/pyrene complexes (electronic files):
C3_Pyr_heptamer.mol2; C4_Pyr_heptamer.mol2; C7_Pyr_heptamer.mol2

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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 diacid 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}, $CHCl_3$/TFE 6:1, v:v): 0.83 dL g^{-1}. GPC: M_n = 30,100 g/mol ; M_w = 62,300 g/mol; $Đ$ = 2.07. T_g (DSC): 109 °C.

FTIR ν_{max} ATR (cm^{-1}): 2961 (aromatic νC-H), 1779 (imide -CO-N-CO-), 1708 (ester νC=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-choronaphthalene (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}, $CHCl_3$/TFE 6:1, v:v): 0.56 dL g^{-1}. GPC: M_n = 20,400 g/mol ; M_w = 39,200 g/mol; $Đ$ = 1.92. T_g (DSC): 72 °C.

^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$/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 νC-H), 1779 (imide -CO-N-CO-), 1709 (ester νC=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 CaH_2), *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}, $CHCl_3$/TFE 6:1, v:v): 0.48 dL g^{-1}. T_m (DSC): 194 °C.

^{1}H 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 νC-H), 1696 (imide -CO-N-CO-, ester νC=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 °C.

^{1}H 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 νC-H), 1698 (imide -CO-N-CO-, ester νC=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 °C.

^{1}H 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, CD_2Cl_2/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 νC-H), 1702 (imide -CO-N-CO-, ester νC=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.

^{1}H 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 νC-H), 1699 (imide -CO-N-CO-, ester νC=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.

^{1}H 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, $CDCl_3$/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 νC-H), 1698 (imide -CO-N-CO-, ester νC=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}, $CHCl_3$/TFE 6:1, v:v): 0.62 dL g^{-1}. T_m (DSC): 217 °C.

^1H NMR (400 MHz, $CDCl_3$/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). ^{13}C NMR (100 MHz, $CDCl_3$/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}, $CHCl_3$/TFE 6:1, v:v): 0.37 dL g^{-1}. T_m (DSC): 203 °C.

^1H NMR (400 MHz, $CDCl_3$/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). ^{13}C 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 νC-H), 1712 (imide -CO-N-CO-, ester νC=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.

^{1}H 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 νC-H), 1709 (imide -CO-N-CO-, ester νC=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 diacid 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}, $CHCl_3$/HFIP 1:1, *v:v*): 0.17 dL g^{-1}. T_g (DSC): 189 °C.

^{1}H NMR (400 MHz, $CDCl_3$/TFA 9:1, *v:v)* δ ppm 8.81 (s, 4H), 4.65–4.34 (m, 8H), 3.47 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$/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 νC-H), 1732 (imide -CO-N-CO-), 1704 (ester νC=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}, $CHCl_3$/HFIP 1:1, *v:v*): 0.56 dL g^{-1}. T_g (DSC): 139 °C.

^{1}H NMR (400 MHz, $CDCl_3$/TFA 9:1, *v:v*) δ ppm 8.82 (s, 4H, C-H), 4.53 (m, 8H, N-CH_2, O-CH_2), 2.64 (m, 4H, CH_2). ^{13}C NMR (100 MHz, CD_2Cl_2/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 νC-H), 1732 (imide -CO-N-CO-), 1703 (ester νC=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}, $CHCl_3$/HFIP 1:1, *v:v*): 1.54 dL g^{-1}. T_g (DSC): 132 °C.

^{1}H NMR (400 MHz, $CDCl_3$/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). ^{13}C NMR (100 MHz, CD_2Cl_2/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 νC-H), 1731 (imide -CO-N-CO-), 1703 (ester νC=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}, $CHCl_3$/HFIP 1:1, v:v): 0.75 dL g^{-1}. T_g (DSC): 116 °C.

^{1}H NMR (400 MHz, $CDCl_3$/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). ^{13}C NMR (100 MHz, CD_2Cl_2/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 νC-H), 1731 (imide -CO-N-CO-), 1703 (ester νC=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}, $CHCl_3$/TFE 6:1, v:v): 0.58 dL g^{-1}. T_g (DSC): 90 °C.

^1H NMR (400 MHz, $CDCl_3$/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). ^{13}C NMR (100 MHz, CD_2Cl_2/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 νC-H), 1731.72 (imide -CO-N-CO-), 1703 (ester νC=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}, $CHCl_3$/HFIP 1:1, v:v): 0.19 dL g^{-1}. T_g (DSC): 73 °C.

^1H NMR (400 MHz, $CDCl_3$/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). ^{13}C NMR (100 MHz, CD_2Cl_2/HFIP 6:1, v:v) ^{13}C NMR (100 MHz, $CDCl_3$/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 νC-H), 1731 (imide -CO-N-CO-), 1703 (ester νC=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}, $CHCl_3$/TFE 6:1, v:v): 1.20 dL g^{-1}. T_g (DSC): 76 °C.

^1H NMR (400 MHz, $CDCl_3$/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). ^{13}C NMR (100 MHz, CD_2Cl_2/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 νC-H), 1732 (imide -CO-N-CO-), 1704 (ester νC=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}, $CHCl_3$/TFE 6:1, v:v): 0.93 dL g^{-1}. T_g (DSC): 50 °C.

^1H NMR (400 MHz, $CDCl_3$/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). ^{13}C NMR (100 MHz, CD_2Cl_2/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 νC-H), 1732 (imide -CO-N-CO-), 1704 (ester νC=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 CaH_2), *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 an acid 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}, $CHCl_3$/TFE 6:1, v:v): 0.20 dL g^{-1}. T_g (DSC): 130 °C.

^{1}H NMR (400 MHz, $CDCl_3$/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-CH_2, O-CH_2), 2.64 (m, 8H, CO-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$/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 νC-H), 1779 (imide -CO-N-CO-), 1707 (ester νC=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}, $CHCl_3$/TFE 6:1, v:v): 0.26 dL g^{-1}. T_g (DSC): 99 °C.

^1H NMR (400 MHz, $CDCl_3$/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-CH_2, O-CH_2), 2.51–2.33 (m, 8H, CO-CH_2), 1.95–1.81 (m, 4H, CO-C-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$/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 νC-H), 1779 (imide -CO-N-CO-), 1701 (ester νC=O), 1388 (imide C-N stretch), 1189 (vs, C–F), 1163 (ester C-O-C), 1140 (imide ring deformation), 768 (imide ring deformation).

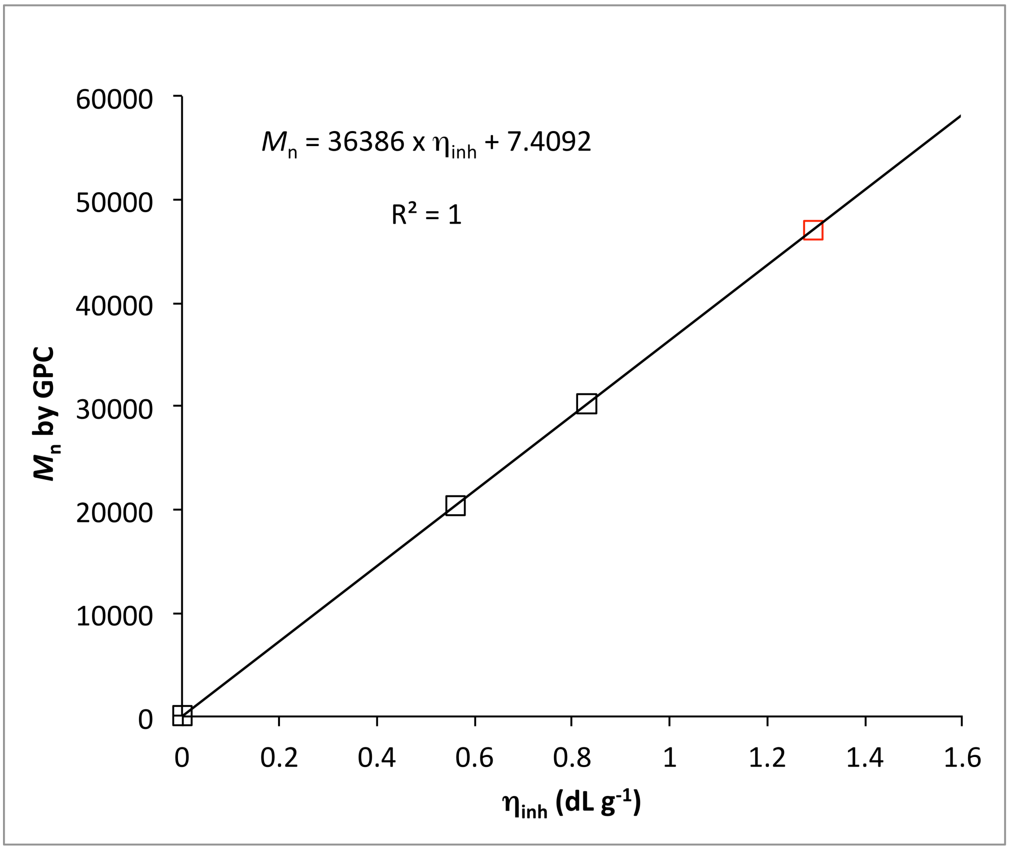
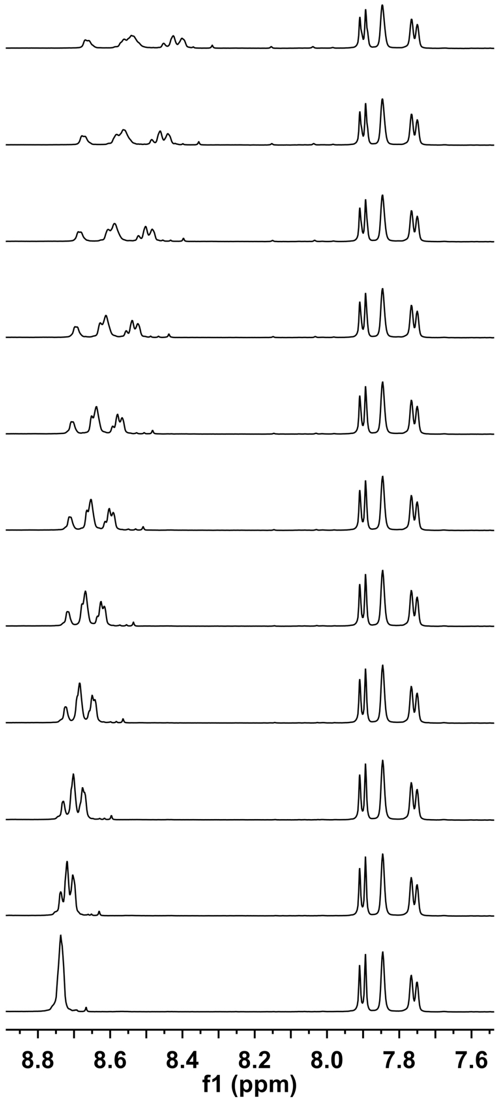


Figure S1. Calibration plot: Inherent viscosity vs M_n (GPC). The straight-line equation of fit is derived from the zero point and the experimental data for HFDI-based poly(ester-imide)s **4** and **5**. The marker point in red is an extrapolation, using the equation of fit for the first three points.

^{1}H 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 uL 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 ^{1}H 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 CDCl$_3$/trifluoroethanol (6:1 v/v).



HFDI-NDI- x = 2, 4 mM	Pyrene-d_{10} 24 mM	NDI:pyrene mole ratio	Conc. of NDI mM
600 uL	300 uL	1:3	2.67
600 uL	250 uL	1:2.5	2.82
600 uL	200 uL	1:2	3.00
600 uL	160 uL	1:1.6	3.16
600 uL	120 uL	1:1.2	3.33
600 uL	100 uL	1:1	3.43
600 uL	80 uL	1:0.8	3.53
600 uL	60 uL	1:0.6	3.64
600 uL	40 uL	1:0.4	3.75
600 uL	20 uL	1:0.2	3.87
600 uL	0 uL	1:0	4.00

TCI cryoprobe 500 MHz, 298 K

Figure S2. Stacked spectra and ^{1}H NMR titration data: Copolymer **22** vs pyrene-d_{10} at 298 K. Solvent was CDCl$_3$/111-trifluoroethanol (6:1 v/v).