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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Knappert, M., Jin, T., Midgley, S. D., Wu, G., Scherman, O. A., Grau-Crespo, R. and Colquhoun, H. M. (2019) Supramolecular complexation between chain-folding poly(ester-imide)s and polycyclic aromatics: a fractal-based pattern of NMR ring-current shielding. Polymer Chemistry, 48. pp. 6641-6650. ISSN 1759-9954 doi: https://doi.org/10.1039/c9py01460h
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To link to this article DOI: http://dx.doi.org/10.1039/c9py01460h

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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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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 (\(\eta_{\text{inh.}}\), 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 \(\nu_{\text{max}}\) ATR (cm\(^{-1}\)): 2961 (aromatic \(\nu_{C-H}\)), 1779 (imide -CO-N-CO-), 1708 (ester \(\nu_{C=O}\)), 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 ($\eta_{inh}$, 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; $D = 1.92$. $T_g$ (DSC): 72 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.93 (d, $J = 8.0$ Hz, 2H), 7.85 (s, 2H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.18 (t, $J = 5.2$ Hz, 4H), 7.36 (d, $J = 5.1$ 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) $\delta$ 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 $\nu_{max}$ ATR (cm$^{-1}$): 2958 (aromatic $\nu$C-H), 1779 (imide $-\text{CO-N-CO}$), 1709 (ester $\nu$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 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); propanediol chloride (0.985 g, 6.991 mmol). Yield: 1.700 g, 68%.

Inherent viscosity ($\eta_{inh}$, 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) $\delta$ 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) $\delta$ ppm 172.56, 166.44, 137.16, 118.30, 65.01, 38.11, 25.67.

FTIR $\nu_{\text{max}}$ ATR (cm$^{-1}$): 2949 (aromatic $\nu$C-H), 1696 (imide -CO-N-CO-, ester $\nu$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), butanediol chloride (1.080 g, 6.97 mmol). Yield: 2.246 g, 84%.

Inherent viscosity ($\eta_{\text{inh}}$, 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) $\delta$ 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) $\delta$ ppm 173.05, 166.45, 137.16, 118.29, 61.85, 38.17, 28.94.

FTIR $\nu_{\text{max}}$ ATR (cm$^{-1}$): 2948 (aromatic $\nu$C-H), 1698 (imide -CO-N-CO-, ester $\nu$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); pentanediol chloride (1.119 g, 6.621 mmol). Yield: 2.331 g, 88%.

Inherent viscosity ($\eta_{\text{inh}}$, 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\(_2\)Cl\(_2\)/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\(_\text{max}\) 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); hexanediol chloride (1.240 g, 6.77 mmol). Yield: 2.7503 g, 96%.

Inherent viscosity (η\(_{\text{inh}}\), 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\(_{\text{max}}\) 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); heptanediol chloride (1.374 g, 6.97 mmol). Yield: 2.442 g, 82%.

Inherent viscosity (η\(_{\text{inh}}\), 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, 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 νmax 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); octanediroyl 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 νmax 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)-pyromellitc diimide (2.029 g, 6.67 mmol); nonanediroyl 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), 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 $\nu_{\text{max}}$ ATR (cm$^{-1}$): 2931 (aromatic $\nu$C-H), 1712 (imide -CO-N-CO-, ester $\nu$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); decanediol chloride (1.705 g, 7.13 mmol). Yield: 3.231 g, 97%.

Inherent viscosity ($\eta_{\text{inh}}$, 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) $\delta$ 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) $\delta$ ppm 174.58, 166.12, 137.12, 118.56, 61.23, 37.70, 33.92, 28.86, 24.50.

FTIR $\nu_{\text{max}}$ ATR (cm$^{-1}$): 2929 (aromatic $\nu$C-H), 1709 (imide -CO-N-CO-, ester $\nu$C=O), 1386 (imide C-N stretch), 1155 (ester C-O-C), 1032 (imide ring deformation), 724 (imide ring deformation).

**NDI-based poly(ester imide)**

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: \(N,N'\text{-bis-(2-hydroxyethyl)-naphthalenetetracarboxylic diimide}\) (0.702 g, 1.98 mmol); propanediol chloride (0.282 g, 2.00 mmol). Yield: 0.32 g, 38%.

Inherent viscosity \((\eta_{inh}, \text{CHCl}_3/\text{HFIP} 1:1, v:v)\): 0.17 dL g\(^{-1}\). \(T_g\) (DSC): 189 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)/TFA 9:1, \(v:v\)) \(\delta\) 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) \(\delta\) ppm 168.09, 164.00, 131.65, 126.73, 126.20, 63.05, 60.90, 39.16.

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

**Homopolymer 15**

Monomers: \(N,N'\text{-bis-(2-hydroxyethyl)-naphthalene tetracarboxylic diimide}\) (0.876 g, 2.47 mmol); butanediol chloride (0.392 g, 2.50 mmol). Yield: 0.67 g, 62%.

Inherent viscosity \((\eta_{inh}, \text{CHCl}_3/\text{HFIP} 1:1, v:v)\): 0.56 dL g\(^{-1}\). \(T_g\) (DSC): 139 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)/TFA 9:1, \(v:v\)) \(\delta\) 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\(_2\)Cl\(_2\)/HFIP 3:1, \(v:v\)) \(\delta\) ppm 174.57, 164.19, 131.91, 127.17, 126.71, 62.58, 39.69, 28.96.

FTIR \(\nu_{\text{max}}\) ATR (cm\(^{-1}\)): 2966 (aromatic \(\nu\text{C-H}\)), 1732 (imide \(-\text{CO-N-CO-}\)), 1703 (ester \(\nu\text{C=O}\)), 1371 (imide C-N stretch), 1188 (ester C-O-C), 1146 (imide ring deformation), 766 (imide ring deformation).
Homopolymer 16
Monomers: \(N,N'\text{-bis}(2\text{-hydroxyethyl})\text{-naphthalene tetracarboxylic diimide}\) (2.005 g, 5.66 mmol); pentanedioyl chloride (0.967 g, 5.72 mmol). Yield: 1.450 g, 56%.

Inherent viscosity (\(\eta_{inh}\), 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) \(\delta\) 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\(_2\)Cl\(_2\)/HFIP 6:1, v:v) \(\delta\)C 175.37, 163.98, 131.81, 127.17, 126.72, 62.36, 39.77, 33.26, 19.48.

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

Homopolymer 17
Monomers: \(N,N'\text{-bis}(2\text{-hydroxyethyl})\text{-naphthalene tetracarboxylic diimide}\) (2.090 g, 5.90 mmol); hexanedioyl chloride (1.091 g, 5.96 mmol). Yield: 2.101 g, 76%.

Inherent viscosity (\(\eta_{inh}\), 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) \(\delta\) 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\(_2\)Cl\(_2\)/HFIP 6:1, v:v) \(\delta\) ppm 175.89, 163.91, 131.77, 127.17, 126.76, 62.23, 39.78, 33.91, 24.10.

FTIR \(\nu_{max}\) ATR (cm\(^{-1}\)): 2959 (aromatic \(\nu\)C-H), 1731 (imide -CO-N-CO-), 1703 (ester \(\nu\)C=O), 1372 (imide C-N stretch), 1192 (ester C-O-C), 1138 (imide ring deformation), 766 (imide ring deformation).
**Homopolymer 18**

Monomers: \( N,N'\text{-bis(2-hydroxyethyl)-naphthalene tetracarboxylic diimide} \) (2.0052 g, 5.66 mmol); heptanediol chloride (1.134 g, 6.80 mmol). Yield: 2.125 g, 78%.

Inherent viscosity \( (\eta_{inh}, \text{CHCl}_3/\text{TFE 6:1, v:v}) \) : 0.58 dL g\(^{-1}\). \( T_g \) (DSC): 90 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)/TFA 9:1, v:v) \( \delta \) 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\(_2\)Cl\(_2\)/HFIP 6:1, v:v) \( \delta \) ppm 176.46, 163.97, 131.82, 127.17, 126.76, 62.19, 39.78, 34.14, 28.52, 24.38.

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

**Homopolymer 19**

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

Inherent viscosity \( (\eta_{inh}, \text{CHCl}_3/\text{HFIP 1:1, v:v}) \) : 0.19 dL g\(^{-1}\). \( T_g \) (DSC): 73 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)/TFA 9:1, v:v) \( \delta \) 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\(_2\)Cl\(_2\)/HFIP 6:1, v:v) \( \delta \) ppm 176.13, 163.59, 131.69, 127.01, 126.57, 61.96, 39.78, 34.15, 28.61, 24.43.

FTIR \( \nu_{\text{max}} \) ATR (cm\(^{-1}\)): 2935 (aromatic \( \nu\text{C-H} \)), 1731 (imide \(-\text{CO-N-CO-}\)), 1703 (ester \( \nu\text{C=O} \)), 1373 (imide C-N stretch), 1161 (ester C-O-C), 1154 (imide ring deformation), 766 (imide ring deformation).
Homo polymer 20

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

Inherent viscosity (\( \eta_{inh} \), CHCl\(_3\)/TFE 6:1, v:v): 1.20 dL g\(^{-1}\). \( T_g \) (DSC): 76 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)/TFA 9:1, v:v) \( \delta \) 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\(_2\)Cl\(_2\)/HFIP 6:1, v:v) \( \delta \) ppm 176.70, 163.92, 131.78, 127.17, 126.76, 62.12, 39.79, 34.40, 28.99, 24.77.

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

Homo polymer 21

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

Inherent viscosity (\( \eta_{inh} \), CHCl\(_3\)/TFE 6:1, v:v): 0.93 dL g\(^{-1}\). \( T_g \) (DSC): 50 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)/TFA 9:1, v:v) \( \delta \) 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\(_2\)Cl\(_2\)/HFIP 6:1, v:v) \( \delta \) ppm 178.30, 165.43, 133.31, 128.68, 128.28, 63.64, 41.32, 35.98, 30.69, 26.37).

FTIR \( \nu_{max} \) ATR (cm\(^{-1}\)): 2929 (aromatic \( \nu_{C-H} \)), 1732 (imide -CO-N-CO-), 1704 (ester \( \nu_{C=O} \)), 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 CaH$_2$), $N,N'$-bis(2-hydroxyethyl)-naphthalene-tetracarboxylic diimide (dried at 100 °C for 24 h), $N,N'$-bis(2-hydroxyethyl)-hexafluoroisopropylidene-dipthalic 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)-naphthalene-tetracarboxylic diimide (1.011 g, 2.82 mmol), $N,N'$-bis(2-hydroxyethyl)-hexafluoroisopropylidene-dipthalic diimide (1.513 g, 2.82 mmol), butanedioyl dichloride (0.902 g, 5.82 mmol). Yield: 1.853 g, 60%.

Inherent viscosity ($\eta_{inh}$, 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) $\delta$ ppm 8.83 (s, 4H, -CH$_2$-, 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) $\delta$ 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 $\nu_{max}$ ATR (cm$^{-1}$): 2973 (aromatic $\nu$C-H), 1779 (imide -CO-N-CO-), 1707 (ester $\nu$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)-naphthalenetricarboxylic diimide (1.001 g, 2.80 mmol), \(N,N'\)-bis(2-hydroxyethyl)-hexafluoropropylene-diphthalic diimide (1.517 g, 2.90 mmol), pentanediol dichloride (0.980 g, 5.80 mmol). Yield: 1.221 g, 38%.

Inherent viscosity \(\eta_{inh}\), CHCl\(_3\)/TFE 6:1, v:v): 0.26 dL g\(^{-1}\). \(T_g\) (DSC): 99 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)/TFA 9:1, v:v) \(\delta\) 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) \(\delta\) 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 \(\nu_{max}\) ATR (cm\(^{-1}\)): 2958 (aromatic \(\nu C-H\)), 1779 (imide -CO-N-CO-), 1701 (ester \(\nu C=O\)), 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.
\(^1\)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 \(\mu\)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 \(^1\)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 \(\mu\)L          | 300 \(\mu\)L             | 1:3                  | 2.67            |
| 600 \(\mu\)L          | 250 \(\mu\)L             | 1:2.5                | 2.82            |
| 600 \(\mu\)L          | 200 \(\mu\)L             | 1:2                  | 3.00            |
| 600 \(\mu\)L          | 160 \(\mu\)L             | 1:1.6                | 3.16            |
| 600 \(\mu\)L          | 120 \(\mu\)L             | 1:1.2                | 3.33            |
| 600 \(\mu\)L          | 100 \(\mu\)L             | 1:1                  | 3.43            |
| 600 \(\mu\)L          | 80 \(\mu\)L              | 1:0.8                | 3.53            |
| 600 \(\mu\)L          | 60 \(\mu\)L              | 1:0.6                | 3.64            |
| 600 \(\mu\)L          | 40 \(\mu\)L              | 1:0.4                | 3.75            |
| 600 \(\mu\)L          | 20 \(\mu\)L              | 1:0.2                | 3.87            |
| 600 \(\mu\)L          | 0 \(\mu\)L               | 1:0                  | 4.00            |

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).