Principles of sequence-recognition in aromatic polyimides


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ELECTRONIC SUPPLEMENTARY INFORMATION

Contents

1. Synthesis and characterisation data for new compounds and polymers

2. UV-Vis data for tweezer-polymer binding.

3. $^1$H NMR data for complexation of tweezer $1b$ with polymers 6, 7, 9 and 10 and with the model di-imide 2.
1. Synthesis and characterisation data for new compounds and polymers

Pyromellitic dianhydride (PMDA) and 4,4’-bis(3-aminophenoxy)diphenylsulfone (3) were obtained from Acros and were used as received. The diamine 4,4’-bis(3-methyl-4-aminophenoxy)diphenylsulfone (4) was synthesised according to a literature method.\(^1\) The polymerization solvent \(N,N\)-dimethylacetamide (DMAc) was distilled from calcium hydride before use. Proton and \(^{13}\)C NMR spectra were recorded on a Bruker DPX 250 MHz spectrometer with chemical shifts referenced to residual solvent resonances. Assignments of proton resonances were made with reference to 2-dimensional (COSY) spectra. Mass spectra (CI, ES) were run on a VG Autospec instrument. Matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectra were recorded on a SAI LT3 LaserTof spectrometer using 1,8,9-trihydroxyanthracene as matrix and sodium trifluoroacetate as cationising agent. UV-visible spectra were measured at 20 °C on a Perkin Elmer Lambda-25 spectrometer. Polymer glass transition onset temperatures were determined by DSC under nitrogen, at a heating rate of 10 °C min\(^{-1}\), using a Mettler DSC20 system. Inherent viscosities (\(\eta_{inh}\)) of polyimides were measured at 25 °C on 0.1% polymer solutions in 1-methyl-2-pyrrolidinone using a Schott-Geräte CT-150 semi-automated viscometer. Molecular weights of polyimides relative to polystyrene standards were determined by gel permeation chromatography (GPC) on a Polymer Laboratories PL-220 instrument equipped with a differential refractive index detector and 2 x PLgel 10 µm Mixed B columns. Analyses were carried out in DMF/LiBr solution (0.05 M in LiBr) at 60 °C, with a flow rate of 1.0 mL min\(^{-1}\) and with an injection volume of 100 µl. Samples were dissolved in DMF/LiBr at a concentration of 1 mg mL\(^{-1}\), and both eluent and sample solutions were filtered through a 0.02 µm PTFE membrane prior to injection.

\(^1\) German Patent DE1909520 (1961); Chem. Abs. 74, 22554, to Bayer.
Synthesis of 4-(3-aminophenoxyphenyl)-4’-chlorophenyl sulfone (8)

![Chemical structure of 4-(3-aminophenoxyphenyl)-4’-chlorophenyl sulfone (8)](image)

A mixture of 3-aminophenol (8.73 g, 0.08 mole), 4,4’-dichlorodiphenylsulfone (68.92 g, 0.24 mole), potassium carbonate (22.11 g, 0.16 mol), N,N-dimethylacetamide (DMAc, 300 mL) and toluene (100 mL) was heated to reflux under nitrogen, with azeotropic distillation of water. After 3.5 h the toluene was distilled off and the temperature raised to 160 °C. After a further 4 h the reaction mixture was cooled to room temperature, poured into water (900 mL) and the precipitate was filtered off. After washing with water and then methanol, the solid was dried at 100 °C for 2 h and purified by chromatography (dichloromethane eluent) to give colourless, crystalline 8 (14.5 g, 50% yield), m.p. 139 °C; ¹H NMR (CDCl₃) δ (ppm) = 7.87 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.11 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 6.54 (dm, 1H), 6.41 (dm, 1H), 6.36 (t, J = 2.2 Hz, 1H), 3.83 (s, 3H); ¹³C NMR (CDCl₃) δ (ppm) = 162.8, 156.2, 148.6, 141.0, 150.1, 134.6, 131.2, 130.3, 130.0, 129.3, 118.2, 112.4, 110.5, 107.3; IR (Nujol): 3386 (ν N-H), 1243 (ν C-O-C) cm⁻¹; MS (CI) calc. for [C₁₈H₁₄ClNO₃S + H]⁺, m/z = 359.04, found 359.04.

Synthesis of 2,6-Bis[(3-(4’-chlorobenzenesulfonyl)phenoxy)phenyl]pyrrolo[3,4-f]isoindole-1,3,5,7 (2H,6H)-tetrone (2)

![Chemical structure of 2,6-Bis[(3-(4’-chlorobenzenesulfonyl)phenoxy)phenyl]pyrrolo[3,4-f]isoindole-1,3,5,7 (2H,6H)-tetrone (2)](image)

A solution of 8 (11.57 g, 0.031 mol) and pyromellitic dianhydride (3.32 g, 0.0152 mol) was heated to refluxing in dry DMAc (485 mL) under nitrogen for 16 h. The clear, pale yellow solution was cooled, poured into water (1 L), filtered, washed with water and methanol. The crude product was purified by recrystallization from N,N-dimethylformamide/isopropanol (5:1 v/v) to afford pale yellow crystalline 3 (7.2 g, 53% yield), m.p. 313.4 °C; ¹H NMR (CDCl₃/TFA) δ (ppm) = 8.62 (s, 2H), 8.02 (d, J = 9.0 Hz, 4H), 7.94 (d, J = 9.0 Hz, 4H), 7.67 (t, J = 8.3 Hz, 2H), 7.60 (d, J = 9.0 Hz, 4H), 7.38 (dm, 2H), 7.33 (dm, 2H), 7.27 (t, J = 2.2 Hz, 2H), 7.25 (d, J = 9.0 Hz, 4H);
\(^{13}\)C NMR (CDCl\(_3\)/TFA) \(\delta\) (ppm) = 166.7, 156.0, 141.9, 138.4, 137.5, 133.5, 131.7, 131.6, 130.4, 130.3, 128.9, 123.7, 121.8, 120.5, 119.1, 118.9; IR (Nujol): 1777, 1717 (imide \(\nu\)C=O), 1377 (\(\nu\)C-N), 1242 (\(\nu\)C-O-C), 1106, 727 cm\(^{-1}\); MS (MALDI-TOF) calc. for \([\text{C}_{46}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_{10}\text{S}_2 + \text{Na}]^{+}\), \(m/z = 923\), found 923. Anal. Calc. for \(\text{C}_{46}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_{10}\text{S}_2\) C 61.27, H 2.91, N 3.11; found C 61.03, H 2.80, N 3.37%.

**Synthesis of 4-(3-aminophenoxyphenyl)-4'-(3'-amino-4''-methylphenoxyphenyl) sulfone (5)**

![Chemical structure](image)

A mixture of 1 (3.6 g, 0.01 mole), 4-amino-\(m\)-cresol (1.36 g, 0.011 mole), potassium carbonate (1.52 g, 0.011mol), N,N-dimethylacetamide (DMAc, 100 mL) and toluene (60 mL) was heated to reflux under nitrogen, with Dean-Stark distillation of water. After 3.5 h the toluene was distilled off and the temperature raised to 160 °C. After a further 12 h the reaction mixture was cooled to room temperature, poured into water (500 mL) and the precipitate was filtered off. After washing with water and then methanol, the solid was dried at 80 °C for 2 h and purified by chromatography (dichloromethane) to give pale brown amorphous solid 5 (2.00 g, 45% yield), amorphous; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) (ppm) = 7.83 (d, \(J = 8.9\) Hz, 2H), 7.81 (d, \(J = 8.9\) Hz, 2H), 7.13 (t, \(J = 8.0\) Hz, 1H), 7.01 (d, \(J = 8.9\) Hz, 2H), 6.94 (d, \(J = 8.9\) Hz, 2H), 6.76 (s, 1H), 6.68 (m, 2H), 6.50 (dm,1H), 6.39 (dm,1H), 6.33 (t, \(J = 2.2\) Hz, 1H),3.67 (s, 4H), 2.15 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) (ppm) = 163.7, 162.3, 156.5, 148.8, 146.7, 142.5, 135.9, 134.8, 131.1, 130.0, 129.9, 124.5, 123.2, 119.7, 118.2, 117.1, 116.3, 112.1, 110.4, 107.1, 18.0; IR (Nujol): 3362 (\(\nu\)N-H), 1235 (\(\nu\)C-O-C) cm\(^{-1}\); MS (ES) calc. for \([\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_4\text{S} + \text{H}]^{+}\), \(m/z = 447.1\), found 447.1; Anal. Calc. for \(\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_4\text{S}\) C 67.25, H 4.97, N 6.27; found C 66.98, H 4.92, N 6.16%.

**Synthesis and characterisation of polyimides 6, 7, 9 and 10**

The synthesis of polyimide 7 is taken as an example. Diamine 5 (0.447 g, 1 mmol) was dissolved in DMAc (3 mL) by stirring at room temperature, and when the diamine was dissolved completely, pyromellitic dianhydride (0.218 g, 1 mmol) was added in one portion. The dianhydride gradually dissolved and the mixture became viscous after 0.5 h. The pale yellow viscous solution was stirred for a further 22 h,
then transferred to a Petri dish and heated at 80 °C under vacuum for 2 h to remove the solvent. The resulting film of polyamic acid was imidized by heating sequentially at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 210 °C for 10 min and finally at 250 °C for 30 min. The polyimide film was dissolved in DMF and re-precipitated twice in methanol to give uniform beads of polyimide 7 which were dried at 80 °C for 4 h.

**Polyimide 7**: Yield 84%, T₆ 295 °C, η₀ = 0.83 dL g⁻¹; Mₐ = 112,000, Mₙ = 157,000; 

¹H NMR (CDCl₃/hexafluoropropan-2-ol 6:1 v/v): δ (ppm) = 8.49 (t, J = 6.5 Hz), 7.86 (d, 8.6 Hz), 7.61 (t, J = 7.5 Hz), 7.31 (d, J = 7.7 Hz), 7.25 – 7.02 (m), 2.16 (s); ¹³C NMR (CDCl₃/hexafluoropropan-2-ol 6:1 v/v): δ (ppm) = 166.3, 165.8, 162.1, 156.9, 156.0, 139.5, 137.6, 137.4, 134.7, 132.2, 131.5, 130.5, 130.1, 125.8, 123.3, 123.0, 120.2, 119.1, 118.9, 118.7, 17.9; IR (film from DMF): 1778, 1728 (imide νC=O), 1375 (νC-N), 1245 (νC-O-C), 1106, 727 cm⁻¹.

![Polyimide 7](image)

**Polyimide 6**: Yield 88%, T₆ 293 °C, η₀ = 0.95 dL g⁻¹; Mₐ = 143,000, Mₙ = 244,000; 

¹H NMR (CDCl₃/hexafluoropropan-2-ol 6:1 v/v): δ (ppm) = 8.48 (t, J = 8.3 Hz), 7.85 (m), 7.59 (t, J = 7.9 Hz), 7.37 – 7.02 (m), 2.16 (s); ¹³C NMR (CDCl₃/hexafluoropropan-2-ol 6:1 v/v): δ (ppm) = 166.3, 165.8, 162.1, 156.8, 156.0, 139.5, 137.6, 137.4, 134.8, 132.2, 131.5, 130.6, 130.1, 125.9, 123.3, 123.0, 120.2, 119.1 118.9, 118.7, 18.0; IR (film from DMF): 1777, 1735 (imide νC=O), 1375 (νC-N), 1244 (νC-O-C), 1106, 727 cm⁻¹.

![Polyimide 6](image)
**Polyimide 9:** Yield 96%, $T_g$ 274 °C, $\eta_{inh} = 0.88$ dL·g$^{-1}$, $M_n = 145,000$, $M_w = 268,000$; $^1$H NMR (CDCl$_3$/hexafluoropropan-2-ol 6:1 v/v): $\delta$ (ppm) = 8.44 (s), 7.84 (d, $J = 8.9$ Hz), 7.58 (t, $J = 8.4$ Hz), 7.31 (d, $J = 8.9$ Hz), 7.17 – 7.12 (m); $^{13}$C NMR (CDCl$_3$/hexafluoropropan-2-ol 6:1 v/v): $\delta$ (ppm) = 165.7, 162.1, 156.0, 137.4, 134.8, 132.3, 131.5, 130.1, 123.2, 121.1, 120.0, 118.9, 118.7; IR (film from DMF): 1778, 1728 (imide $\nu$C=O), 1372 ($\nu$C-N), 1243 ($\nu$C-O-C), 1106, 725 cm$^{-1}$.

![Polyimide 9](image)

**Polyimide 10:** Yield 70%, $T_g$ 335 °C, $M_n = 75,000$, $M_w = 116,000$; $^1$H NMR (CDCl$_3$/hexafluoroisopropanol 6:1 v/v): $\delta$ (ppm) = 8.52 (s), 7.88 (d, $J = 8.9$ Hz), 7.27 – 7.03 (m), 2.18 (s); $^{13}$C NMR (CDCl$_3$/hexafluoropropan-2-ol 6:1 v/v): $\delta$ (ppm) = 166.2, 162.0, 156.7, 139.4, 137.5, 134.8, 130.5, 130.0, 125.8, 122.9, 120.2, 119.0, 118.9, 17.9.

![Polyimide 10](image)
2. UV-Vis and $^1$H NMR data for tweezer-polymer complexation

*Determination of the 1:1 binding constant for tweezer 1a with model di-imide 2*

A standard solution containing equimolar amount of di-imide 2 (2 mM) and tweezer 1 in CHCl₃/hexafluoro-propan-2ol (6:1, v/v) was made up in a 10 mL volumetric flask, and the absorbance “A” of this solution at 500 nm was recorded. The solution was then diluted accurately and the absorbance re-measured. This process of accurate dilution and remeasurement of absorbance was repeated six times to obtain seven sets of data. The experiment was repeated with a second standard solution (1.75 mM), and seven-fold dilution yielded eight sets of data. The linear regression analysis for determination of the binding constant ($6 \times 10^3$ M⁻¹) is shown below. See ref. 2.

\[
y = 0.5231x + 1.7075
\]

\[
R^2 = 0.901
\]

\\[
1/A^{1/2} \quad 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2 \quad 2.5 \quad 3 \quad 3.5
\]

A = absorbance; c = concentration (mole L⁻¹) of imide units (equimolar with tweezer)
Intercept, $y_0 = 1.708 \times 10^3$; Slope, $\alpha = 0.523$

So that:  
\[
K_a = \frac{y_0}{\alpha^2} = 6244 \text{ M}^{-1}
\]

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3. $^1$H NMR data for complexation of 1b with polymers 6, 7, 9 and 10 and with the model di-imide 2.

$^1$H NMR studies of the binding of tweezer 1a to polyimides 6, 7, 9 and 10.

A stock solution of each polyimide (4mM with respect to total imide residues) in CHCl$_3$/hexafluoropropan-2-ol (6:1 v/v) was prepared in a 5 mL volumetric flask, and 0.8 mL of this solution was added to an NMR tube using a micropipette. The solution was slowly evaporated under a flow of nitrogen, and the residue was dried at 80 °C under vacuum for 4 h. A solution of the tweezer molecule 1a in CDCl$_3$/hexafluoropropan-2-ol (6:1 v/v), having the required concentration of tweezer, was similarly prepared in a 5 mL volumetric flask. An aliquot of this solution (0.8 mL) was added to the NMR tube by micropipette and mixed well to re-dissolve the polyimide before carrying out NMR analysis. Peak assignments were made by 2-dimensional (COSY) analyses, by evaluation of integrals, and by tracking incremental changes in peak positions on progressive addition of tweezer 1a.

Supplementary Figures 1 - 6 (following) show the effects of tweezer complexation, over the range 1.25 - 200 mol%, relative to pyromellitimide residues in the polymer or model compound, on the $^1$H NMR spectra of polyimides 6 and 7 and, as control experiments, on the homo-polyimides 9 and 10 and the model di-imide 2.
**Supplementary Fig. 1.** $^1$H NMR spectra of copolymer 6 in the aromatic region (CDCl$_3$/hexafluoropropan-2-ol, 6:1 v/v), showing the effects of adding an increasing proportion of tweezer 1a. Sequence-assignments for the imide resonances are shown in Fig.3 and Supplementary Fig. 2. Corresponding plots for the two homopolymers (9 and 10), as controls, are shown in Supplementary Figs. 4 and 5.
**Supplementary Fig. 2.** Expansion of the imide region for the upper three $^1$H NMR spectra shown in Supplementary Fig. 1. The separations of the UIU resonance into an apparent 1:2:1 triplet, and the HIU resonance into an apparent 1:1 doublet, are both fully consistent with the adjacent-binding model, as shown in the sequence-assignments. The splitting of the HIH resonance (which in this copolymer can, by definition, have no adjacent UIU binding-sequences) reflects the existence of non-interconverting syn and anti conformers of this sequence. Assignments of the two HIH resonances are based on the premise that the syn isomer has one unhindered face and can therefore, unlike the anti-isomer, undergo at least a weak interaction with the outer face of one of the pyrene arms of the tweezer.
Supplementary Fig. 3. $^1$H NMR spectra of polyimide 7 in the aromatic region (CDCl$_3$/hexafluoro-propan-2-ol, 6:1 v/v), showing the effect on the imide resonances of adding an increasing proportion of tweezer 1a. The singlet due to sequence UIU undergoes a major shift on complexation, but exhibits no development of fine-structure because the sequence-restrictions in polymer 7 forbid adjacent binding (i.e. UIU cannot be adjacent to UIU). In contrast, signals from the unbound or very weakly-bound sequences HIH and HIU do develop fine structure, as a consequence of tweezer binding to adjacent UIU sequence, as shown. The doubling of the HIH resonance at high tweezer-concentration is again ascribed to the existence of non-interconverting syn and anti conformers.
Supplementary Fig. 4. Control experiment. $^1$H NMR spectra of the unhindered homopolyimide 9 in the aromatic region (CDCl$_3$/hexafluoro-propan-2-ol, 6:1 v/v), showing the effect on the imide resonance of adding an increasing proportion of tweezer 1a. The very large complexation shift demonstrates strong tweezer binding at the sequence UIU, and the absence of any fine structure development at high tweezer concentrations confirms that such structure, observed in polymers 6 and 7, represents long-range, chain-sequence information.
Supplementary Fig. 5. Control experiment. $^1$H NMR spectra of the methyl-hindered homopolyimide 10 in the aromatic region (CDCl$_3$/hexafluoro-propan-2-ol, 6:1 v/v), showing the effect on the imide resonance of adding an increasing proportion of tweezer 1a. The very small complexation shift indicates extremely weak tweezer binding to the sequence HIH, and the absence of any fine structure development at high tweezer concentrations again confirms that such structure, observed in polymers 6 and 7, represents long-range, chain-sequence information. The splitting of the imide resonance is, as described in Supplementary Fig. 2, attributed to a marginally stronger interaction of the tweezer with the syn- than with the anti-conformer of HIH.
Supplementary Fig. 6. Control experiment. $^1$H NMR spectra of the model compound 2 in the aromatic region (CDCl$_3$/hexafluoro-propan-2-ol, 6:1 v/v), showing the effect on the imide resonance of adding an increasing proportion of tweezer 1a.