Supporting Information for

Binding and Supramolecular Organization of Homo- and Heterotelechelic Oligomers in Solutions

Jessalyn Cortese, Corinne Soulié-Ziakovic* and Ludwik Leibler*

I. Synthesis and NMR of Thy-PPO-460-DAT 5a

II. MALDI-TOF of NH₂-PPO-2200-NH₂ 1b, Thy-PPO-2200-Thy 6b, DAT-PPO-2200-DAT 7b, 50/50-M2200 8b and Thy-PPO-460-DAT 5a

III. Association constants determination by ¹H NMR

IV. Viscosity models
I. Synthesis of Thy-PPO-460-DAT

**Chart 1.** (i) NH₂-PPO-X-NH₂ 1a, (ii) NH₂-PPO-X-BOC 2a, (iii) Thy-PPO-X-BOC 3a, (iv) Thy-PPO-X-NH₂ 4a, and (v) Thy-PPO-X-DAT 5a (X = 460).

**Step 1.** A solution of di-tertio-butyl dicarbonate (BOC₂O, 4.94 g - 22.6 mmol - 1 eq.) in dichloromethane (DCM, 100 mL) was added dropwise to a solution of purified (by liquid-liquid extraction, in order to eliminate the bigger molecules which prefer the organic phase to the acidic aqueous phase) NH₂-PPO-X-NH₂ (1a, 22.6 mmol - 1 eq.) in DCM (100 mL), under nitrogen flow, and cooled in an ice bath (0°C). The reaction mixture was allowed to stir, under nitrogen flow, for 6 hrs, in the ice bath, and was subsequently washed with a 0.1 M acetic acid solution (pH ~ 3, 3 x 200 mL) to extract the unreacted diamine. The solvent was then removed by rotary evaporation. Water (150 mL) was added to the resultant oily material. Non solubilized di-BOC-protected diamine was filtered from the mixture (filter pores diameter = 0.45 µm). A 2N sodium hydroxide solution was added to the aqueous filtrate (pH ~ 4) until pH reached 10. The mixture was then extracted with DCM, dried over anhydrous magnesium sulfate, filtered, and evaporated, affording 2a (0.37 eq.).

**RMN** ¹H (CDCl₃ / TMS) δ/ppm = 0.97 (d, 3H, b) - 1.08 (m, 28H, a, b) - 1.38 (s, 14H, f) - 1.92 (s, 2H, g) - 2.8 to 4.0 (m, 31H, c, d, d, e, f, f) - 3.69 (s, 2H, f) - 4.87 (s, 0.8H, g).

**RMN** ¹³C (CDCl₃ / TMS) δ/ppm = 17.1 (a) - 18.1 (b) - 19.8 (b) - 28.5 (f) - 46.5, 47.0 (f, f) - 72.3 to 79.0 (d, d, c, e, 2) - 155.6 (3).
Step 2. Thymine-1-acetic acid (0.88 g - 4.8 mmol - 1 eq.) was dissolved in DMF (15 mL). 2a (4.8 mmol - 1 eq.), TBTU (3.08 g - 9.6 mmol - 2 eq.) and triethylamine (TEA, 2.7 mL - 19.4 mmol - 4 eq.) were then added. The reaction stirred at room temperature for 2.5 days, and was subsequently quenched by adding water (100 mL). The reaction mixture was extracted with toluene (2 x 100 mL), washed with water (100 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated, affording 3a (1 eq.).

\[ ^1\text{H NMR (DMSO-d_6 /TMS)} \delta/\text{ppm} = 0.84 \text{ (m, 0.3H, b)} - 1.04 \text{ (m, 30H, a, b, b)} - 1.37 \text{ (s, 12H, I)} - 1.75 \text{ (s, 3H, A)} - 3.1 \text{ to 3.8 (m, } c, d, d, e, f) - 3.84 \text{ (m, 1H, f)} - 4.26 \text{ (s, 2H, B)} - 6.54 \text{ (d, 1H, g)} - 7.40 \text{ (s, 1H, C)} - 7.99 \text{ (m, 1H, I)} - 11.24 \text{ (s, 1H, D)}. \]

\[ ^{13}\text{C NMR (DMSO-d_6 /TMS)} \delta/\text{ppm} = 11.9 \text{ (A)} - 17.0 \text{ to 18.5 (a, b, b)} - 28.2 \text{ (I)} - 44.8, 45.8 (f, f) - 49.2 \text{ (B)} - 71 \text{ to 75, 77.4 (c, d, e, 2)} - 107.4 \text{ (E)} - 142.5 \text{ (C)} - 151.0 \text{ (F)} - 155.0 \text{ (D)} - 164.5 \text{ (G)} - 166.2 \text{ (H)}. \]

Step 3. 3a (8.1 mmol - 1 eq.) was dissolved in DCM (20 mL) at 0°C. Trifluoroacetic acid (TFA, 25 mL - 337 mmol - 42 eq.) was then added. The reaction stirred at room temperature for 2 days, and the solvents were subsequently removed by rotary evaporation. The amino functions were then neutralized by adding a 2M sodium hydroxide solution saturated with sodium chloride until pH reached 14. The product was extracted with toluene (3 x 20 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated, affording 4a (0.23 eq.).

\[ ^1\text{H NMR (DMSO-d_6 /TMS)} \delta/\text{ppm} = 0.89 \text{ (m, 4H, b)} - 1.04 \text{ (m, 27H, a, b)} - 1.68 \text{ (s, 3H, A)} - 3.0 \text{ to 3.7 (m, e, d, d, e, f)} - 3.80 \text{ (m, 1H, f)} - 4.15 \text{ (s, 2H, B)} - 6.99 \text{ (s, 1H, C)} - 7.81 \text{ (d, 1H, I)}. \]

Step 4. 4a (2.4 mmol - 1 eq.) was dissolved in 60 mL of a water / absolute ethanol mixture (v/v 50/50). NaHCO₃ (0.47 g - 4.9 mmol - 2 eq.) and 2-chloro-4,6-diamino-1,3,5-triazine (0.43 g - 2.9 mmol - 1.2 eq.) were added, and the resulting suspension was stirred under reflux for 48h. Since DAT-Cl was only partially soluble in this solvent, the reaction mixture started as a white suspension that transformed into a transparent solution as the reaction progressed. The solvent was removed in vacuo from the reaction mixture. DCM (50 mL) was added, the suspension was filtered, dried over anhydrous magnesium sulfate, filtered, evaporated, and dried under vacuum at 100°C, affording 5a (0.66 eq.).

\[ ^1\text{H NMR (DMSO-d_6 /TMS)} \delta/\text{ppm} = 1.04 \text{ (m, 29H, a, b, b)} - 1.75 \text{ (s, 3H, A)} - 2.9 \text{ to 3.7 (m, e, d, d, e)} - 3.84 \text{ (m, 1H, f)} - 4.04 \text{ (m, 1H, f)} - 4.26 \text{ (s, 2H, B)} - 5.8 \text{ to 6.3 (m, 5H, } \Phi, \Psi, \Omega) - 7.42 \text{ (s, 1H, C)} - 7.98 \text{ (d, 1H, I)}. \]

\[ ^{13}\text{C NMR (DMSO-d_6 /TMS)} \delta/\text{ppm} = 11.9 \text{ (A)} - 17 \text{ to 19 (a, b, b)} - 44.8 (f, f) - 49.3 \text{ (B)} - 71 \text{ to 75 (e, d, d, e)} - 107.8 \text{ (E)} - 142.6 \text{ (C)} - 151.1 \text{ (F)} - 164.6 \text{ (G)} - 165.9 \text{ (G)} - 166.1 \text{ (H)} - 168.3 \text{ (A, } \Sigma). \]
II. MALDI-TOF mass spectra

The samples (0.20 mg) were dissolved in acetone (1.0 mL) and mixed 1:2 (v:v) with a saturated solution of 2,5-dihydroxibenzoic acid matrix in acetone. The spectra were recorded in positive mode on a PerSeptive Voyager RP-DE MALDI-TOF mass spectrometer.

Figure 1. MALDI-TOF mass spectrum of NH$_2$-PPO-2200-NH$_2$ 1b

$M_n = 1925.51$ ; $M_z = 2039.91$ ; $M_w = 1982.06$

Polymer Dispersion Index = 1.03

Figure 2. MALDI-TOF mass spectrum of Thy-PPO-2200-Thy 6b:

$M_n = 2156.51$ ; $M_z = 2333.60$ ; $M_w = 2247.28$

Polymer Dispersion Index = 1.04
Figure 3. MALDI-TOF mass spectrum of DAT-PPO-2200-DAT 7b

\[ \text{Mn} = 1925.51; \quad \text{Mz} = 2039.91; \quad \text{Mw} = 1982.06 \]

Polymer Dispersion Index = 1.03

Figure 4. MALDI-TOF mass spectrum of 50/50-M2000 8b

\[ \text{Mn} = 2121.64; \quad \text{Mz} = 2284.45; \quad \text{Mw} = 2204.92 \]

Polymer Dispersion Index = 1.04
Figure 5. MALDI-TOF mass spectrum of Thy-PPO-2200-DAT 5b

\[ \text{Mn} = 2186.20 \; ; \; \text{Mz} = 2402.13 \; ; \; \text{Mw} = 2297.94 \]

\[ \text{Polymer Dispersion Index} = 1.05 \]
III. Association constants determination

(i) by NMR titration

The association constants $K_{AA}$ of an AA complex ($A + A \rightleftharpoons AA$) and $K_{AB}$ of an AB complex ($A + B \rightleftharpoons AB$) can be determined by $^1$H NMR titration, assuming isodesmic mechanisms. Indeed, the chemical shifts of the A protons implicated in the hydrogen bonds vary greatly between the free, self-associated, and AB associated states. If the equilibria are faster than the NMR spectroscopic time scale, the observed chemical shift is a weighted average between the chemical shifts of the associated $\delta_{AB}$, self-associated $\delta_{AA}$, and free states $\delta_A$. Thus, at a given temperature, $K_{AA}$ and $K_{AB}$ can be measured by monitoring the A protons implicated in the hydrogen bonds chemical shift as a function of species concentration. The titration curves are then analyzed by computer fitting with least-squares methods (EQNMR program).

For solutions containing only A’s:

$$\delta = \delta_A \frac{[A]}{C_A} + 2\delta_{AA} \frac{[AA]}{C_A}$$

(1)

$$C_A = [A] + 2[AA]$$

(2)

$$K_{AA} = \frac{[AA]}{[A]^2}$$

(3)

$$\delta^A = \delta_{AA} + (\delta_{AA} - \delta_A) \frac{1 - \sqrt{1 + 8K_{AA}C_A}}{4K_{AA}C_A}$$

(4)

For solutions containing A and B, and where the AA dimerization can be neglected:

$$\delta = \delta_A \frac{[A]}{C_A} + \delta_{AB} \frac{[AB]}{C_A}$$

(5)

$$C_A = [A] + [AB]$$

(6)

$$K_{AB} = \frac{[AB]}{[A][B]}$$

(7)

$$\delta^A = \delta_{AB} + (\delta_A - \delta_{AB}) \frac{C_A - 1/K_{AB} - C_B + \sqrt{(C_A + 1/K_{AB} + C_B)^2 - 4C_A C_B}}{2C_A}$$

(8)
**Figure 2.** $^1$H NMR titration in DMSO-$d_6$ at 25°C of Thy-C$_4$ (9.0*10^{-2} \text{ mol/L})$ by MeDAT (from 0 to 2.3*10^{-1} \text{ mol/L}) (K$_{\text{Thy-DAT}}$ = 1.3 L/mol, $\delta_{\text{freeThy}} = 11.25$ ppm, $\delta_{\text{bondedThy}} = 12.10$ ppm).

**Figure 3.** $K_{\text{Thy-Thy}}$ determination by NMR titration in CDCl$_3$ at 25°C of Thy-PPO-460-Thy 6a ($K_{\text{Thy-Thy}}$ = 2.0 L/mol, $\delta_{\text{freeThy}} = 9.3$ ppm, $\delta_{\text{dimerizedThy}} = 10.9$ ppm).
**Figure 4.** $K_{\text{DAT-DAT}}$ determination by NMR titration in CDCl$_3$ at 25°C of DAT-PPO-460-DAT 7a ($K_{\text{DAT-DAT}} = 2.8$ L/mol, $\delta_{\text{freeDAT}} = 5.03$ ppm, $\delta_{\text{dimerizedDAT}} = 6.47$ ppm).

**Figure 5.** $K_{\text{Thy-DAT}}$ determination by NMR titration in CDCl$_3$ at 25°C of DAT-PPO-460-DAT 7a by Thy-PPO-460-Thy 6a ($K_{\text{Thy-DAT}} = 846.5$ L/mol, $K_{\text{DAT-DAT}} = 4.7$ L/mol, $\delta_{\text{freeDAT}} = 4.52$ ppm, $\delta_{\text{dimerizedDAT}} = 6.81$ ppm, $\delta_{\text{bondedDAT}} = 6.28$ ppm).
**Figure 6.** $K_{\text{Thy-DAT}}$ determination by NMR titration in CDCl$_3$ at 25°C of DAT-PPO-460-DAT 7a by Thy-PPO-460-Thy 6a ($K_{\text{Thy-DAT}} = 1255.7$ L/mol, $K_{\text{DAT-DAT}} = 3.2$ L/mol, $\delta_{\text{freeDAT}} = 4.70$ ppm, $\delta_{\text{dimerizedDAT}} = 6.88$ ppm, $\delta_{\text{bondedDAT}} = 6.24$ ppm).

**Figure 7.** $K_{\text{Thy-Thy}}$ determination by NMR titration in toluene-d$_8$ at 25°C of Thy-PPO-2200-Thy 6b ($K_{\text{Thy-Thy}} = 26.5$ L/mol, $\delta_{\text{freeThy}} = 9.35$ ppm, $\delta_{\text{dimerizedThy}} = 10.98$ ppm).
Figure 8. $K_{\text{DAT-DAT}}$ determination by NMR titration in toluene-$d_8$ at 25°C of DAT-PPO-2200-DAT 7b

($K_{\text{DAT-DAT}} = 42.5 \text{ L/mol}$, $\delta_{\text{free DAT}} = 4.91$ ppm, $\delta_{\text{dim DAT}} = 6.35$ ppm).

(ii) Association constant as a function of temperature

Although $K_{\text{Thy-DAT}}$ could not be measured in toluene-$d_8$ by NMR titration, temperature-dependent NMR measurements of solutions of Thy-PPO-2200-Thy, DAT-PPO-2200-DAT, and Thy-PPO-2200-DAT allowed estimation of $K_{\text{Thy-DAT}}$, as well as $K_{\text{Thy-Thy}}$ and $K_{\text{DAT-DAT}}$, as a function of temperature.

To this end, the extreme chemical shifts of Thy NH (D) and DAT NH$_2$ (Φ, Ψ) in the free ($\delta_{\text{free Thy}}$, $\delta_{\text{free DAT}}$) and self-associated ($\delta_{\text{dim Thy}}$, $\delta_{\text{dim DAT}}$) states (i.e. the extreme values, which are temperature-independent and solvent-independent) can be estimated by temperature-dependent $^1$H NMR measurements of solutions of Thy-PPO-2200-Thy and DAT-PPO-2200-DAT (in CDCl$_3$ and in toluene-$d_8$). Indeed, sigmoid fitting on the observed chemical shift for Thy NH (D) ($\delta_{\text{Thy exp solvent}}$, Figure 9a) and DAT NH$_2$ (Φ, Ψ) ($\delta_{\text{DAT exp solvent}}$, Figure 9b) in those experiments, yielded the values of 7.90 ppm for $\delta_{\text{free Thy}}$, 11.17 ppm for $\delta_{\text{dim Thy}}$, in agreement with literature data,$^1$ and 4.40 ppm for $\delta_{\text{free DAT}}$, 7.63 ppm for $\delta_{\text{dim DAT}}$.

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$^1$ Salas, M.; Gordillo, B.; Gonzalez, F.; ARKIVOC 2003, 11, 72.
Figure 9. Determination of the extreme chemical shifts (temperature-independent and solvent-independent) of: (a) Thy NH (D) in the free (δ_{free Thy}) and self-associated (δ_{dim Thy}) states by temperature-dependent ¹H NMR of Thy-PPO-2200-Thy in CDCl₃ and toluene-d₈, and (b) DAT NH₂ (Φ, Ψ) in the free (δ_{free DAT}) and self-associated (δ_{dim DAT}) states by temperature-dependent ¹H NMR of DAT-PPO-2200-DAT in CDCl₃ and toluene-d₈.

Knowing δ_{free Y} and δ_{dim Y} with Y = Thy or DAT, knowing δ_{exp Y}^{T,solvent} of a Y-PPO-2200-Y solution at a given temperature T and in a given solvent, and knowing the total concentration of Y groups (C_Y) in this solution, one could estimate K_{Y-Y}^{T,solvent} from equations (9), (10), (11) (three equations, three unknowns parameters {[Y], [Y=Y] and K_{Y,Y}}).

\[
\delta_{exp Y}(T) = \frac{[Y]}{C_Y} \delta_{free Y} + \frac{2[Y=Y]}{C_Y} \delta_{dim Y} \quad (9)
\]

\[
C_Y = [Y] + 2[Y=Y] \quad (10)
\]

\[
K_{Y-Y} = \frac{[Y=Y]}{[Y]^2} \quad (11)
\]

With this method, at 24°C, K_{Thy-Thy}^{24°C} was estimated at 7 M⁻¹ in CDCl₃ and 95 M⁻¹ in toluene-d₈ and K_{DAT-DAT}^{24°C} at 4 M⁻¹ in CDCl₃ and 17 M⁻¹ in toluene-d₈. Values were in the same ballpark but somewhat different than those determined by NMR titration where δ_{free Thy}, δ_{dim Thy}, δ_{free DAT}, δ_{dim DAT}, K_{Thy-Thy}, and K_{DAT-DAT} were adjustable parameters (see above).

Following the same method, extreme chemical shifts (temperature-independent and solvent-independent) of Thy NH (D) in the Thy-DAT associated (δ_{asso Thy}) state could be estimated by temperature-dependent ¹H NMR measurements on Thy-PPO-2200-DAT solutions in CDCl₃ and
toluene-d₈. Indeed, sigmoid fitting on the observed chemical shift for Thy NH (D) \( \delta_{\text{exp}}^{T, \text{solvent}} \) in those experiments yielded the value of 14.50 ppm for \( \delta_{\text{asso}}^{\text{Thy}} \) (Figure 10).

**Figure 10.** Determination of the chemical shifts of Thy NH (D) in the free (\( \delta_{\text{free}}^{\text{Thy}} \)) and associated with DAT (\( \delta_{\text{asso}}^{\text{Thy}} \)) states by temperature-dependent \(^1\text{H} \) NMR of Thy-PPO-2200-DAT 10a in CDCl₃ and toluene-d₈.

Using previously determined \( \delta_{\text{free}}^{\text{Thy}}, \delta_{\text{dim}}^{\text{Thy}}, \) and \( \delta_{\text{asso}}^{\text{Thy}}, K_{\text{Thy}}^{T, \text{solvent}} \) and \( K_{\text{DAT}}^{T, \text{solvent}} \) for a given temperature \( T \) and in a given solvent, knowing \( \delta_{\text{asso}}^{T, \text{solvent}} \) in a Thy-PPO-2200-DAT 10a solution, and knowing the total concentration of Thy and DAT groups in this solution (\( C_{\text{Thy}} = C_{\text{DAT}} \)), one could estimate, by iteration, \( K_{\text{Thy}}^{T, \text{solvent}}, K_{\text{DAT}}^{T, \text{solvent}} \) from equations (12) to (17) (six equations, six unknowns parameters \{[\text{Thy}], [\text{DAT}], [\text{Thy}=\text{Thy}], [\text{DAT}=\text{DAT}], [\text{Thy}=\text{DAT}] \) and \( K_{\text{Thy}}^{T, \text{solvent}} \}). At 24°C, we obtained \( K_{\text{Thy}}^{24\degree \text{C}, \text{chloroform}} = 835 \text{ M}^{-1} \) in CDCl₃, in accordance with our NMR titration and with the literature, and \( K_{\text{Thy}}^{24\degree \text{C}, \text{toluene}} = 22061 \text{ M}^{-1} \) in toluene-d₈, a very high value as expected.

\[
\delta_{\text{exp}}^{\text{Thy}}(T) = \left[ \frac{\text{Thy}}{C_{\text{Thy}}} \right] \delta_{\text{free}}^{\text{Thy}} + \left[ \frac{\text{Thy} = \text{Thy}}{C_{\text{Thy}}} \right] \delta_{\text{dim}}^{\text{Thy}} + \left[ \frac{\text{Thy} = \text{DAT}}{C_{\text{Thy}}} \right] \delta_{\text{asso}}^{\text{Thy}} \tag{12}
\]

\[
C_{\text{Thy}} = \left[ \text{Thy} \right] + 2\left[ \text{Thy} = \text{Thy} \right] + \left[ \text{Thy} = \text{DAT} \right] \tag{13}
\]

\[
C_{\text{DAT}} = \left[ \text{DAT} \right] + 2\left[ \text{DAT} = \text{DAT} \right] + \left[ \text{Thy} = \text{DAT} \right] \tag{14}
\]
\[
K_{\text{Thy-DAT}} = \frac{[\text{Thy} = \text{DAT}]}{[\text{Thy}][\text{DAT}]} \quad (15)
\]

\[
K_{\text{Thy-Thy}} = \frac{[\text{Thy} = \text{Thy}]}{[\text{Thy}]^2} \quad (16)
\]

\[
K_{\text{DAT-DAT}} = \frac{[\text{DAT} = \text{DAT}]}{[\text{DAT}]^2} \quad (17)
\]
III. Viscosity Models

(i) Viscosity model for linear supramolecular polymers

In the diluted regime, the specific viscosity of a monodisperse polymer solution can be expressed as a function of the polymer radius of gyration $R_g$, its weight concentration $C_g$, and its molecular weight $M$, according to the Zimm model (equation (18), with $N_a$ the Avogadro number and $\kappa$ a constant, equal to 6.93 according to the original Zimm prediction, or 6.1 from experiments on linear polymers in theta-conditions and more recent theories).²

\[
\eta_{sp} = \frac{\eta_0 - \eta_s}{\eta_s} = \kappa \frac{C_g N_a R_g^3}{M} \tag{18}
\]

Assuming that the supramolecular polymerization is under thermodynamic control with an isodesmic mechanism, then the average degree of polymerization (DP = $N$) can be expressed with equations (19) for a self-association (AA) and (20) for a complementary association (AB), $C$ being the concentration of supramolecular solution, and $K_{AA}$ and $K_{AB}$ the association constants.

\[
N = \frac{2[AA]}{[A]} + 1 = \frac{8CK_{AA}}{-1 + \sqrt{1 + 16CK_{AA}}} (\approx 2\sqrt{K_{AA}C}) \tag{19}
\]

\[
N = \frac{2[AB]}{[A] + [B]} + 1 = \frac{[AB]}{[A]} + 1 = \frac{\beta + 2C - \sqrt{(\beta + 2C)^2 - 4C^2}}{-\beta + \sqrt{(\beta + 2C)^2 - 4C^2}} + 1 \tag{20}
\]

with $\beta = \frac{1}{K_{AB}}$

The supramolecular polymer size distribution can be expressed with equations (22) for the numbered-average distribution and (24) for the weighted-average distribution, by analogy to step growth polymerization. $X_i$ is the number-fraction, $w_i$ the weight-fraction of supramolecular polymers constituted of $i$ chains, $p$ the extent of reaction (i.e. the fraction of stickers that have reacted), and $\gamma$ a normalization constant fixed by equation (23).³⁴ Indeed, although the associations constantly break and reform, the mean size $N$ and the size distribution remain constant at equilibrium.

\[
X_i = (1 - p)p^{i-1} \approx \frac{1}{\gamma} \exp\left(-\frac{i}{N}\right) \tag{22}
\]


The specific viscosity of a supramolecular polymer solution \( \eta_{sp} \) can then be considered to be a weighted sum on all sizes (i.e. an integral) of equation (28). This approach yields equation (25) which expresses \( \eta_{sp} \) as a function of the supramolecular polymer’s weight concentration \( C_g \) and mean size \( N \). Equation (25) also contains a constant \( \alpha \) characteristic of the supramolecular polymer unit [equation (26), with \( M_1 \) the unit’s molecular weight and \( R_1 \) the unit’s radius of gyration], and a function of \( N \). \( f(N) \) is actually an infinite integral that can be approximated to an integral to 10 000 [equation (27)], since there are virtually no supramolecular polymer made of more than 10 000 units given the order of magnitude of our association constants. Besides, \( \nu \) is equal to 0.5 for short chains or in \( \Theta \)-solvent.\(^5\)

\[
\eta_{sp} = \frac{\alpha C_g}{N \gamma} f(N) \tag{25}
\]

with \( \alpha = \kappa \frac{N_g R_1^3}{M_1} \) \tag{26}

with \( f(N) = \int_1^{10000} i^{3\nu} \exp\left(\frac{-i}{N}\right) \, di \) \tag{27}

The specific viscosity \( \eta_{sp} \) could then be calculated as follows. Knowing \( C \) and using the values of association constants previously estimated by \(^1\)H NMR measurements at room temperature (Table 1), \( N \) could be calculated from equation (19) or (20). Knowing \( N \), the integral \( f(N) \) could be numerically calculated with the mathematical software Maxima. \( \alpha \) was estimated from concentration-dependent viscosity measurements of NH\(_2\)-PPO-2200-NH\(_2\). Indeed, assuming there were no association in NH\(_2\)-PPO-2200-NH\(_2\), \( \alpha \) was the slope of the \( \eta_{sp} \) vs \( C_g \) linear curve (Figure 11, without association: \( \eta_{sp} = \alpha C_g \)).

<table>
<thead>
<tr>
<th>( K )</th>
<th>DMSO-d(_6)</th>
<th>CDCl(_3)</th>
<th>Toluene-d(_8)</th>
</tr>
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<tbody>
<tr>
<td>( K_{\text{Thy-Thy}} )</td>
<td>-</td>
<td>2.0 (^b)</td>
<td>26.5 (^c)</td>
</tr>
<tr>
<td>( K_{\text{DAT-DAT}} )</td>
<td>-</td>
<td>2.8 (^c)</td>
<td>42.5 (^f)</td>
</tr>
<tr>
<td>( K_{\text{Thy-DAT}} )</td>
<td>1.3 (^a)</td>
<td>~1000 (^d)</td>
<td>~22 000 (^g)</td>
</tr>
</tbody>
</table>

**Table 1.** Association constants (in L/mol), measured by \(^1\)H NMR: \(^a\) BuThy with MeDAT; \(^b\) Thy-PPO-460-Thy; \(^c\) DAT-PPO-460-DAT; \(^d\) DAT-PPO-460-DAT with Thy-PPO-460-Thy; \(^e\) Thy-PPO-2200-Thy; \(^f\) DAT-PPO-2200-DAT; \(^g\) Thy-PPO-2200-DAT.

Figure 11. Concentration-dependent specific viscosity of NH$_2$-PPO-2200-NH$_2$ 1a in toluene, allowing determination of $\alpha$ as the slope of the linear curve ($\alpha = 7.17$ cm$^3$/g).

Another way to modelize viscosity of supramolecular polymers without using the Zimm equation (18) has been illustrated by Bouteiller and his coworker. However, their method requires synthesis of a model covalent polymer to determine its viscosimetric parameters (Mark-Houwink and Huggins constants).

(ii) Viscosity for ring supramolecular polymers

Cyclic supramolecular polymers obey the same Zimm equation (18) as linear supramolecular ones. The difference is that, for the same molecular weight, a ring has a lower radius of gyration than a chain (see equations (28), (29), and (30), with $a$ the monomer size, $i$ the number of monomers, and $\nu$ equal to 0.5 for short chains or in $\Theta$-solvent).

\[
R_{g,\text{chain},i} = \frac{a(i)^{\nu}}{\sqrt{6}} \quad (28)
\]

\[
R_{g,\text{ring},i} = \frac{a(i)^{\nu}}{\sqrt{12}} \quad (29)
\]

\[
R_{g,\text{ring},i} = \frac{R_{g,\text{chain},i}}{\sqrt{2}} \quad (30)
\]

(iii) Ring-chain equilibrium

The weight fraction of rings $\rho_w$ can be estimated with the Jacobson-Stockmayer theory (equations (31), (32) and (33), with $x$ the fraction of reacted end-groups in the chain fraction, $\nu$ the

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number of chain atoms per monomer unit, and $b$ the effective link length of the polymer chain).

**Bookmark not defined.** The function $\phi(x,s)$ can be calculated numerically with the mathematical software Maxima, using expression (34) more suited for numerical calculation than equation (33). $x$ is assumed to be equal to what it would be without rings, *i.e.* it is just a function of the association constant and of the concentration.

$$\rho_w = \frac{B'}{C} \phi(x, \frac{3}{2}) \tag{31}$$

with $$B' = \frac{1}{N_A} \left( \frac{3}{2\pi\nu} \right)^{\frac{3}{2}} \frac{1}{2b^3} \tag{32}$$

and $$\phi(x, s) = \sum_{i=1}^{\infty} x^i s^i \tag{33}$$

$$\phi(x, s) = \Gamma(1-s)(-\log x)^{s-1} + \sum_{i=0}^{\infty} \zeta(s-i) \frac{(\log x)^i}{i!} \tag{34}$$

The weight fraction of rings $\rho_w$ was plotted against concentration of the supramolecular polymer in Figure 12. $\rho_w$ was very high, especially for low concentrations and high association constants.

![Figure 12. Weight fraction of rings as a function of concentration for an association constant of 1000 L/mol (◆) and 22 000 L/mol (■).](image)

(iii) Viscosity for ring-chain equilibrium

Taking into account the presence of rings, the specific viscosity becomes a weighted average following equation (35). The results of this second model, also mostly applying at low concentrations

---

(below 0.06 g cm\(^{-3}\)), are plotted in the article, assuming all rings are made of the two supramolecular units (by far the predominant form in 50/50-M-2200, see Table 2).

\[
\eta_{sp} = \rho_w \eta_{sp}^{\text{rings}} + (1 - \rho_w) \eta_{sp}^{\text{chains}}
\]

<table>
<thead>
<tr>
<th>C (g/cm(^3))</th>
<th>% of i = 2</th>
<th>% of i = 3</th>
<th>% of i = 4</th>
<th>% of i = 5</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>in chloroform</td>
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<tr>
<td>0.013</td>
<td>97.2</td>
<td>2.5</td>
<td>0.8</td>
<td>0.3</td>
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<tr>
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<td>94.9</td>
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<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>0.041</td>
<td>94.1</td>
<td>3.3</td>
<td>1.3</td>
<td>0.6</td>
</tr>
<tr>
<td>0.055</td>
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<td>3.5</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>0.075</td>
<td>93.1</td>
<td>3.7</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td>0.096</td>
<td>92.7</td>
<td>3.8</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>In toluene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.9</td>
<td>1.0</td>
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<tr>
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<td>90.4</td>
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<td>4.6</td>
<td>2.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 2. Distribution of ring sizes. Percentages are defined as the number of rings made of \(i\) supramolecular units divided by the total number of rings.