Supporting Information for

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

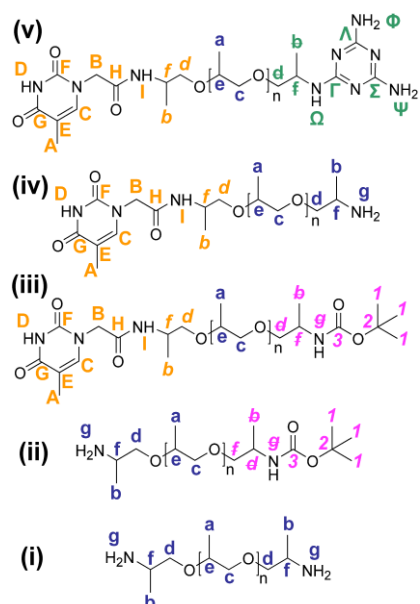Jessalyn Cortese, Corinne Soulié-Ziakovic* and Ludwik Leibler*

I. Synthesis of Thy-PPO-460-DAT

Chart 1. (i) NH$_2$-PPO-X-NH$_2$ **1a**, (ii) NH$_2$-PPO-X-BOC **2a**, (iii) Thy-PPO-X-BOC **3a**, (iv) Thy-PPO-X-NH$_2$ **4a**, and (v) Thy-PPO-X-DAT **5a** (X = 460).

Step 1. A solution of di-*tertio*-butyl dicarbonate (BOC$_2$O, 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) NH$_2$-PPO-X-NH$_2$ (**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 ^{1}H (CDCl$_3$ / TMS) δ/ppm = **0.97** (d, 3H, **b**) - **1.08** (m, 28H, **a**, **b**) - **1.38** (s, 14H, **1**) - **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 ^{13}C (CDCl$_3$ / TMS) δ/ppm = **17.1** (**a**) - **18.1** (**b**) - **19.8** (**b**) - **28.5** (**1**) - **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.). **RMN ^{1}H** (DMSO-d_6 /TMS) δ/ppm = **0.84** (m, 0.3H, **b**) - **1.04** (m, 30H, **a**, *b*, *b̶*) - **1.37** (s, 12H, *1*) - **1.75** (s, 3H, **A**) - **3.1 to 3.8** (m, **c**, *d*, *d̶*, **e**, *f*) - **3.84** (m, 1H, *f*) - **4.26** (s, 2H, **B**) - **6.54** (d, 1H, *g*) - **7.40** (s, 1H, **C**) - **7.99** (m, 1H, **I**) - **11.24** (s, 1H, **D**).

RMN ^{13}C (DMSO-d_6 /TMS) δ/ppm = **11.9** (**A**) - **17.0 to 18.5** (**a**, *b*, *b̶*) - **28.2** (*1*) - **44.8, 45.8** (*f*, *f̶*) - **49.2** (**B**) - **71 to 75, 77.4** (**c**, *d*, *d̶*, **e**, *2*) - **107.8** (**E**) - **142.5** (**C**) - **151.0** (**F**) - **155.0** (*3*) - **164.5** (**G**) - **166.2** (**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.).

RMN ^{1}H (DMSO-d_6 /TMS) δ/ppm = **0.89** (m, 4H, **b**) - **1.04** (m, 27H, **a**, *b*) - **1.68** (s, 3H, **A**) - **3.0 to 3.7** (m, **c**, **d**, *d*, **e**, **f**) - **3.80** (m, 1H, *f*) - **4.15** (s, 2H, **B**) - **6.99** (s, 1H, **C**) - **7.81** (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). NaHCO$_3$ (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.).

RMN ^{1}H (DMSO-d_6 /TMS) δ/ppm = **1.04** (m, 29H, **a**, *b̶*, *b*) - **1.75** (s, 3H, **A**) - **2.9 to 3.7** (m, **c**, *d̶*, *d*, **e**) - **3.84** (m, 1H, *f*) - **4.04** (m, 1H, *f̶*) - **4.26** (s, 2H, **B**) - **5.8 to 6.3** (m, 5H, **Φ**, **Ψ**, **Ω**) - **7.42** (s, 1H, **C**) - **7.98** (d, 1H, **I**).

RMN ^{13}C (DMSO-d_6 /TMS) δ/ppm = **11.9** (**A**) – **17 to 19** (**a**, *b̶*, *b*) - **44.8** (*f*, *f̶*, *f*) – **49.3** (**B**) – **71 to 75** (**c**, *d̶*, *d*, **e**) - **107.8** (**E**) – **142.6** (**C**) – **151.1** (**F**) – **164.6** (**G**) - **165.9** (**Γ**) - **166.1** (**H**) – **168.3** (**Λ**, **Σ**).

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-dihydroxbenzoic acid matrix in acetone. The spectra were recorded in positive mode on a PerSeptive Voyager RP-DE MALDI-TOF mass spectrometer.
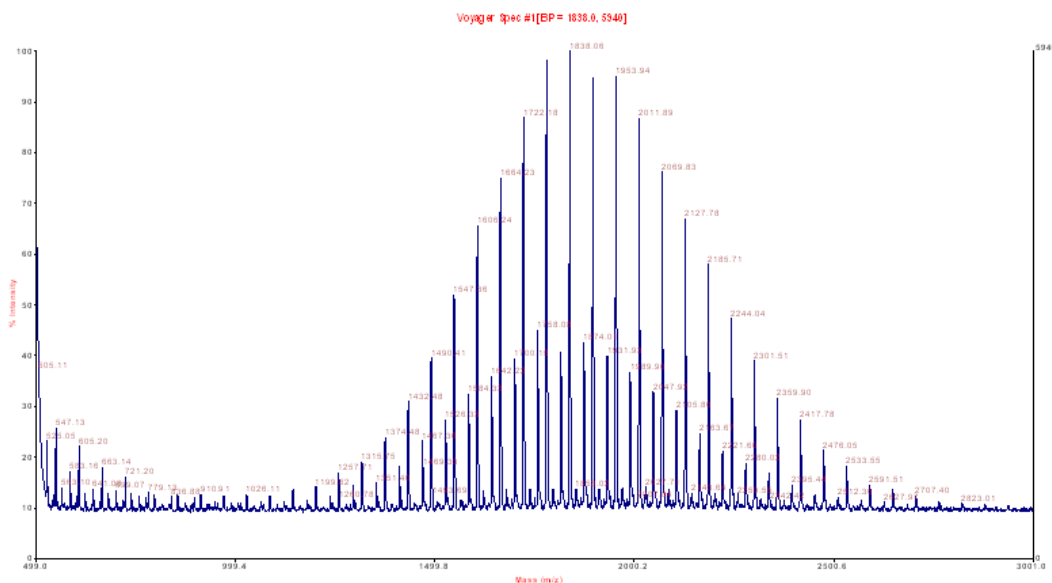

Figure 1. MALDI-TOF mass spectrum of NH_2-PPO-2200-NH_2 **1b**

Mn = 1925.51 ; **Mz** = 2039.91 ; **Mw** = 1982.06
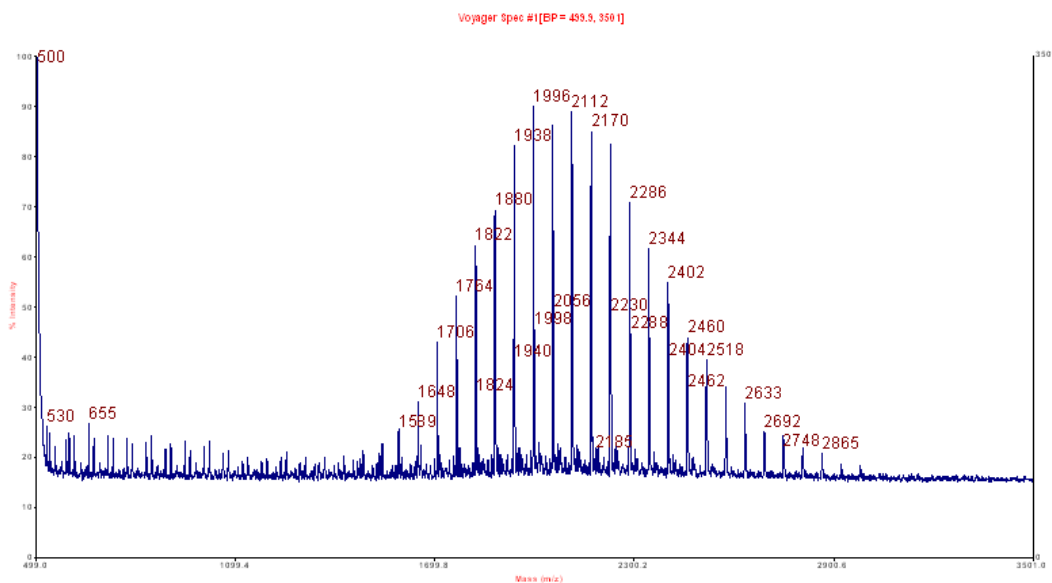
Polymer Dispersion Index = 1.03

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

Mn = 2156.51 ; **Mz** = 2333.60 ; **Mw** = 2247.28
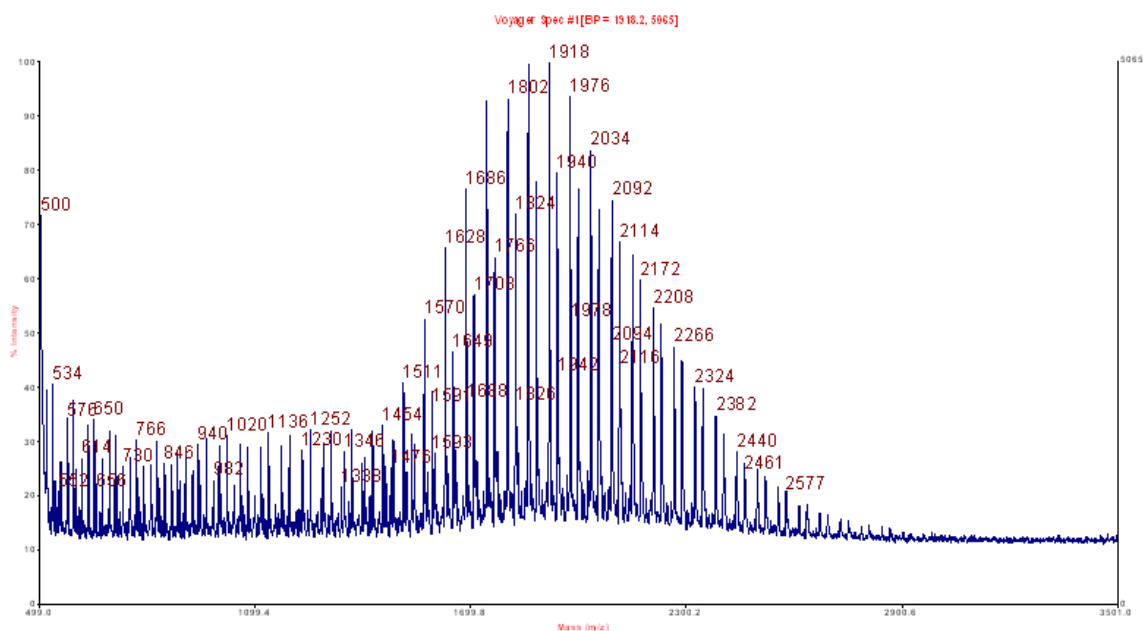
Polymer Dispersion Index = 1.04

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Figure 3. MALDI-TOF mass spectrum of DAT-PPO-2200-DAT **7b**

Mn = 1925.51 ; Mz = 2039.91 ; Mw = 1982.06
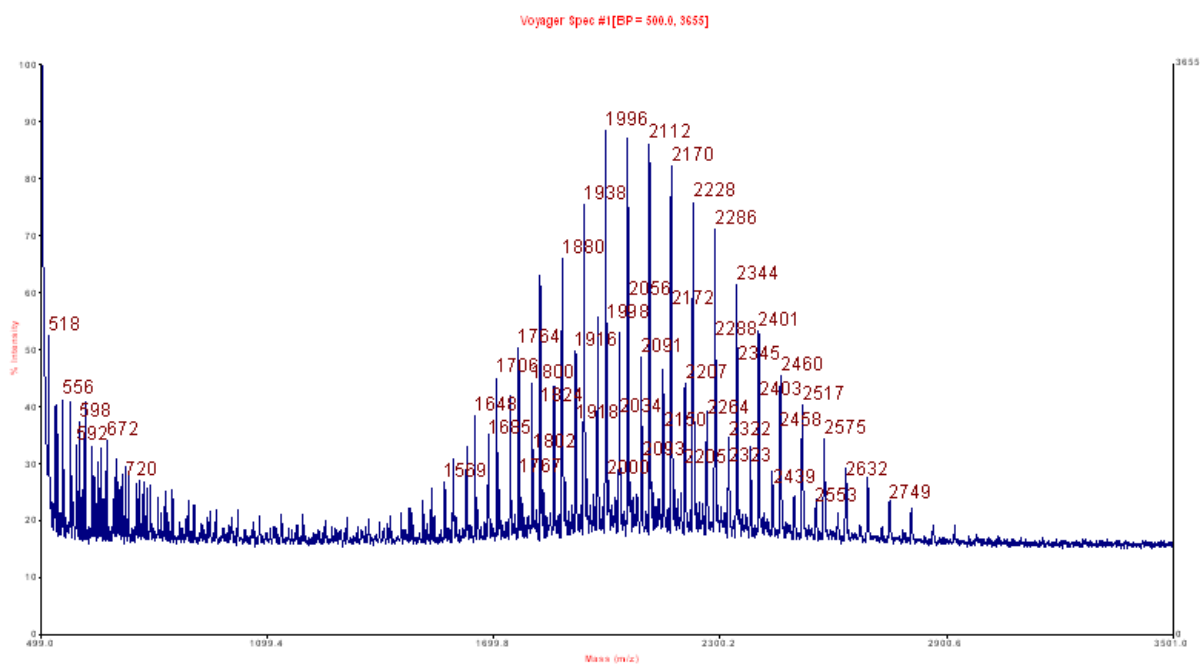
Polymer Dispersion Index = 1.03

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

Mn = 2121.64 ; Mz = 2284.45 ; Mw = 2204.92

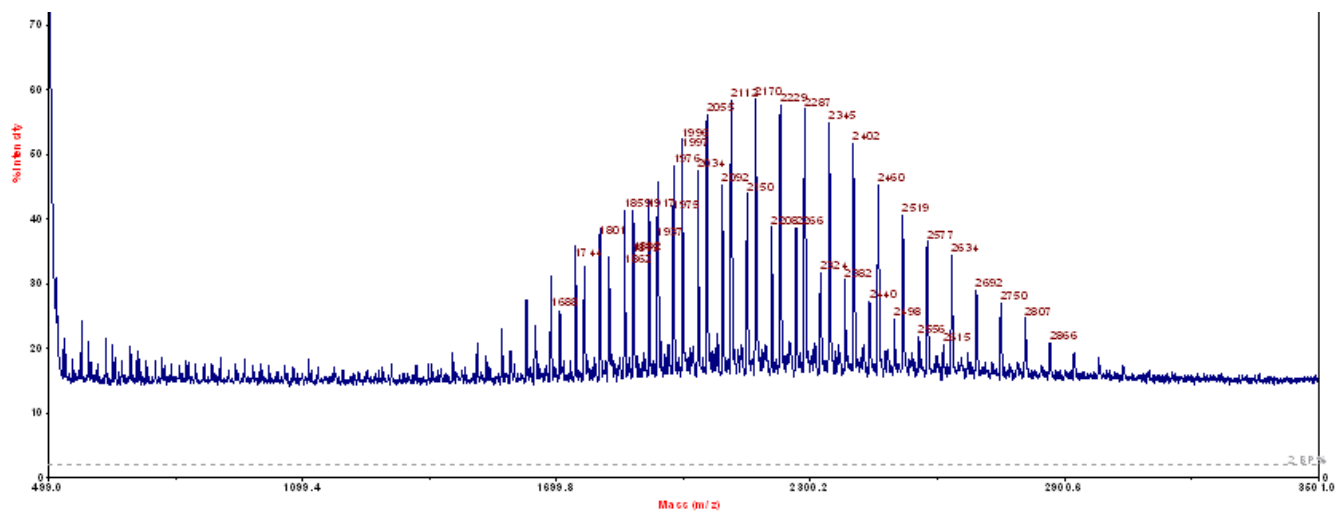**Polymer Dispersion Index** = 1.04

Figure 5. MALDI-TOF mass spectrum of Thy-PPO-2200-DAT **5b**

Mn = 2186.20 ; **Mz** = 2402.13 ; **Mw** = 2297.94

Polymer Dispersion Index = 1.05

III. Association constants determination

(i) by NMR titration

The association constants K_{AA} of an AA complex (A + A $\leftrightarrows$ AA) and K_{AB} of an AB complex (A + B $\leftrightarrows$ 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 δ_{AB}, self-associated δ_{AA}, and free states δ_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:

$$\delta = \delta_A \frac{[A]}{C_A} + 2\delta_{AA} \frac{[AA]}{C_A} \tag{1}$$

$$C_A = [A] + 2[AA] \tag{2}$$

$$K_{AA} = \frac{[AA]}{[A]^2} \tag{3}$$

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

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

$$\delta = \delta_A \frac{[A]}{C_A} + \delta_{AB} \frac{[AB]}{C_A} \tag{5}$$

$$C_A = [A] + [AB] \tag{6}$$

$$K_{AB} = \frac{[AB]}{[A][B]} \tag{7}$$

$$\delta^A = \delta_{AB} + (\delta_A - \delta_{AB}) \frac{C_A - 1/K_{AB} - C_B + \sqrt{(C_A + 1/K_{AB} + C_B)^2 - 4C_A C_B}}{2C_A} \tag{8}$$
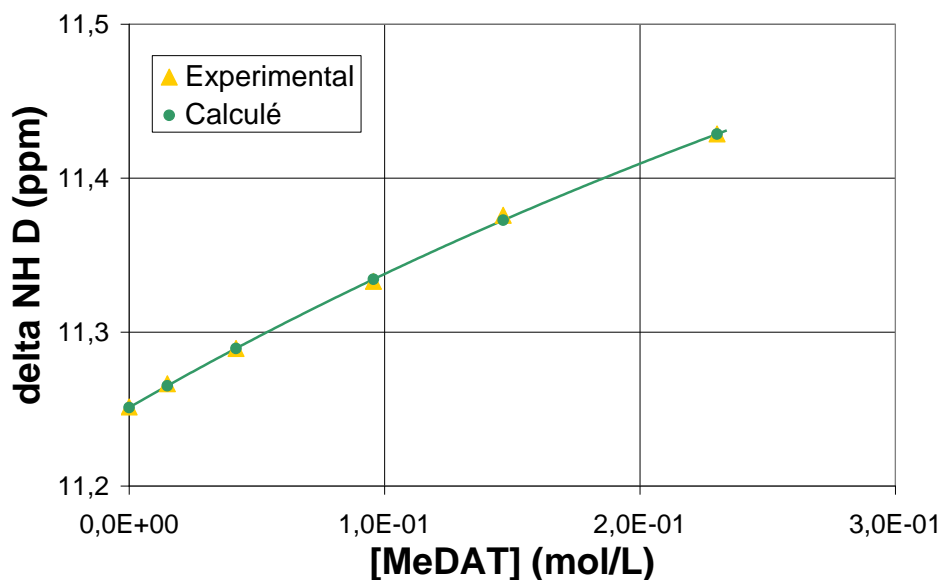
Figure 2. ^{1}H NMR titration in DMSO-d_6 at 25°C of Thy-C_4 ($9.0*10^{-2}$ mol/L) by MeDAT (from 0 to $2.3*10^{-1}$ mol/L) (**$K_{Thy-DAT}$ = 1.3 L/mol**, $\delta_{freeThy}$ = 11.25 ppm, $\delta_{bondedThy}$ = 12.10 ppm).
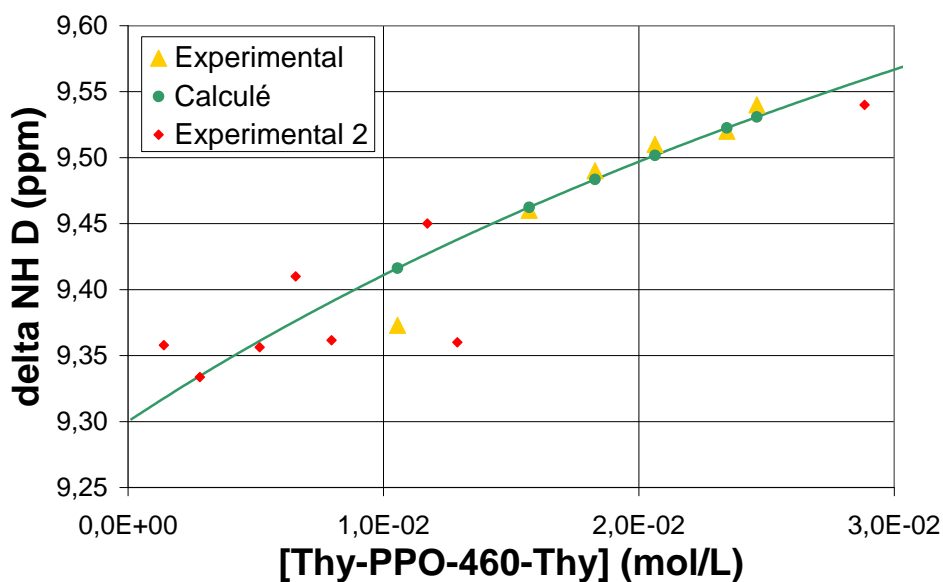

Figure 3. $K_{Thy-Thy}$ determination by NMR titration in CDCl$_3$ at 25°C of Thy-PPO-460-Thy **6a**

(**$K_{Thy-Thy}$ = 2.0 L/mol**, $\delta_{freeThy}$ = 9.3 ppm, $\delta_{dimerizedThy}$ = 10.9 ppm).

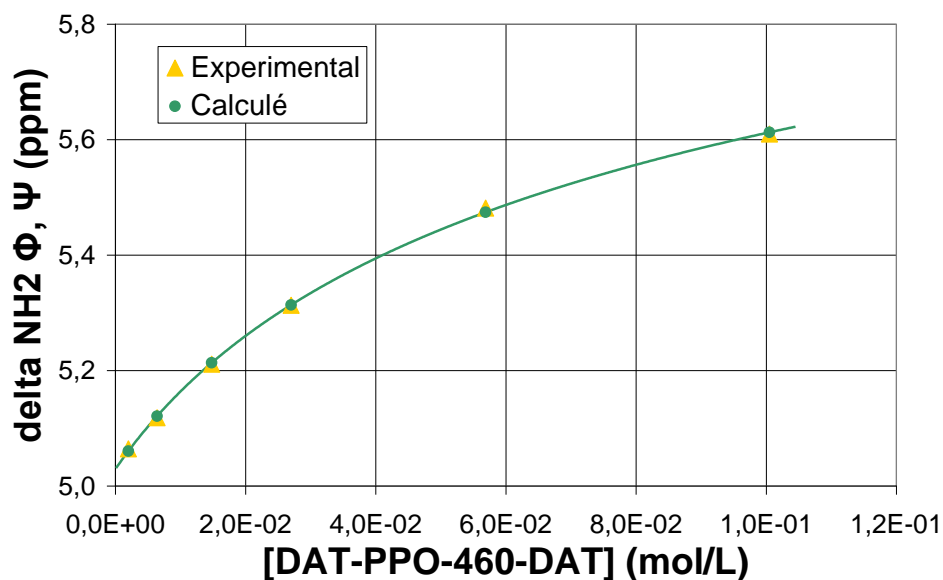**Figure 4**. $K_{\text{DAT-DAT}}$ determination by NMR titration in CDCl$_3$ at 25°C of DAT-PPO-460-DAT **7a**

($\boldsymbol{K_{\text{DAT-DAT}} = 2.8}$ **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** ($\boldsymbol{K_{\text{Thy-DAT}} = 846.5}$ **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).
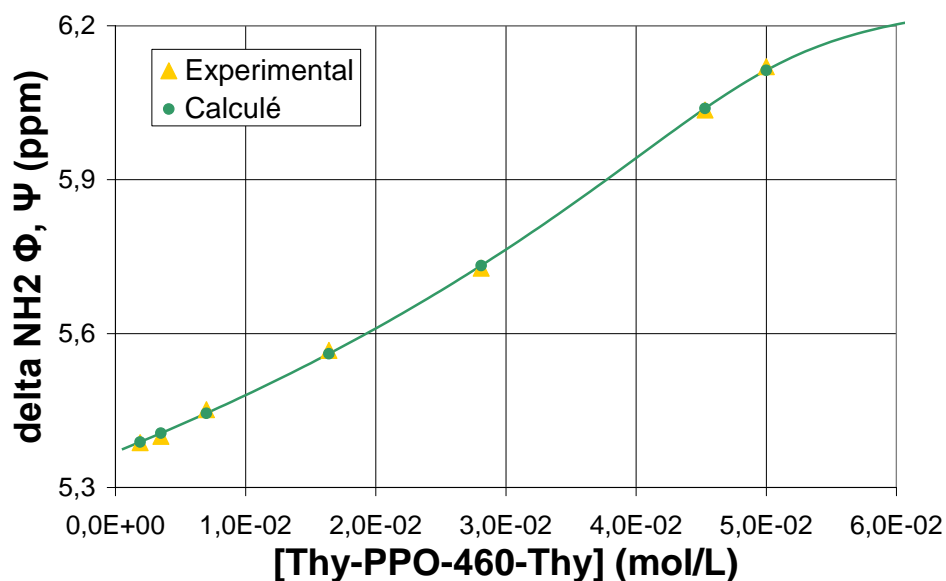
Figure 6. $K_{\text{Thy-DAT}}$ determination by NMR titration in CDCl$_3$ at 25°C of DAT-PPO-460-DAT **7a** by Thy-PPO-460-Thy **6a** ($K_{\text{Thy-DAT}}$ = **1255.7 L/mol**, $K_{\text{DAT-DAT}}$ = 3.2 L/mol, δ_{freeDAT} = 4.70 ppm, $\delta_{\text{dimerizedDAT}}$ = 6.88 ppm, $\delta_{\text{bondedDAT}}$ = 6.24 ppm).

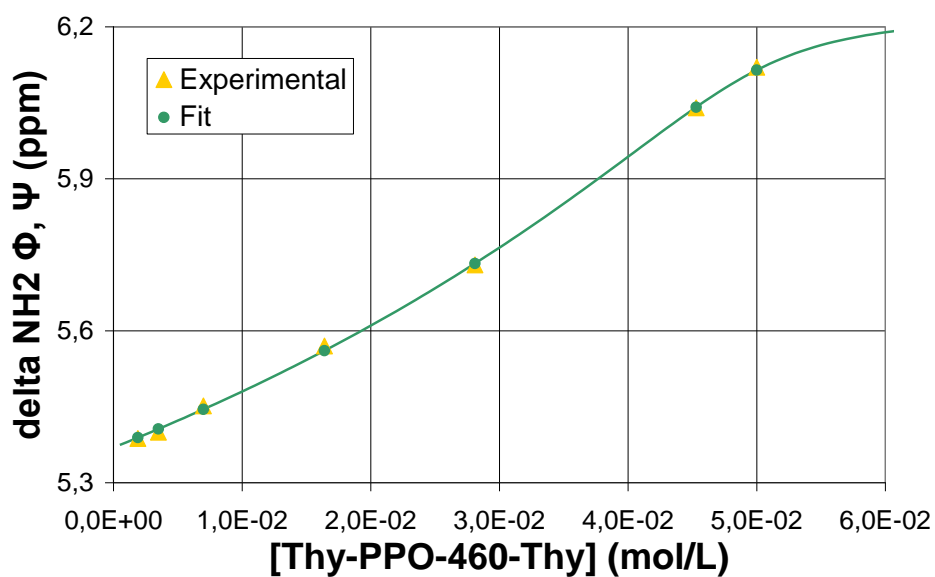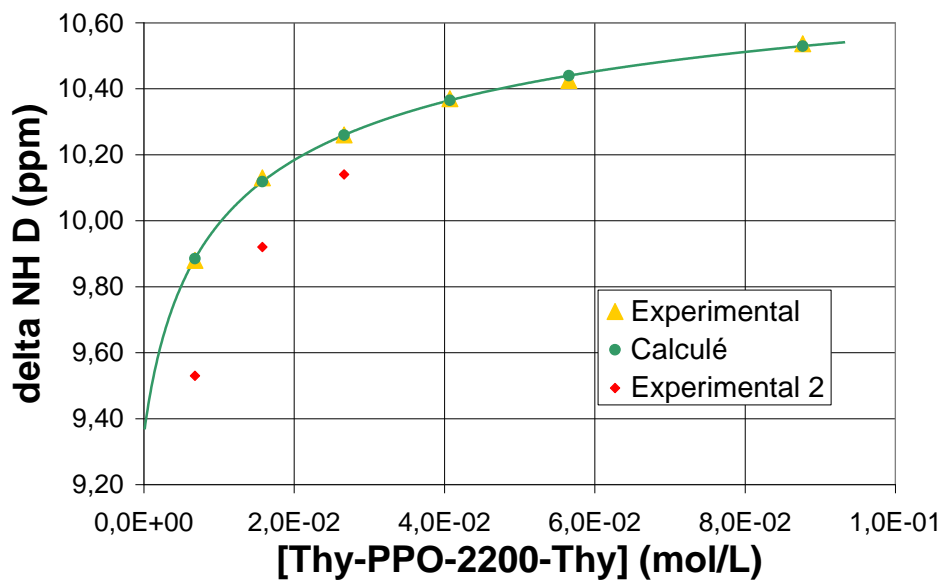**Figure 7**. $K_{\text{Thy-Thy}}$ determination by NMR titration in toluene-d$_8$ at 25°C of Thy-PPO-2200-Thy **6b** ($K_{\text{Thy-Thy}}$ = **26.5 L/mol**, δ_{freeThy} = 9.35 ppm, $\delta_{\text{dimerizedThy}}$ = 10.98 ppm).
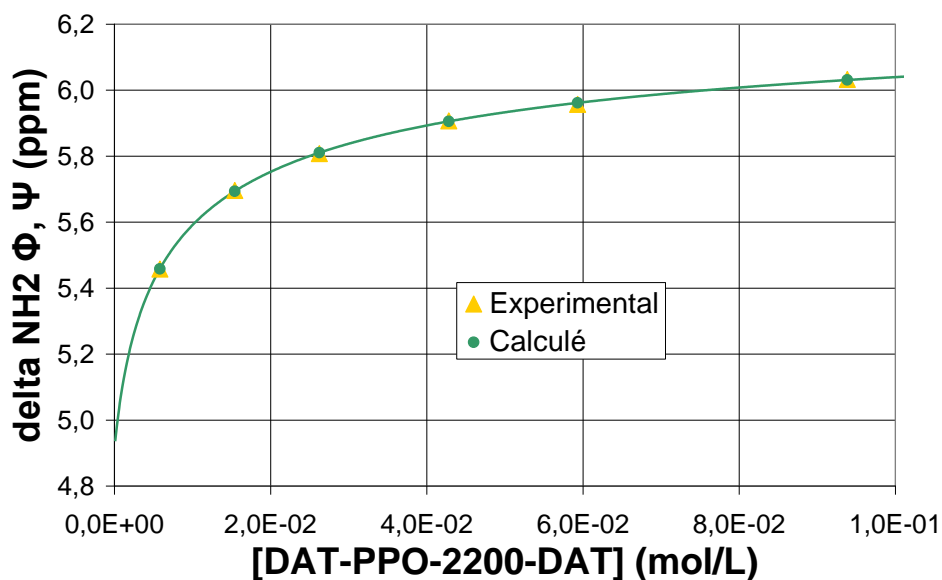
Figure 8. $K_{\text{DAT-DAT}}$ determination by NMR titration in toluene-d_8 at 25°C of DAT-PPO-2200-DAT **7b**

($K_{\text{DAT-DAT}}$ = **42.5 L/mol**, δ_{freeDAT} = 4.91 ppm, $\delta_{\text{dimerizedDAT}}$ = 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**) ($\delta_{\text{expThy}}^{\text{T,solvent}}$, **Figure 9**a) and DAT NH$_2$ (**Φ**, **Ψ**) ($\delta_{\text{expDAT}}^{\text{T,solvent}}$, **Figure 9**b) 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 $\delta_{\text{dim DAT}}$.

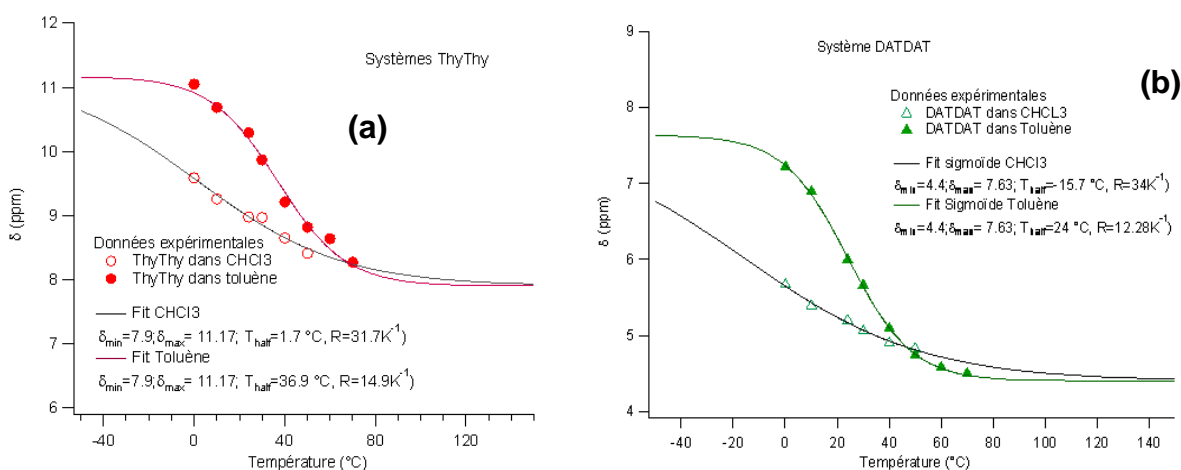[1] Salas, M.; Gordillo, B.; Gonzalez, F.; *ARKIVOC* **2003**, *11*, 72.

Figure 9. Determination of the extreme chemical shifts (temperature-independent and solvent-independent) of: (a) Thy NH (**D**) in the free ($\delta_{\text{free Thy}}$) and self-associated ($\delta_{\text{dim Thy}}$) states by temperature-dependent ^{1}H NMR of Thy-PPO-2200-Thy in CDCl$_3$ and toluene-d$_8$, and (b) DAT NH$_2$ (**Φ**, **Ψ**) in the free ($\delta_{\text{free DAT}}$) and self-associated ($\delta_{\text{dim DAT}}$) states by temperature-dependent ^{1}H NMR of DAT-PPO-2200-DAT in CDCl$_3$ and toluene-d$_8$.

Knowing $\delta_{\text{free Y}}$ and $\delta_{\text{dim Y}}$ with Y = Thy or DAT, knowing $\delta_{\text{exp Y}}^{\text{T,solvent}}$ 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 $K_{Y-Y}^{\text{T,solvent}}$ from equations (9), (10), (11) (three equations, three unknowns parameters {[Y], [Y=Y] and K_{Y-Y}}).

$$\delta_{\text{expY}}(\text{T}) = \frac{[\text{Y}]}{C_Y}\delta_{\text{freeY}} + \frac{2[\text{Y} = \text{Y}]}{C_Y}\delta_{\text{dimY}} \qquad (9)$$

$$C_Y = [\text{Y}] + 2[\text{Y} = \text{Y}] \qquad (10)$$

$$K_{Y-Y} = \frac{[\text{Y} = \text{Y}]}{[\text{Y}]^2} \qquad (11)$$

With this method, at 24°C, $K_{Thy-Thy}^{24°C}$ was estimated at 7 M^{-1} in CDCl$_3$ and 95 M^{-1} in toluene-d$_8$ and $K_{DAT-DAT}^{24°C}$ at 4 M^{-1} in CDCl$_3$ and 17 M^{-1} in toluene-d$_8$. Values were in the same ballpark but somewhat different than those determined by NMR titration where $\delta_{\text{free Thy}}$, $\delta_{\text{dim Thy}}$, $\delta_{\text{free DAT}}$, $\delta_{\text{dim DAT}}$, $K_{\text{Thy-Thy}}$, and $K_{\text{DAT-DAT}}$ 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 ($\delta_{\text{asso Thy}}$) state could be estimated by temperature-dependent ^{1}H NMR measurements on Thy-PPO-2200-DAT solutions in CDCl$_3$ and

toluene-d_8. Indeed, sigmoid fitting on the observed chemical shift for Thy NH (**D**) $\delta_{\exp Thy}^{T,solvent}$ in those experiments yielded the value of 14.50 ppm for $\delta_{asso\ Thy}$ (**Figure 10**).
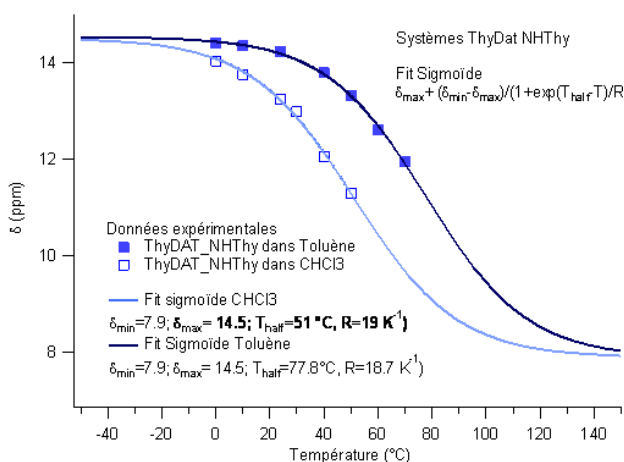

Figure 10. Determination of the chemical shifts of Thy NH (**D**) in the free ($\delta_{free\ Thy}$) and associated with DAT ($\delta_{asso\ Thy}$) states by temperature-dependent ^{1}H NMR of Thy-PPO-2200-DAT **10a** in CDCl$_3$ and toluene-d_8.

Using previously determined $\delta_{free\ Thy}$, $\delta_{dim\ Thy}$, and $\delta_{asso\ Thy}$, $K_{Thy-Thy}^{T,solvent}$ and $K_{DAT-DAT}^{T,solvent}$ for a given temperature T and in a given solvent, knowing $\delta_{\exp Thy}^{T,solvent}$ in a Thy-PPO-2200-DAT **10a** solution, and knowing the total concentration of Thy and DAT groups in this solution ($C_{Thy} = C_{DAT}$), one could estimate, by iteration, $K_{Thy-DAT}^{T,solvent}$ from equations (12) to (17) (six equations, six unknowns parameters {[Thy], [DAT], [Thy=Thy], [DAT=DAT], [Thy=DAT] and $K_{Thy-DAT}$}). At 24°C, we obtained $K_{Thy-DAT}^{24°C,chloroform} = 835$ M^{-1} in CDCl$_3$, in accordance with our NMR titration and with the literature, and $K_{Thy-DAT}^{24°C,toluene} = 22061$ M^{-1} in toluene-d_8, a very high value as expected.

$$\delta_{\exp\ Thy}(T) = \frac{[Thy]}{C_{Thy}}\delta_{free Thy} + \frac{2[Thy = Thy]}{C_{Thy}}\delta_{dim\ Thy} + \frac{[Thy = DAT]}{C_{Thy}}\delta_{asso Thy} \qquad (12)$$

$$C_{Thy} = [Thy] + 2[Thy = Thy] + [Thy = DAT] \qquad (13)$$

$$C_{DAT} = [DAT] + 2[DAT = DAT] + [Thy = DAT] \qquad (14)$$

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$$K_{Thy-DAT} = \frac{[Thy=DAT]}{[Thy][DAT]} \qquad (15)$$

$$K_{Thy-Thy} = \frac{[Thy=Thy]}{[Thy]^2} \qquad (16)$$

$$K_{DAT-DAT} = \frac{[DAT=DAT]}{[DAT]^2} \qquad (17)$$

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 κ 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.

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

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

$$\text{with } \beta = \frac{1}{K_{AB}} \tag{21}$$

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 γ a normalization constant fixed by equation (23).[3,4] Indeed, although the associations constantly break and reform, the mean size N and the size distribution remain constant at equilibrium.

$$X_i = (1-p)p^{i-1} \approx \frac{1}{\gamma} \exp(\frac{-i}{N}) \tag{22}$$

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[2] Graessley, W. W.; *Polymer liquids & networks: dynamics and rheology*; Taylor & Francis Group: New York, **2008**.

[3] Flory, P.J.; *Principles of polymer chemistry*; Cornell University Press: Ithaca, NY, **1953**.

[4] Knoben, W.; Besseling, N. A. M.; Stuart, M. A. C.; *J. Chem. Phys.* **2007**, *126*, 24907.

$$\text{with } \int_1^\infty X_i \approx \int_1^{10000} X_i = 1, \text{ so } \gamma = N(e^{-1/N} - e^{-10000/N}) \tag{23}$$

$$w_i = i(1-p)X_i = \frac{i}{N}X_i \tag{24}$$

The specific viscosity of a supramolecular polymer solution η_{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 η_{sp} as a function of the supramolecular polymer's weight concentration C_g and mean size N. Equation (25) also contains a constant α 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, υ is equal to 0.5 for short chains or in Θ-solvent.[5]

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

$$\text{with } \alpha = \kappa \frac{N_a R_1^3}{M_1} \tag{26}$$

$$\text{with } f(N) = \int_1^{10000} i^{3\upsilon} \exp(\frac{-i}{N}) di \tag{27}$$

The specific viscosity η_{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. α 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, α was the slope of the η_{sp} *vs* C_g linear curve (**Figure 11**, without association: $\eta_{sp} = \alpha C_g$).

	DMSO-d_6	CDCl$_3$	Toluene-d_8
$K_{Thy-Thy}$	-	2.0 [b]	26.5 [e]
$K_{DAT-DAT}$	-	2.8 [c]	42.5 [f]
$K_{Thy-DAT}$	1.3 [a]	~ 1000 [d]	~ 22 000 [g]

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.

[5] Rubinstein, M.; Colby, R.; *Polymer physics*; Oxford University Press: USA, **2003**.
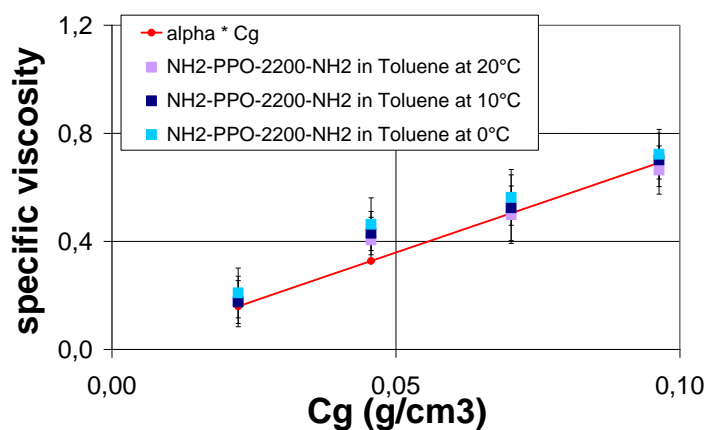
Figure 11. Concentration-dependent specific viscosity of NH_2-PPO-2200-NH_2 **1a** in toluene, allowing determination of α as the slope of the linear curve ($\alpha = 7.17$ cm^3/g).

Another way to modelize viscosity of supramolecular polymers without using the Zimm equation (18) has been illustrated by Bouteiller and his coworker.[6] 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 υ equal to 0.5 for short chains or in Θ-solvent).

$$R_{g,chain,i} = \frac{a(in)^{\nu}}{\sqrt{6}} \qquad (28)$$

$$R_{g,ring,i} = \frac{a(in)^{\nu}}{\sqrt{12}} \qquad (29)$$

$$R_{g,ring,i} = \frac{R_{g,chain,i}}{\sqrt{2}} \qquad (30)$$

(iii) Ring-chain equilibrium

The weight fraction of rings ρ_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, υ the

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[6] Abed, S.; Boileau, S.; Bouteiller, L.; *Polymer* **2001**, *42*, 8613.

number of chain atoms per monomer unit, and b the effective link length of the polymer chain).**Error! 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).[7] 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.

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

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

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

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

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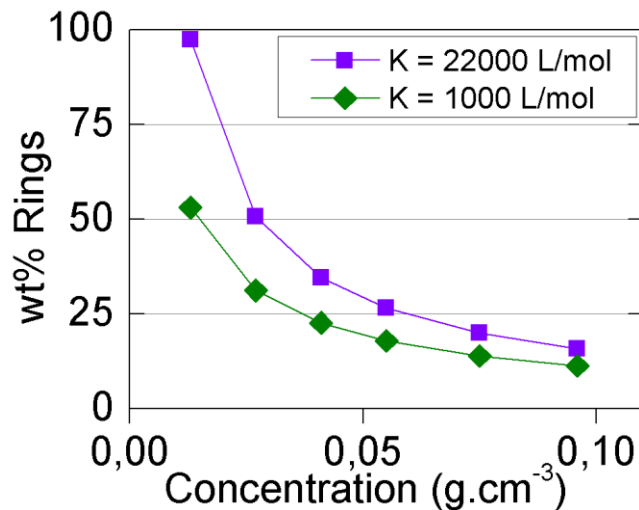

Figure 12. Weight fraction of rings as a function of concentration for an association constant of 1000 L/mol (◆) and 22 000 L/mol (■).

(iv) Viscosity for ring-chain equilibrium

Taking into account the presence of rings, the specific viscosity becomes a weighted average following equation (35).[8] The results of this second model, also mostly applying at low concentrations

[7] Truesdell, C.; *Ann. Math.* **1945**, *46*, 144.
[8] Jacobson, H.; Beckmann, C. O.; Stockmayer, W. H.; *J. Chem. Phys.* **1950**, *18*, 1607.

(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**).

$$\eta_{sp} = \rho_w \eta_{sp}^{rings} + (1 - \rho_w)\eta_{sp}^{chains} \qquad (35)$$

C (g/cm3)	% of i = 2	% of i = 3	% of i = 4	% of i = 5
in chloroform				
0.013	97.2	2.5	0.8	0.3
0.027	94.9	3.0	1.1	0.5
0.041	94.1	3.3	1.3	0.6
0.055	93.8	3.5	1.4	0.7
0.075	93.1	3.7	1.5	0.7
0.096	92.7	3.8	1.6	0.8
In toluene				
0.013	91.2	4.2	1.9	1.0
0.027	90.4	4.4	2.0	1.1
0.041	90.0	4.5	2.1	1.1
0.055	89.7	4.5	2.1	1.2
0.075	89.4	4.6	2.1	1.2
0.096	89.3	4.6	2.2	1.2

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.