Chain stopper assisted characterization of supramolecular polymers

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Supporting Information

Association model used for Figure 2. We consider the simplest model: the association is isodesmic and the chain stopper is bound with the same association constant:[1]

$$M_n + M_1 \underset{}{\overset{K}{\rightleftharpoons}} M_{n+1}$$

$$S + M_n \underset{}{\overset{K}{\rightleftharpoons}} SM_n$$

where M_1, M_n, S and SM_n represent the free monomer, the chain of length n, the free chain stopper and the terminated chain of length n, respectively. The following relationships can be deduced:

$$[M_n] = K^{n-1}[M_1]^n,\ n > 1 \qquad (1)$$

$$[SM_n] = K^n[S][M_1]^n,\ n \geq 1 \qquad (2)$$

The conservation of matter imposes:

$$C_0 = \sum_1^{\infty} n[M_n] + \sum_1^{\infty} n[SM_n] \qquad (3)$$

$$S_0 = [S] + \sum_1^{\infty} [SM_n] \qquad (4)$$

where C_0 and S_0 are the total monomer and chain stopper concentrations respectively. Combining eq 1 to 4 yields

$$[\mathrm{M}_1] = \frac{2\mathrm{C}_0 + \mathrm{S}_0 + \frac{1}{K} - \sqrt{\left(\mathrm{S}_0 + \frac{1}{K}\right)^2 + \frac{4\mathrm{C}_0}{K}}}{2\mathrm{K}(\mathrm{C}_0 + \mathrm{S}_0)} \tag{5}$$

Finally, the number average degree of polymerization is

$$\mathrm{DP}_n = \frac{\mathrm{S}_0 + \mathrm{C}_0}{\mathrm{S}_0 + \sum_1^{\infty}[\mathrm{M}_n]} = \frac{\mathrm{S}_0 + \mathrm{C}_0}{\mathrm{S}_0 + \frac{[\mathrm{M}_1]}{1 - \mathrm{K}[\mathrm{M}_1]}} \tag{6}$$

Viscosimetric data.

Table SI1. Intrinsic viscosity for mixtures of **EHUT** and **DBUT** in CCl_4, in dL g^{-1}.

EHUT/DBUT	[η]
90/10	0.91
95/5	1.38
97/3	1.66

Dynamic light scattering data.

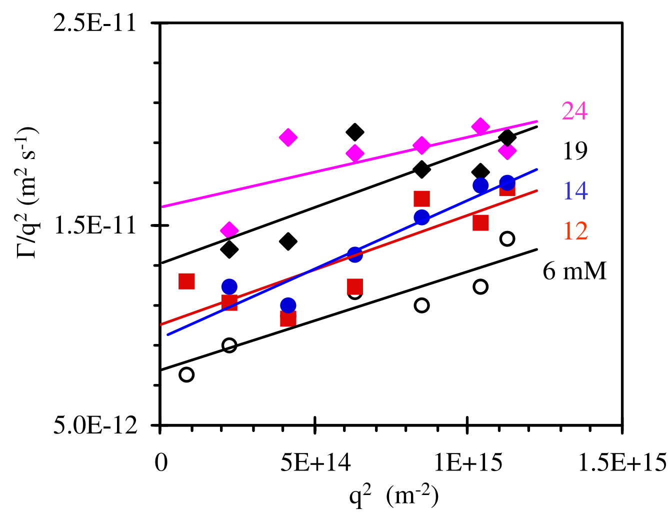

Figure SI1. Angle dependence of the relaxation rate (Γ=1/τ) for 99.5/0.5 **EHUT/DBUT** mixtures, in CCl_4.

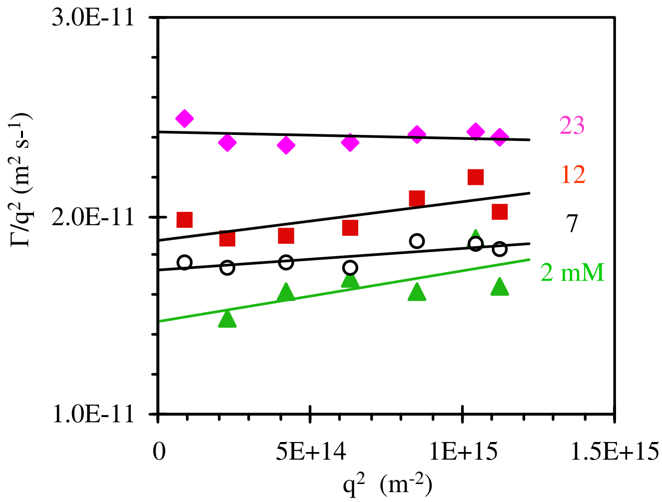

Figure SI2. Angle dependence of the relaxation rate (Γ=1/τ) for 97/3 **EHUT/DBUT** mixtures, in CCl_4.

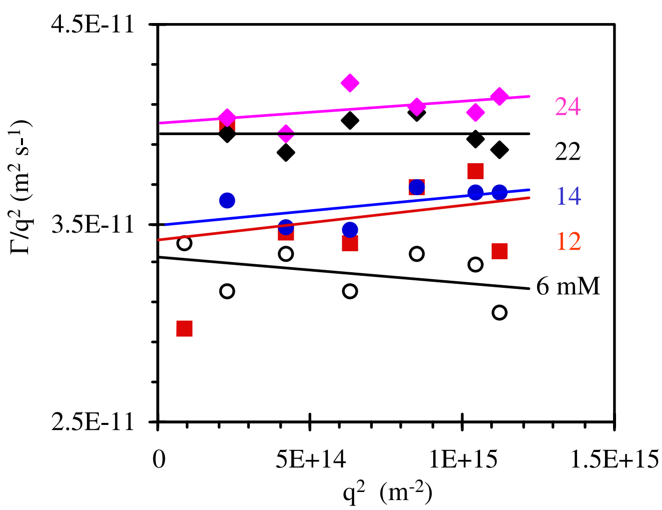

Figure SI3. Angle dependence of the relaxation rate (Γ=1/τ) for 90/10 **EHUT/DBUT** mixtures, in CCl_4.

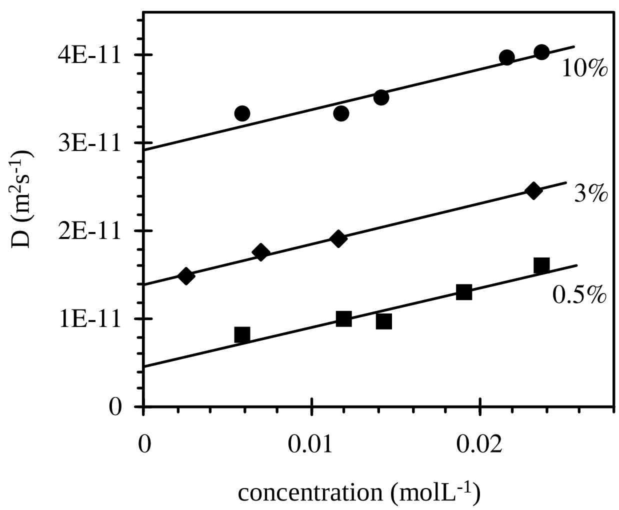

Figure SI4. Diffusion coefficient of 90/10, 97/3 and 99.5/0.5 **EHUT/DBUT** mixtures, versus overall concentration in CCl_4.

Static light scattering data.

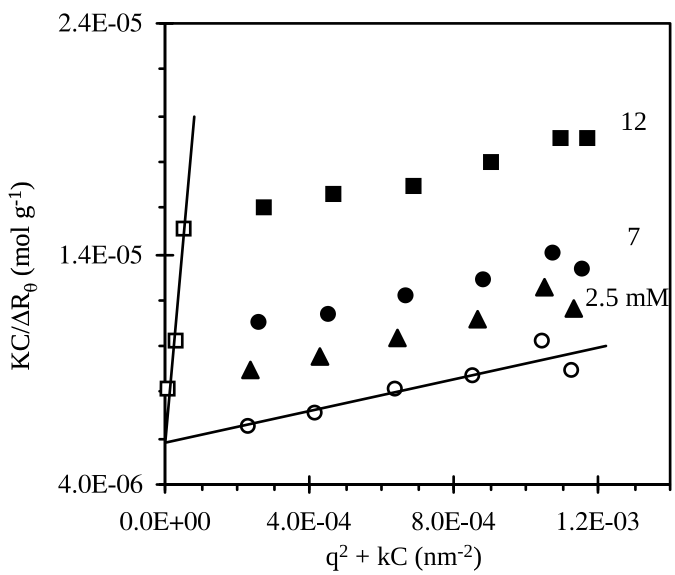

Figure SI5. Static light scattering data (Zimm plot) for 97/3 **EHUT/DBUT** mixtures, in CCl_4 ($k = 0.01$ cm^3 g^{-1} nm^{-2}).

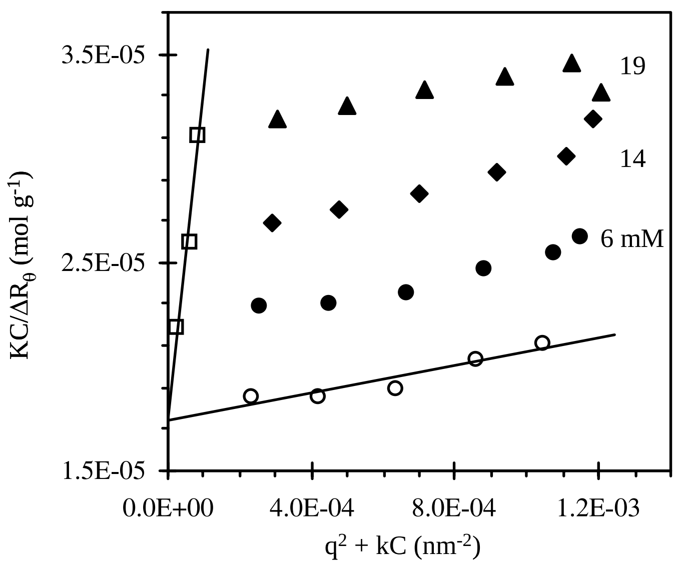

Figure SI6. Static light scattering data (Zimm plot) for 90/10 **EHUT/DBUT** mixtures, in CCl_4 (k = 0.01 cm^3 g^{-1} nm^{-2}).

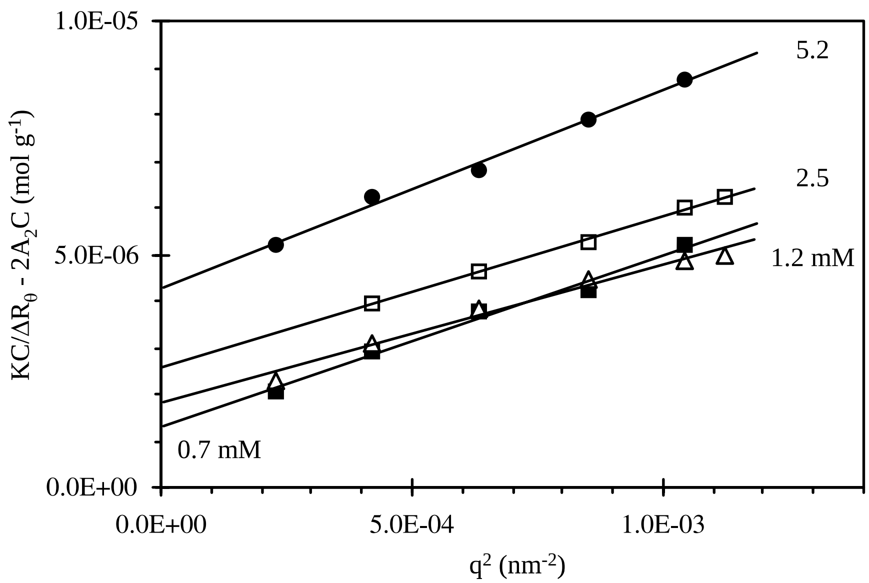

Figure SI7. Angle dependence of the Rayleigh ratio (ΔR_θ) for stopper-free **EHUT** solutions, in CCl_4.

Isothermal titration calorimetry (ITC). The solutions of **EHUT** in carbon tetrachloride were prepared at room temperature, under stirring for at least one day. The solvent was used as received. Heats of dissociation were measured using a MicroCal VP-ITC titration microcalorimeter. The sample cell (1.435 cm^3) was filled with pure solvent. A relatively concentrated **EHUT** solution in the same solvent was placed in a 0.295 cm^3 continuously stirred (310rpm) syringe. A first 2μL aliquot was injected, without taking into account the observed heat, to remove the effect of solute diffusion across the syringe tip during the equilibration period. Subsequent aliquots of the solution (2 to 10μL) were automatically injected into the sample cell every 200s, until the syringe was empty.

Figure SI8 shows the heat flow curve obtained when a 0.15mM **EHUT** solution in CCl_4 is incrementally injected into pure CCl_4 at 40°C. The process is endothermic, in agreement with the fact that hydrogen bonds are dissociated during the dilution. The signal is noisy due to the low concentration (which is imposed by the strong association), but integration of the heat flow peaks is possible and yields the enthalpograms presented in Figure SI9 (4 experiments were performed with a different **EHUT** concentration in the syringe). The 4 curves were simultaneously fitted with the cooperative model described in reference 2, with K_2, K, ΔH and Q_{dil1} to Q_{dil4} as adjustable constants. The quality of the fit over this large concentration range is satisfactory. The values of the constants obtained are listed in Table SI2. The same measurements could be performed in the temperature range between 30 and 60°C (Table SI2), but the data at 25°C were of poor quality, because the association is too strong. Consequently, the values of association constants were determined by extrapolation (Figure SI10 and Table SI2). These values were then used to calculate the weight average molar mass (Figure 8) and the polydispersity (Figure SI11), versus concentration in CCl_4.[3]

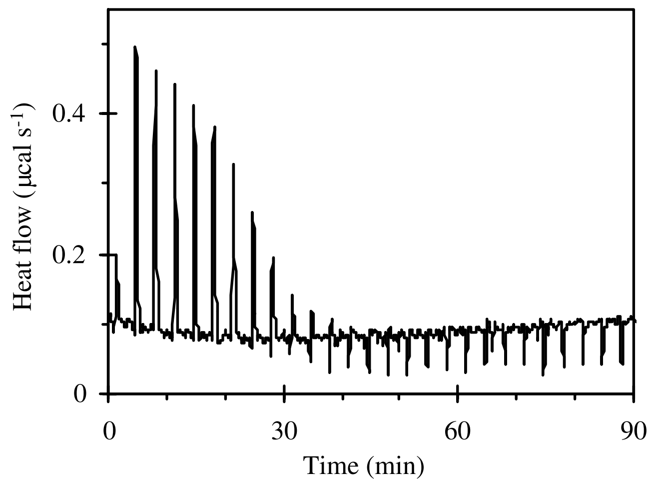

Figure SI8. Heat effect produced by injecting 5μL aliquots of a 0.15mM **EHUT** solution in CCl_4 into CCl_4 (T=40°C).

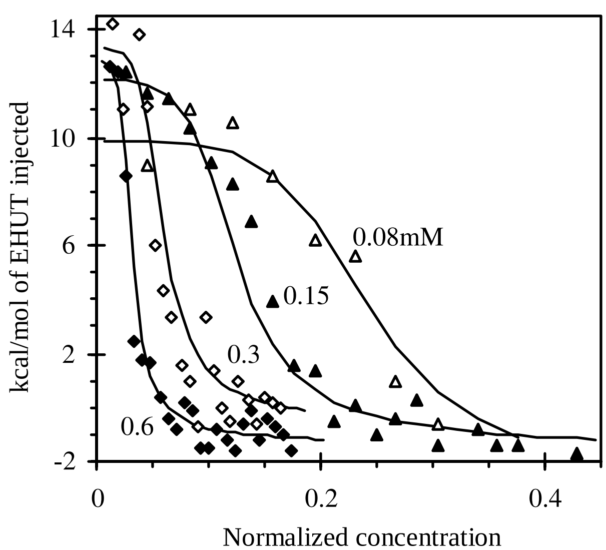

Figure SI9. Enthalpograms of 0.6mM, 0.3mM, 0.15mM, and 0.08mM **EHUT** solutions in CCl_4 versus concentration normalized by the final cell concentration (T=40°C). The plain curves are fits obtained with a cooperative model[2] and parameter values reported in Table SI2.

Table SI2. Thermodynamic parameters determined by ITC, for solutions of **EHUT** in CCl_4.

T [a]	K_2 [b]	K [c]	K/K_2 [d]	K^2/K_2 [e]	ΔH [f]	C_0^s [g]
25	*9.2 10^3* [h]	*780 10^3* [h]	*85* [h]	*6.6 10^7* [h]	–	–
30	5.9 10^3	550 10^3	93	5.1 10^7	-61	0.3/0.15/0.1/0.06
40	3.9 10^3	257 10^3	66	1.7 10^7	-61	0.6/0.3/0.15/0.08
50	3.7 10^3	148 10^3	40	5.9 10^6	-60	1.3/0.6/0.3/0.15
60	1.0 10^3	74 10^3	74	5.5 10^6	-64	2.5/1.2/0.7/0.3

[a] Temperature, in °C.

[b] Dimerization constant, in $Lmol^{-1}$. Uncertainty ±40%.

[c] Oligomerization constant, in $Lmol^{-1}$. Uncertainty ±20%.

[d] Measure of the cooperativity along the supramolecular chain.

[e] Association constant between long oligomers, in $Lmol^{-1}$.

[f] Enthalpy of oligomerization, in kJ mol^{-1}. Uncertainty ±10%.

[g] Concentrations used, in 10^{-3} $molL^{-1}$.

[h] By extrapolation.

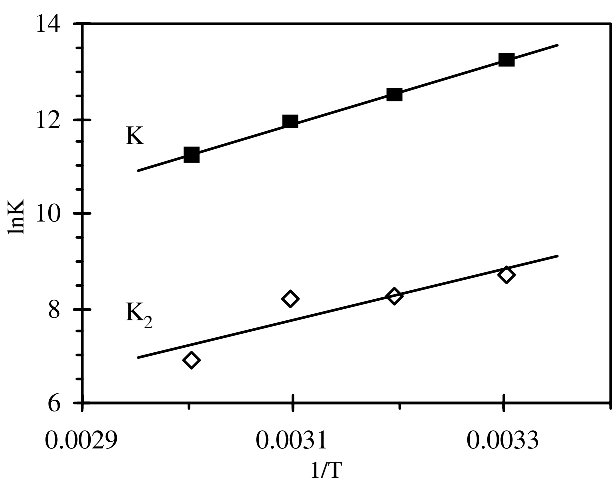

Figure SI10. van't Hoff plot for **EHUT** in CCl_4.

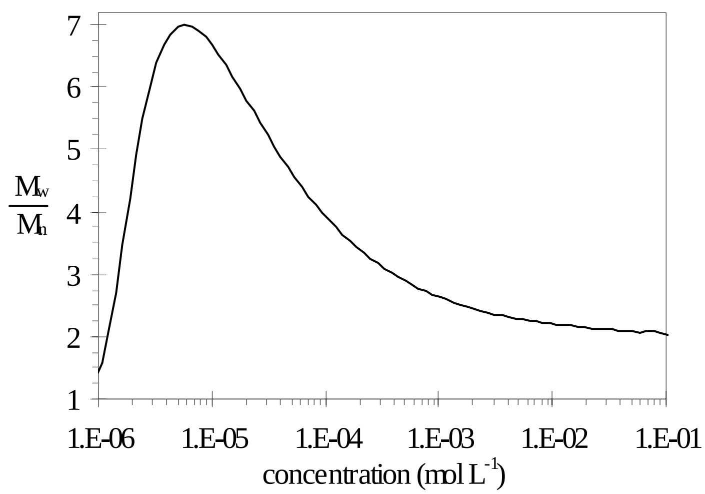

Figure SI11. Determination by calorimetry of the polydispersity for **EHUT**, versus concentration in CCl_4, at 25°C.

References

(1) A non-isodesmic behavior yields the same qualitative results.

(2) Arnaud, A.; Bouteiller, L. *Langmuir* **2004**, *20*, 6858-6863.

(3) Simic, V.; Bouteiller, L.; Jalabert, M. *J. Am. Chem. Soc.* **2003**, *125*, 13148-13154.