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Highly Cooperative Formation of Bis-Urea Based Supramolecular Polymers

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Abstract: Eleven bis-ureas have been synthesized, and some of their properties are reported. Several of these compounds form supramolecular polymers in organic solvents. The self-association is shown by FTIR spectroscopy to display cooperativity at two levels. The first level of cooperativity is due to the synergistic association of the two urea functions of a single molecule. The second level of cooperativity is revealed by the fact that the formation of dimers is less favored than that of long oligomers.

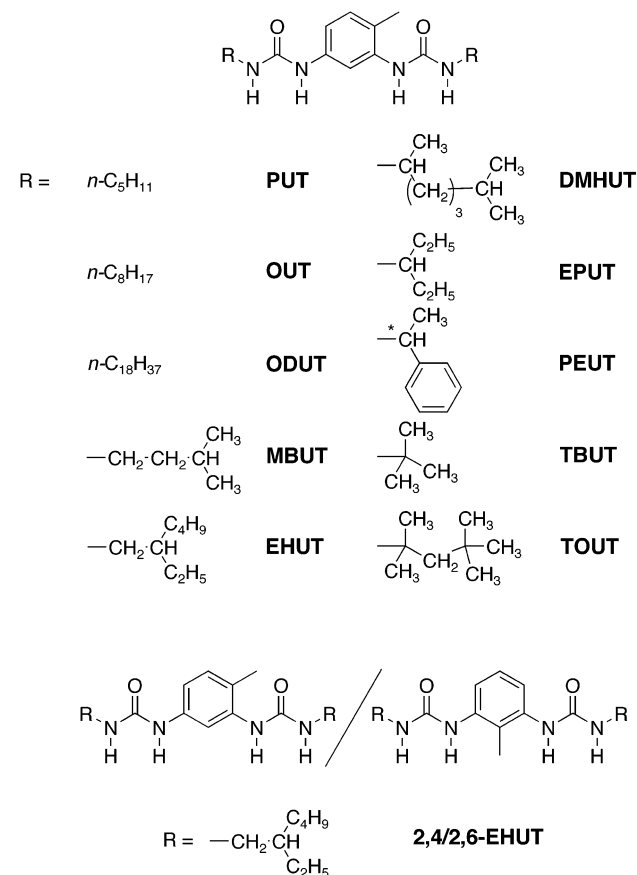
Introduction

Supramolecular polymers are chains of small molecules held together through reversible noncovalent interactions.^{1–3} This reversibility is responsible for the appearance of new properties, as compared to those of usual covalent polymers. For instance, the molar mass dependence of supramolecular polymers on concentration, solvent polarity and temperature leads to unusual rheological properties, which are potentially useful for a wide range of applications.

We have recently described a new supramolecular polymer (**EHUT**, see Chart 1), based on the bis-urea moiety.⁴ **EHUT** has been shown to form highly viscoelastic solutions in toluene, due to self-association through hydrogen bonding, leading to the formation of very long cylindrical wires.^{4b}

Interestingly, the properties of **EHUT** are quite different from similar bis-ureas described in the literature.^{5–9} Indeed, 1,2-

Chart 1. Structures of Bis-Ureas Studied



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cyclohexyl^{5,6c,f,g,8,9} or phenylene^{6c,7b} based bis-ureas are very efficient organogelators,¹⁰ meaning that after dissolution at high temperature, a gel is formed at room temperature due to solvent entrapment in a network of crystalline fibers. The main

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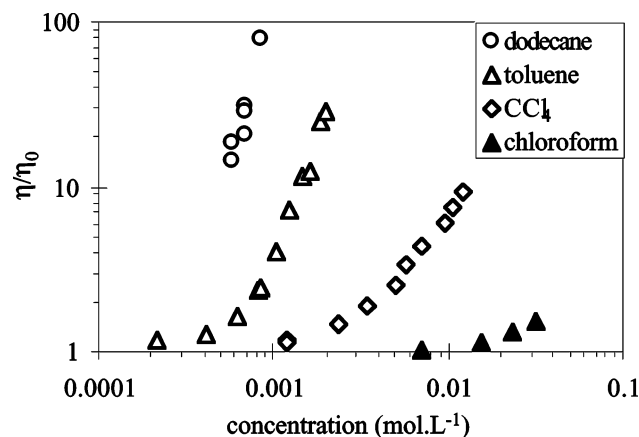


Figure 1. Relative viscosity of **EHUT** solutions in different solvents, at 25 °C.

differences between these kinds of compounds are first the fact that, unlike organogelators, **EHUT** dissolves at room temperature, without any activation, in solvents where it forms a viscoelastic solution. Therefore, these solutions are thermodynamically stable. As a consequence, the length of the wires formed by **EHUT** can be altered by a slight change in experimental conditions, which is not the case for organogels below their melting point (once the gel is formed). Second, the cross-section of **EHUT** wires has been shown to be 2.6 nm in diameter, which corresponds to the largest dimension of the molecule, whereas the cross-sections of the fibers reported for organogelators are at least an order of magnitude larger. Consequently, the organogels display a much stronger elastic modulus than the viscoelastic solutions of **EHUT**.

Considering the singular properties of **EHUT** compared to bis-urea organogelators, we investigated the influence of small structural variations to see if other supramolecular polymers could be obtained (see the second part of this paper). Characterization was performed by capillary viscometry to qualitatively reveal the high molar mass of the assemblies and by FTIR spectroscopy, because it is ideally suited to measure the degree of association of substituted ureas.¹¹ The FTIR characterization of **EHUT** is described in the first part of this work.

Results and Discussion

1. Characterization of EHUT. Figure 1 qualitatively shows the influence of solvent on the formation of high molar mass supramolecular assemblies. The lower the polarity and the hydrogen bonding ability of the solvent, the higher the viscosity of the solutions of **EHUT** became, due to stronger self-association by hydrogen bonding.

It would be desirable to perform the spectroscopic characterization of the association in the solvents where the association is the strongest. Unfortunately, FTIR spectra of solutions of **EHUT** in dodecane, toluene, or carbon tetrachloride show only a hydrogen bonded N–H peak, down to the lowest concentration accessible. The intensity of the free N–H vibration is too small to be detected, so that the quantitative characterization of any equilibrium is impossible by FTIR.¹² Chloroform, however, presents a good compromise because the association of **EHUT** is here sufficiently disfavored to allow quantitative measure-

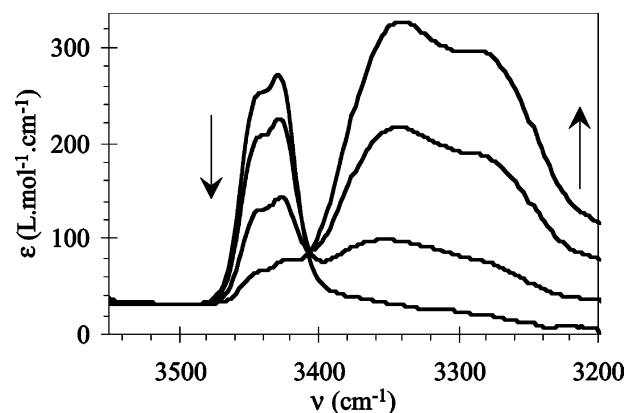


Figure 2. Normalized FTIR spectra of solutions of **EHUT** in CDCl_3 , versus concentration (4.0×10^{-4} , 8.9×10^{-4} , 1.8×10^{-3} , and $8.9 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$). Arrows indicate the direction of change with increasing concentration.

ments, but still significant to be informative. CDCl_3 was used instead of CHCl_3 , to minimize the solvent absorption in the N–H stretching vibration region. Figure 2 shows FTIR spectra of solutions of **EHUT** at several concentrations in CDCl_3 . Four bands can be distinguished: the two bands at 3444 and 3429 cm^{-1} can be attributed to free N–H groups, and the two bands at 3340 and 3280 cm^{-1} to hydrogen bonded N–H groups.¹¹ This assignment is in agreement with an increase of molar mass of the assemblies with concentration (Figure 1), because the relative magnitude of the free N–H vibration decreases with increasing concentration. Before analyzing these curves more quantitatively, it is desirable to assign more precisely each vibration. Figure 3 compares the spectrum of **EHUT** to those of model mono-ureas (Chart 2).

Symmetrical mono-ureas **EHU** and **BPU** were chosen as aliphatic and aromatic references, respectively, and **2T/EHU** and **4T/EHU** were selected to assess the influence of the position of the methyl group. All of the solutions considered in Figure 3 are sufficiently diluted, so that only the free N–H vibrations are present. Comparison of the spectra of this figure affords the following assignment for **EHUT**: the band at 3444 cm^{-1} corresponds to the free aliphatic N–H group and the band at 3429 cm^{-1} corresponds to the free aromatic N–H group. No significant influence of the position of the methyl group on the aromatic bridging group is detected. A precise assignment of the hydrogen bonded N–H vibrations is potentially more complicated, because the shift of the N–H vibration due to self-association depends not only on the molecular structure, but also on the strength of the association and thus on the supramolecular structure, which is not the same for mono-ureas and **EHUT**. Proton/deuterium (H/D) exchange kinetics is a powerful technique used to derive information on hydrogen bonded systems.¹³ At time $t = 0$, D_2O was added to a **EHUT** solution in chloroform, and the decrease of the N–H bands was monitored. Figure 4a shows that the intensity of the 3280 cm^{-1} vibration band decreases faster than the intensity of the 3340 cm^{-1} vibration band. Moreover, Figure 4b shows that, for a **4T/EHU** mono-urea solution, the free aromatic N–H band (3431 cm^{-1}) decreases faster than the free aliphatic N–H band (3446 cm^{-1}).

The present behavior of the mono-urea means that the stronger acidity of the aromatic N–H group leads to an increase

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(12) ^1H NMR spectroscopy has not been used, because the N–H resonances of **EHUT** (in these solvents) are extremely broad.

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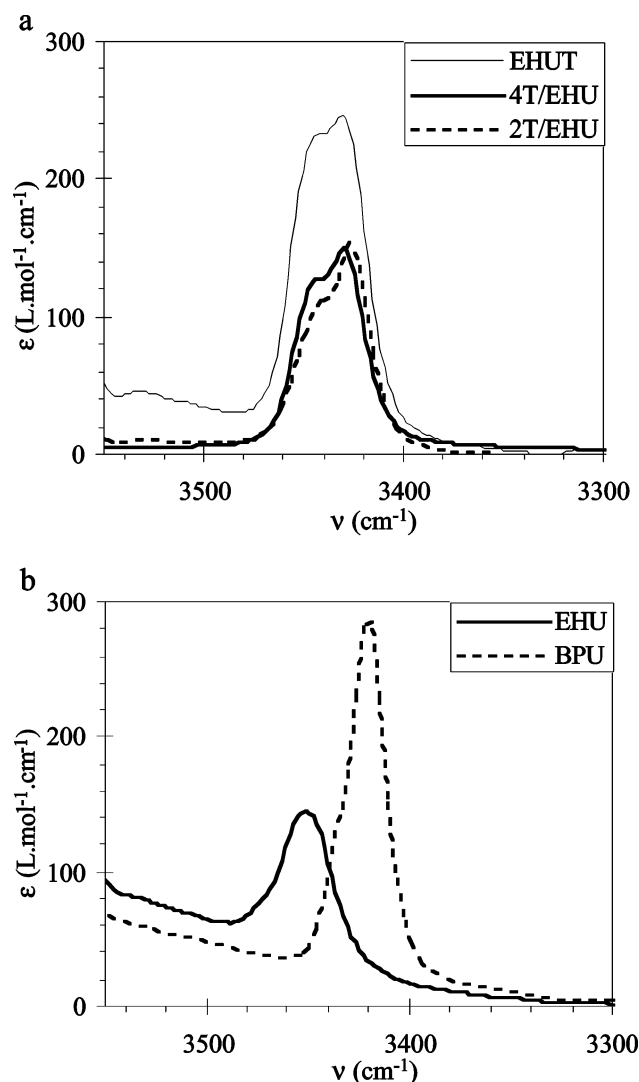
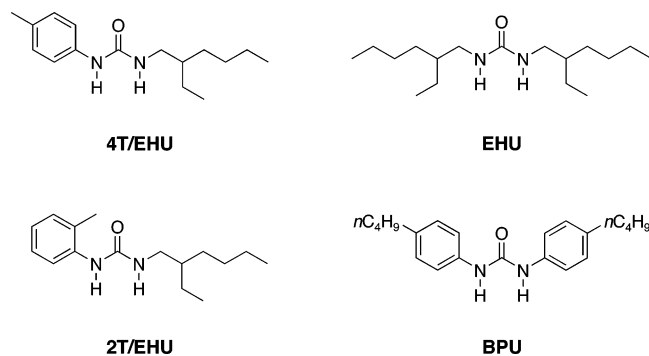


Figure 3. FTIR spectra of solutions of **EHUT** and model mono-ureas at a concentration of about 10^{-4} mol·L $^{-1}$, in CDCl $_3$.

Chart 2. Structures of Model Mono-Ureas Studied



of the exchange dynamics. The same is to be expected for the bis-urea. Consequently, in the case of the bis-urea (Figure 4a), the 3280 cm $^{-1}$ band can be attributed to the hydrogen bonded aromatic group and the 3340 cm $^{-1}$ band can be attributed to the hydrogen bonded aliphatic group of **EHUT**. This assignment has been confirmed by following the H/D exchange by ^1H NMR in very similar conditions. Indeed, the two aromatic N–H resonances at (7.5 and 7.1 ppm) decrease at the same rate and

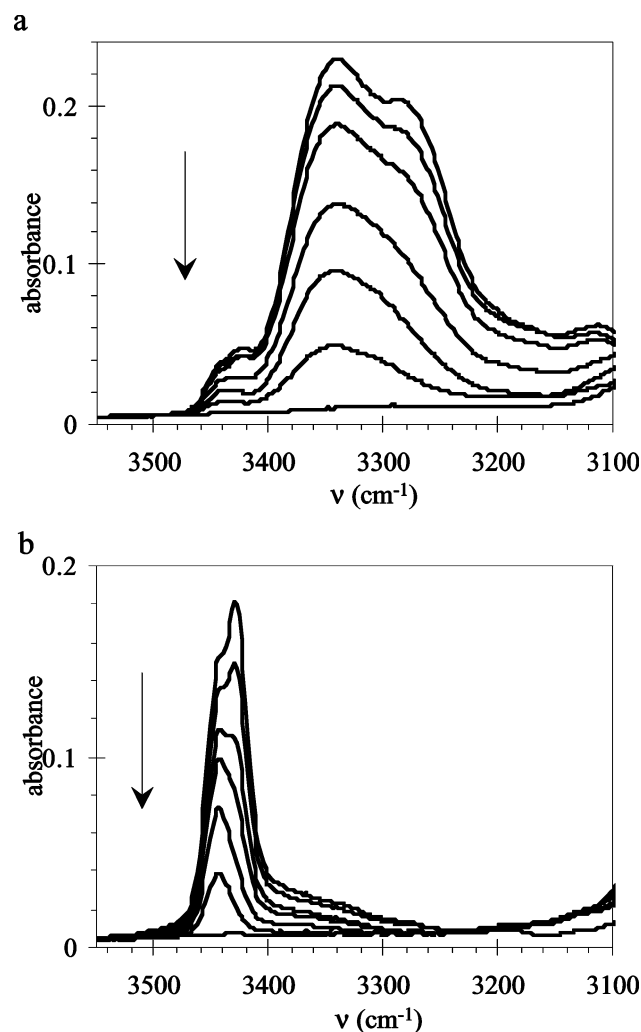


Figure 4. FTIR spectra of solutions of (a) bis-urea **EHUT** (7×10^{-3} mol·L $^{-1}$) and (b) model mono-urea **4T/EHU** (11×10^{-3} mol·L $^{-1}$) in CDCl $_3$, versus time after addition of D $_2$ O. Arrows indicate the direction of change with time. The half-life time is approximately 2 h for (a) and 40 min for (b).

faster than the two aliphatic N–H resonances at (6.1 and 5.9 ppm).

A quantitative analysis of the spectra of Figure 2 was based on the measurement of the intensity of the free N–H stretching vibrations, according to previous work on mono-ureas.^{11,14} At very low concentration (2.6×10^{-4} mol·L $^{-1}$), the spectrum of the totally dissociated bis-urea is obtained. This spectrum can then be used to determine the fraction of free N–H groups in spectra of more concentrated solutions (see the Experimental Section). The results are displayed in Figure 5, and compared to the results for solutions of model mono-ureas **4T/EHU** and **2T/EHU**.

This figure shows that the two model mono-ureas behave similarly, with **2T/EHU** being less associated than **4T/EHU**, probably due to the steric hindrance of the methyl substituent. More importantly, this figure also proves that the association of bis-urea **EHUT** is more cooperative than the association of model mono-ureas at two levels. First of all, the curves for **EHUT** and for the mono-ureas are separated by 2 orders of

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Table 1. Characteristics of Solutions of Mono and Bis-Ureas in CDCl₃ at Room Temperature

	2T/EHU	4T/EHU	MBUT	EHUT	DMHUT
$\nu_{\text{N-H}}^a$	3444/3427	3446/3431	3442/3431	3444/3429	3435/3427
$\nu_{\text{N-H}}^b$	3355	3350	3335/3290	3340/3280	3325/3280
K_2^b	1.8 ± 0.5	4.5 ± 0.5	7 ± 4	21 ± 3	14 ± 7
K^b	8.0 ± 1.0	16.6 ± 3.0	2300 ± 200	1400 ± 200	1700 ± 100
K/K_2^c	4.4 ± 1.8	3.7 ± 0.7	330 ± 230	70 ± 20	120 ± 60
K^2/K_2^d	36 ± 10	60 ± 20	$(8 \pm 5) \times 10^5$	$(1.0 \pm 0.5) \times 10^5$	$(2.1 \pm 0.9) \times 10^5$

^a N–H stretching frequencies (ν_{b} : hydrogen bonded; ν_{f} : free), in cm⁻¹. ^b Dimerization (K_2) and multimerization (K) constants, in L·mol⁻¹. ^c Measure of the cooperativity along the supramolecular chain. ^d Association constant between long oligomers, in L·mol⁻¹.

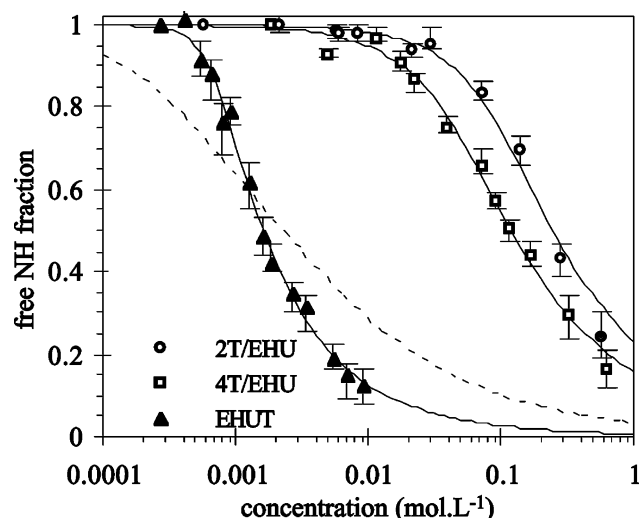


Figure 5. Fraction of free NH groups of bis-urea **EHUT** and model mono-ureas **4T/EHU** and **2T/EHU**, versus concentration in CDCl₃, at room temperature. The full curves are calculated with the nonisodesmic model and the values of the constants reported in Table 1. The dotted curve is the best fit of the **EHUT** data with the isodesmic model.

Scheme 1. Association Equilibria Involved in the Formation of a Supramolecular Polymer (M = monomer, M_n = Oligomer of Degree of Polymerization n)



magnitude on the concentration scale. If the two urea functions of bis-urea **EHUT** assembled independently from each other, then we would only expect a separation of a factor 2 between the curves (because the concentration scale is in molecules and not in urea functions). Thus, the additional 50-fold shift proves that hydrogen bonding of the first urea function of a molecule of **EHUT** facilitates the association of the second urea function in the supramolecular assembly. Second, the decrease of the free N–H fraction is steeper for **EHUT** than for mono-ureas. This means that the transition from monomer to long supramolecular polymers through the sequence of association equilibria (Scheme 1) is sharper for the bis-urea than for mono-ureas. In other words, the formation of short oligomers (dimers, trimers, ...) triggers the formation of long chains in the case of bis-urea.¹⁵ This is the manifestation of cooperativity at a second level.

These descriptions can be made more precise by fitting a particular model to the data of Figure 5. The simplest (isodesmic) model (i.e., $K_n = K$, for $n \geq 2$)¹⁶ does not yield a good

description of the data, as already reported for mono-ureas,^{11,14} but the second simplest model ($K_2 \neq K = K_n$, for $n \geq 3$) yields an excellent fit of all the data. The values of the constants derived are reported in Table 1. The value of K/K_2 is a measure of the second level of cooperativity (along the supramolecular chain). The fact that the association of mono-ureas is cooperative and can be described by the two constant model (K_2 , K) has already been reported and attributed to polarization of the urea function after the formation of dimers.¹¹ The K/K_2 value for bis-urea **EHUT** shows that the association of **EHUT** is even more cooperative than the association of mono-ureas, as has been deduced from the shape of the curves. The reason for the higher cooperativity (K/K_2) of the association of **EHUT** compared to mono-ureas is certainly related to significant differences in the respective molecular arrangements. For example, the bimolecular structure previously proposed for **EHUT**^{4b} is in agreement with such an observation.¹⁷

To compare the strength of the association, the best parameter is neither K_2 nor K , but K^2/K_2 . Indeed, the association constant between two oligomers M_p and M_q (p and $q \geq 2$) is $k(p,q) = [M_{p+q}]/([M_p] \cdot [M_q])$. Introducing in this relationship the step by step association constants ($[M_n] = K_2 \cdot K^{n-2} \cdot [M]^n$, for $n \geq 2$) yields $k(p,q) = K^2/K_2$, for p and $q \geq 2$. Table 1 shows that the association constant between oligomers (K^2/K_2) is more than 3 orders of magnitude larger for bis-urea **EHUT** than for mono-ureas. This huge difference is the result of the two levels of cooperativity previously mentioned. The value for **EHUT** ($K^2/K_2 = 1.0 \times 10^5$ L·mol⁻¹) can be compared to the association constant of a well-known quadruple hydrogen bonded supramolecular polymer based on dimerization of ureidopyrimidone units. For this system in chloroform and at room temperature, values of about 5×10^7 L·mol⁻¹ have been reported.¹⁸ The less strong association of **EHUT** can possibly be attributed to a lower degree of preorganization, due to the presence of two rotatable covalent bonds in the self-assembling unit.

Furthermore, the knowledge of the association constants makes it possible to compute the whole distribution of oligomers present at a given concentration and thus enhances our understanding of the system. Figure 6a represents the variation

(17) In the case of bis-urea **EHUT**, a more elaborate model (such as $K_2 \neq K = K_n$, for $n > 3$) could have been anticipated, because the cross section of the supramolecular chains has been proposed to contain two (or three) molecules,^{4b} which means that the association pattern must be more complex for **EHUT** than for mono-ureas, which form monomolecular wires. However, the fit to the (K_2 , K) model is already very good at the precision of the present measurements (Figure 5); it is thus not possible to derive any additional constant. The two constants K_2 and K deduced from the fit must consequently be considered as apparent values of a simple model describing a probably more complex process.

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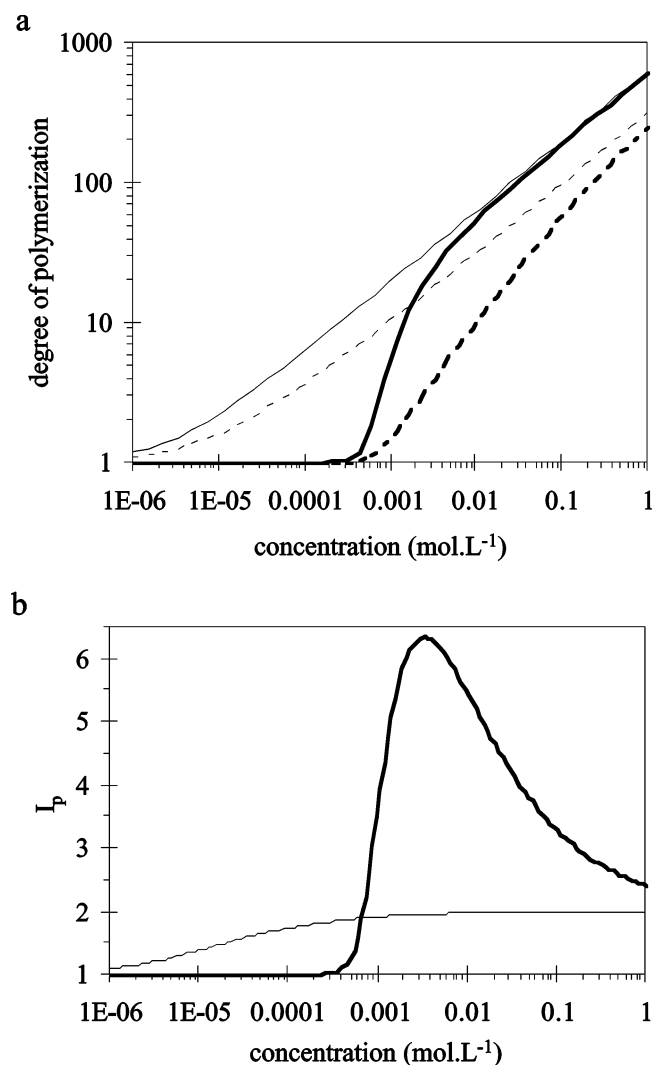


Figure 6. (a) Calculated weight average (full curves) and number average (dotted curves) degrees of polymerization of supramolecular polymers, versus concentration. (b) Calculated polydispersity index of supramolecular polymers, versus concentration. These curves correspond to **EHUT** ($K_2 = 21 \text{ L} \cdot \text{mol}^{-1}$, $K = 1400 \text{ L} \cdot \text{mol}^{-1}$) (bold curves) and an isodesmic reference compound ($K_2 = K = 1.0 \times 10^5 \text{ L} \cdot \text{mol}^{-1}$) (plain curves).

of the number average and weight average degrees of polymerization of **EHUT** versus concentration in chloroform. A useful reference is a virtual compound which would obey the simple isodesmic model, with an association constant equal to the value of K^2/K_2 for **EHUT**: $K_n = 1.0 \times 10^5 \text{ L} \cdot \text{mol}^{-1}$, for $n \geq 2$. At high concentrations, **EHUT** and the reference have the same DP_n and DP_w , which is expected, because at high concentrations, the influence of monomers and dimers is negligible. At lower concentrations though, the contrast is striking. The growth of the supramolecular chains is much sharper for **EHUT** than for the noncooperative reference. In particular, DP_w increases from 2 to 100 in a 40-fold concentration increase in the case of **EHUT**, whereas it takes a 3000-fold increase in the case of the noncooperative reference. This very sharp transition can be an advantage for applications where switching between polymer-like behavior and monomer-like behavior is desired. A possible drawback is the increased polydispersity of the cooperative system in the region of high chain growth (Figure 6b). The high polydispersity is due to the bimodality of the distribution: a

Table 2. Solubility of Bis-Ureas^a

	DMSO	EtOH	CHCl ₃	toluene	heptane
PUT	S	S	I	I	I
OUT	S	I	I	I	I
ODUT	I	I	I	I	I
MBUT	S	S	S	I	I
EHUT	S	S	S	S	S
DMHUT	S	S	S	$S = 8 \text{ g} \cdot \text{L}^{-1}$	S
EPUT	S	S	I	I	I
PEUT	S	I	I	I	I
TBUT	S	I	I	I	I
TOUT	S	S	I	I	I
2,4/2,6-EHUT	S	I	I	I	I

^a I: insoluble, S: soluble. Solubility was tested at a concentration of $10 \text{ g} \cdot \text{L}^{-1}$ (unless otherwise mentioned) and at room temperature.

polymer fraction, which has a usual polydispersity of about 2, is in equilibrium with a relatively high monomer concentration.¹¹

2. Influence of Structure. The properties of bis-ureas can be expected to be extremely sensitive to the nature of the bridging group between the two urea functions, because this bridging group is responsible for the first level of cooperativity. Consequently, we synthesized a series of bis-ureas having in common the same meta-substituted phenylene core, but either with different side-groups, or with a different position of the methyl group.

2.1 Influence of the Side-Groups. Ten different bis-ureas were synthesized by reaction of 2,4-toluenediisocyanate with the corresponding amines (Chart 1). None of the three bis-ureas with linear alkyl substituents **R** (**PUT**, **OUT**, and **ODUT**) are soluble in the low polarity solvents tested (Table 2). Introducing branching expectedly improves solubility, because three branched bis-ureas are soluble in chloroform (**MBUT**, **EHUT**, and **DMHUT**) and two of them are even soluble in heptane, at room temperature (**EHUT** and **DMHUT**). Branching thus seems to be a necessary condition for solubilizing bis-ureas, but it is not a sufficient condition, because **EPUT**, **PEUT**, **TBUT**, and **TOUT** are not soluble in low polarity solvents. It has to be noted that the two most soluble bis-ureas synthesized (**EHUT** and **DMHUT**) are in fact mixtures of isomers, obtained from racemic amines.

The self-assembling ability of the three chloroform soluble bis-ureas was first evaluated by FTIR spectroscopy. The values of the free N–H fractions (Figure 7) and the association constants derived from them (Table 1) show that the behavior of **MBUT**, **EHUT**, and **DMHUT** are very similar. This indicates that the self-assembling mechanism is probably the same for the three compounds. Furthermore, the strength of the association (K^2/K_2) increases significantly in the order **EHUT** \leq **DMHUT** $<$ **MBUT**. The stronger association of **MBUT** probably results from a reduced steric hindrance of the 3-methylbutyl substituent compared to the 2-ethylhexyl and 1,5-dimethylhexyl groups. A similar trend has been observed in the case of mono-ureas.¹¹ The influence of the structure on the strength of the association is confirmed by the increase in viscosity in the order **EHUT** $<$ **DMHUT** $<$ **MBUT** (Figure 8).

2.2 Influence of the Position of the Methyl Group. All of the previous bis-ureas described here were synthesized from 2,4-toluene diisocyanate containing less than 4% of the 2,6 isomer, and were then checked by NMR to contain negligible

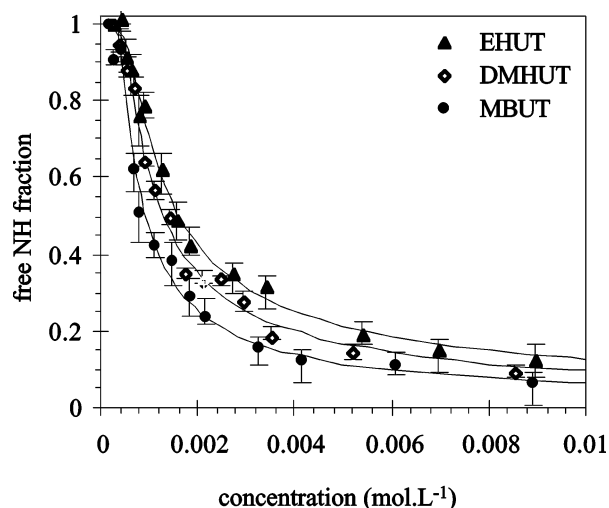


Figure 7. Fraction of free NH groups of bis-ureas, versus concentration in CDCl_3 , at room temperature. The curves are calculated with the constants reported in Table 1.

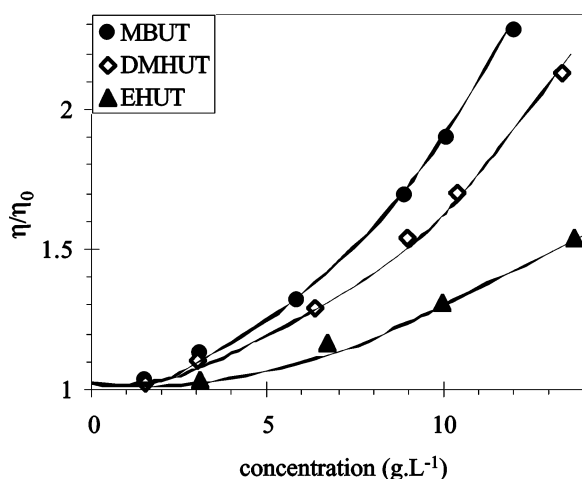


Figure 8. Relative viscosity of bis-ureas, versus concentration in chloroform, at 25 °C.

amounts of the 2,6 bis-urea isomer. The influence of the position of the methyl group was assessed by synthesizing **2,4/2,6-EHUT** from the technical mixture of toluene diisocyanate isomers, which contains 80% 2,4- and 20% 2,6-isomers. In fact, the purification by recrystallization changes the proportion, because NMR analysis shows that **2,4/2,6-EHUT** is a 50/50 mixture of the two bis-urea isomers. Table 2 shows that the solubility of **2,4/2,6-EHUT** is remarkably lower than the solubility of **EHUT**. Even though **2,4/2,6-EHUT** is not a pure compound, it can be concluded that the position of the methyl substituent has a very strong influence on the properties of this family of bis-ureas. It is possible that the more symmetrical structure of **2,6-EHUT**, compared to **2,4-EHUT**, is responsible for the formation of a more stable crystalline structure, which would in turn be responsible for a lower solubility.

Conclusion

Our results provide an unambiguous assignment of the FTIR spectra of solutions of **EHUT** in the N–H region, which makes

a quantitative analysis possible. From this analysis, it has been shown that the self-assembly of bis-ureas displays cooperativity at two levels. The first level of cooperativity is due to the synergistic association of the two urea functions of a single molecule. The second level of cooperativity is revealed by the fact that the formation of dimers is less favored than the formation of long oligomers. The consequences of these features are a strong association, a sharp transition between monomer-like and polymer-like properties and a polydispersity larger than 2. Finally, **EHUT** is not the only compound having such remarkable properties: three bis-ureas with similar behaviors have been identified. This fact paves the way for the rational optimization of the properties of these supramolecular polymers.

Experimental Section

Viscometry. Solutions were prepared 1 day prior to the measurements and filtered on Millex membranes ($\Phi = 0.45 \mu\text{m}$) in the case of chloroform and carbon tetrachloride solutions, but could not be filtered in the case of toluene and dodecane solutions. Dodecane, toluene, and carbon tetrachloride were used as received. Chloroform (stabilized with amylenes) was dried over molecular sieves. However, it was checked that the use of this dried CHCl_3 , or water saturated CHCl_3 , or CDCl_3 , yielded the same results within experimental error. Measurements were performed at 25 ± 0.1 °C with a Cannon–Manning semi-micro capillary viscometer, except for dodecane solutions, which were characterized with a Low Shear 30 Couette rheometer.

IR Spectroscopy. Infrared spectra were recorded at room temperature on a Perkin–Elmer 1760 spectrometer in KBr cells of 0.05 to 2.5 cm path length. Solutions in CDCl_3 (dried on molecular sieves) were prepared 1 day prior to the measurements. Quantitative data analysis was based on the N–H vibration, because the intensity of the C=O vibration was not precise enough, due to high solvent absorption at this wavelength. The shape of the free N–H stretching vibration was determined on sufficiently dilute solutions, such that only the free component was detected (reference curve). At higher concentrations, the fraction of free N–H groups was deduced from the proportion of the reference curve necessary to remove completely free N–H component. Then, the association constants were determined by nonlinear curve fitting, using the following equations [the main source of uncertainty (which is mentioned in Table 1 and Figures 5 and 7) is due to the uncertainty of the deconvolution, because the shape of the hydrogen bonded N–H band is ill-defined]. In the case of mono-ureas, the fraction of free N–H groups, f , is given by eq 1,¹⁴ where C_0 is the mono-urea total molar concentration, and C_1 is the molar concentration of unassociated mono-urea, which is calculated numerically by solving eq 2 (mass balance equation)¹⁴

$$f = \frac{C_1}{C_0} \cdot \left(1 + \frac{K_2 C_1}{1 - K C_1} \right) \quad (1)$$

$$K(K - K_2)C_1^3 + (2K_2 - 2K - K^2 C_0)C_1^2 + (1 + 2K C_0)C_1 - C_0 = 0 \quad (2)$$

Then, the number-average and weight-average degrees of polymerization DP_n and DP_w are computed from eqs 3 and 4

$$\text{DP}_n = \frac{C_0}{C_1} \cdot \left(\frac{1 - (K - K_2)C_1}{1 - K C_1} \right) \quad (3)$$

$$\text{DP}_w = \frac{1 + K C_1}{1 - K C_1} - \frac{2(K - K_2)C_1^2}{C_0(1 - K C_1)} \quad (4)$$

In the case of bis-ureas, fibrillar supramolecules are formed, which

have been proposed to be either bi- or tri-molecular wires, but not mono-molecular wires.^{4b} Consequently, eq 1 does not apply. If the structure is supposed to be bimolecular, then the fraction of free N–H groups, f , is given by eq 5

$$f = \frac{C_1}{C_0} \left(1 - \frac{K_2 C_1}{2} + \frac{2K_2 C_1}{1 - K C_1} \right) \quad (5)$$

Equations 2–4 also apply to the bimolecular case.

Proton/deuterium exchange experiments were performed by adding D₂O to a solution of **EHUT** in CHCl₃. FTIR spectra of the organic phase were recorded in a CaF₂ cell of 0.1 cm path length.

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Supporting Information Available: Synthesis and characterization of mono-ureas and bis-ureas. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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