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Selective synthesis of non-symmetrical bis-ureas and their self-assembly†

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Symmetrical bis-ureas composed of two urea functions linked together by a toluene ring were previously shown to form long supramolecular polymers and thus highly visco-elastic solutions, thanks to cooperative self-assembly involving four hydrogen bonds. In this paper, we report the direct and selective synthesis of non-symmetrical bis-ureas. Mono-isocyanate/mono-ureas were first obtained from a one-step selective reaction between one aromatic amine and one isocyanate function of 2,4-toluene diisocyanate. Then, non-symmetrical bis-ureas, tetra-ureas, and bis-urea functional polydimethylsiloxanes (PDMS) were obtained by reacting the mono-isocyanate/mono-ureas with well chosen amines. The chloroform solutions of these compounds were characterised by quantitative FTIR spectroscopy and viscosimetry. It was shown that non-symmetrical bis-ureas substituted on one side by an aromatic moiety and on the other by an aliphatic group combine the solubility of aliphatic bis-ureas and the strong association of aromatic ones. Moreover, the association of bis-ureas grafted onto polydimethylsiloxanes is efficient and leads to the physical cross-linking of these polymers, even in chloroform.

Introduction

Supramolecular polymers result from the self-assembly of small molecules, which are held together by weak interactions and lead to polymer-like structures.[1–4] These systems are increasingly studied because of the reversible character of the process through various stimuli, including temperature, solvent and concentration.

Among these systems, we have focused on bis-ureas (Scheme 1), whose two urea functions are linked together by a rigid spacer. Some of these molecules dissolve spontaneously at room temperature in apolar solvents and lead to visco-elastic solutions at concentrations as low as 1% by weight. This is due to their self-assembly into long and rigid wires, by four strong cooperative hydrogen bonds.[5] A range of symmetrical bis-ureas‡ has previously been synthesised by reacting 1 equiv. of 2,4-toluene diisocyanate (2,4-TDI) with 2 equiv. of a primary amine.[6] Up to now, no dissymetrical bis-ureas based on 2,4-TDI have been obtained.

On the other hand, bis-urea grafted polymers may form self-assembled materials with unique rheological properties, both in bulk and solution. Furthermore, multifunctional compounds such as tetra-ureas can be expected to show extremely efficient association.

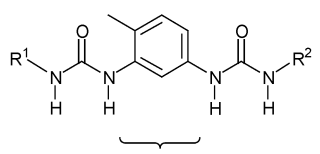
To obtain these new molecules, the selective reaction of an amine with only one isocyanate function of 2,4-TDI is required (Scheme 2). The previously cited products may then be obtained by reacting the remaining isocyanate function of the mono-adduct with a well-chosen amino-functional molecule (Schemes 3–5).

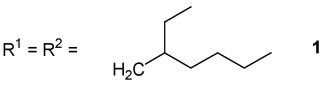
According to the literature, the ortho isocyanate function of 2,4-TDI is slightly less reactive than the para one.[7–9] Moreover, when one of the two isocyanates is converted to a urea or a urethane function, the reactivity of the remaining isocyanate significantly decreases.[9,10] Thus, mono-isocyanate/mono-urethane may be obtained by reacting an alcohol with an excess of 2,4-TDI.[10] However, amines being more reactive than alcohols, the selectivity of the reaction with 2,4-TDI is expected to decrease. In fact, no detailed selective synthesis of mono-isocyanate/mono-urea based on 2,4-TDI has been reported yet, even though clues have been given by some authors.[8,11] This paper presents such a selective synthesis with aromatic amines, which are less reactive than aliphatic ones.[7]

Results and discussion

1. Synthesis of mono-isocyanate/mono-ureas

Analysis. The unselective reaction of equimolar amounts of 2,4-TDI and 4-*n*-butylaniline (BuA) leads to a mixture of 4 products (Scheme 6). The moisture sensitivity of these products, caused by the remaining isocyanate function, complicates their analysis. Thus, the product of the first step was reacted with an excess of 2-ethylhexylamine (EHA). After this





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Scheme 1 General formula of bis-ureas.

† Electronic supplementary information (ESI) available: NMR spectra in the 2 ppm region for the products, before and after recrystallisation, from runs OC105 and OC072, having different product distributions. See http://www.rsc.org/suppdata/nj/b3/b316913h/

‡ The word symmetrical refers to R^1 and R^2 substituents and neglects the presence of the methyl group on the central ring.

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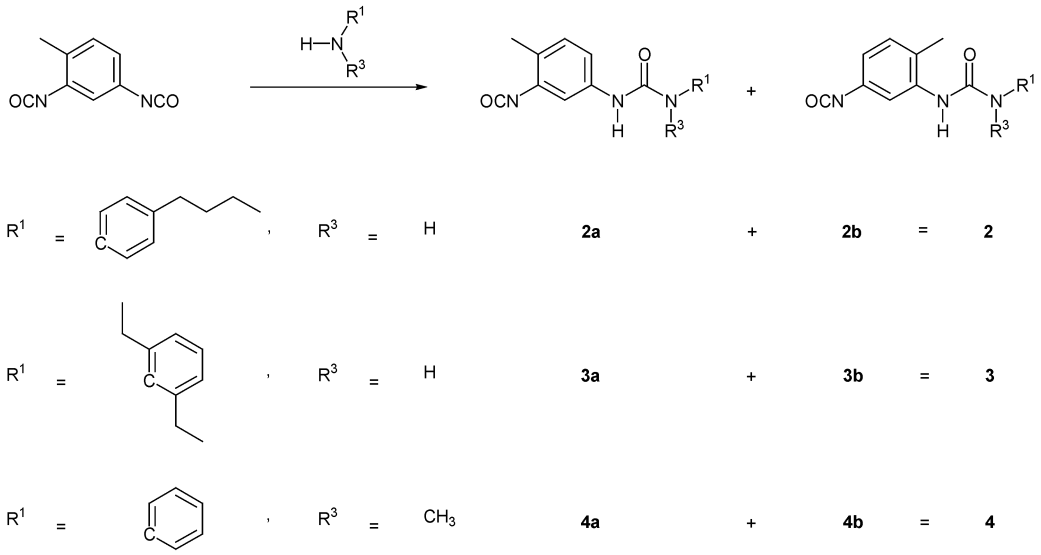


Scheme 2 Synthesis of mono-isocyanate/mono-ureas.

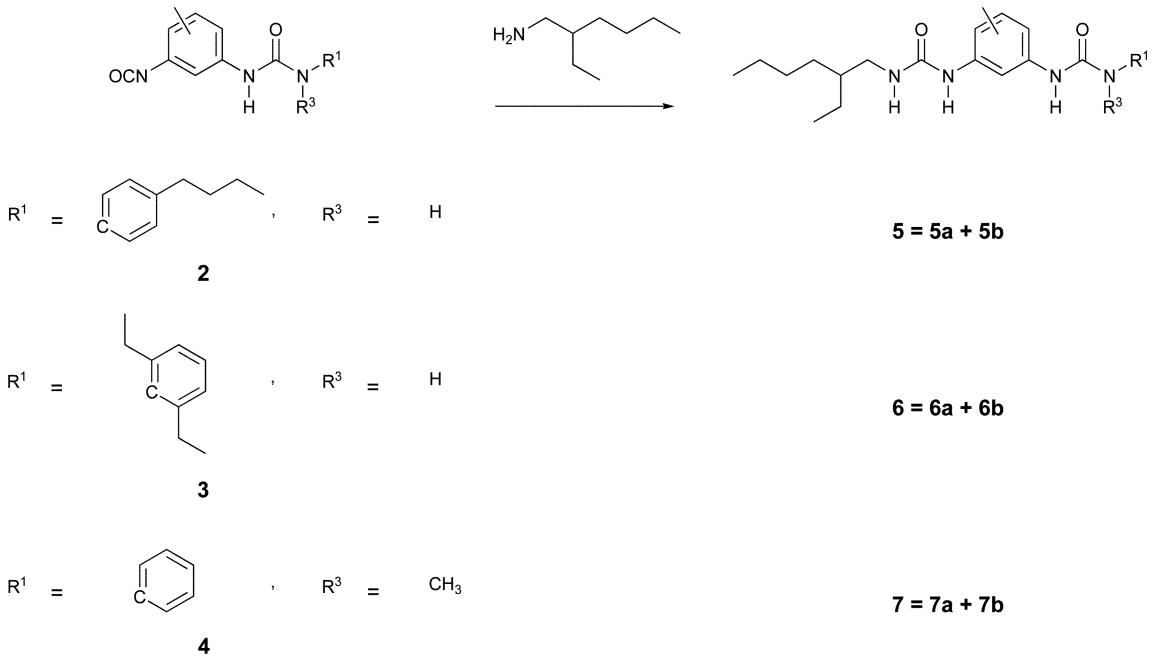
second step, the final mixture is free of isocyanate functions and can be analysed directly by ^{1}H NMR.

The composition of the mixture after the first step can then be deduced from the analysis of the crude product of the second step. Indeed, according to Scheme 6, the proportions of **5a**, **5b**, **1** and **16** in the second step correspond to the amounts of **2a**, **2b**, 2,4-TDI, and **16**, respectively, in the first step. Moreover, the four bis-ureas potentially obtained at the end of the second step are easily identified by ^{1}H NMR (spectra a–d in Fig. 1) even for proportions of symmetrical bis-ureas as low as 5 mol % (spectra e and f in Fig. 1). Finally, deconvolution of the 4 peaks, corresponding to the four different bis-ureas, gives an accurate determination of the amount of each bis-urea. Thus, the selective formation of mono-isocyanate/mono-urea from 2,4-TDI and BuA can be accurately and easily evaluated by this two-step method.

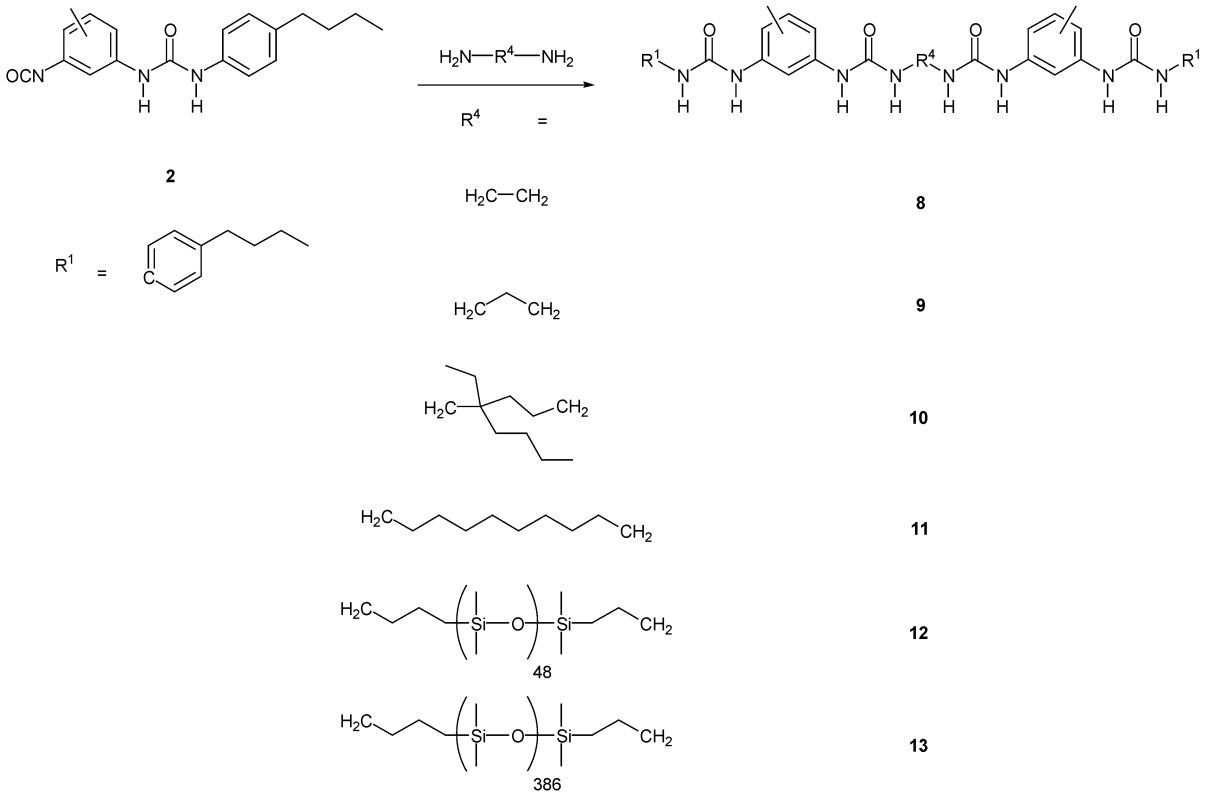
Influence of solvent and stoichiometry. The influence of the solvent and of the 2,4-TDI : BuA ratio on the selectivity of the first step was investigated. Three solvents were tested (THF, heptane, dichloromethane) with 2,4-TDI : BuA ratios varying from 1 : 1 to 5 : 1 (Fig. 2). In heptane or dichloromethane, **2** precipitates during the first step, which makes it possible to remove the excess of 2,4-TDI by filtration. In THF however, the mono-isocyanate/mono-ureas are soluble and the excess of 2,4-TDI was not removed. The composition of the final product was evaluated for all runs (Table 1).

According to Table 1 and Fig. 2, the reaction is not selective in stoichiometric conditions since small amounts of **16** are detected at the end of the second step for OC103, OC134 and OC108. This is caused by the fact that the **2** : 2,4-TDI ratio becomes very high at the end of the reaction, and thus the probability for BuA to react with **2** and form **16** becomes significant.[10]

Moreover, several differences are observed when the solvent is changed. First, almost no **1** can be detected when the first step is conducted in heptane or dichloromethane. Indeed, **2** is not soluble in these solvents, unlike 2,4-TDI. Thus, the products of the first step are filtered at the end of the reaction, and



Scheme 3 Synthesis of non-symmetrical bis-ureas.

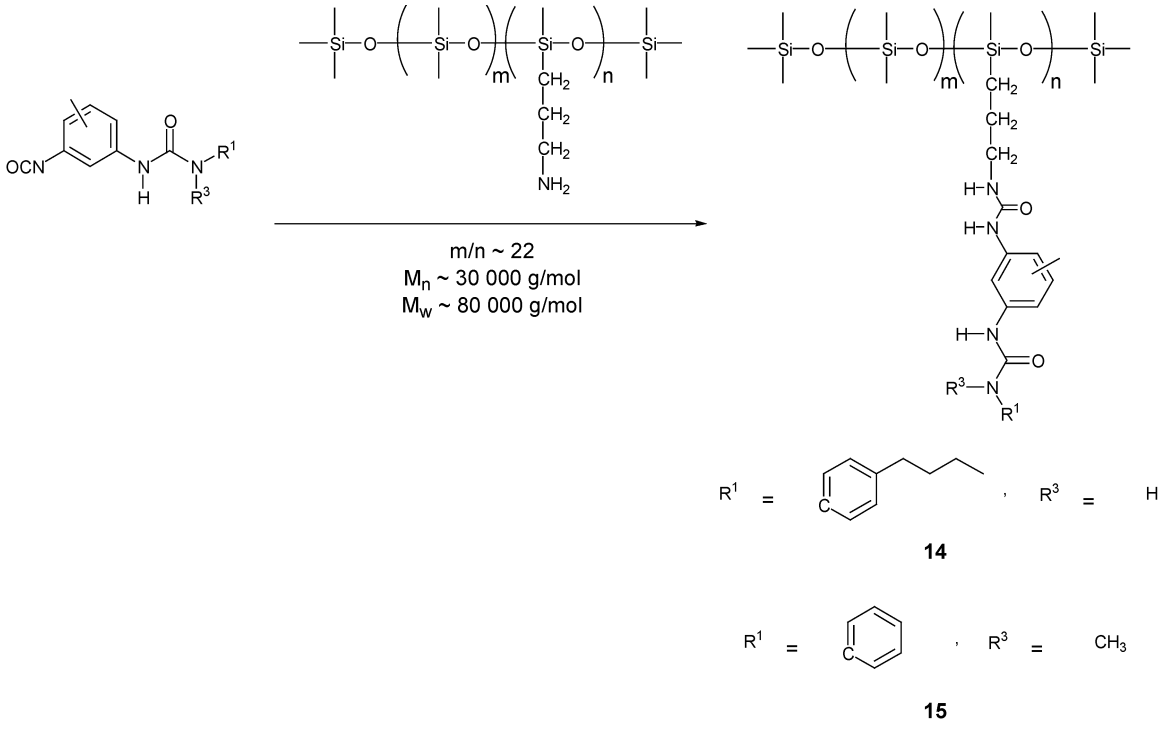


Scheme 4 Synthesis of tetra-ureas.

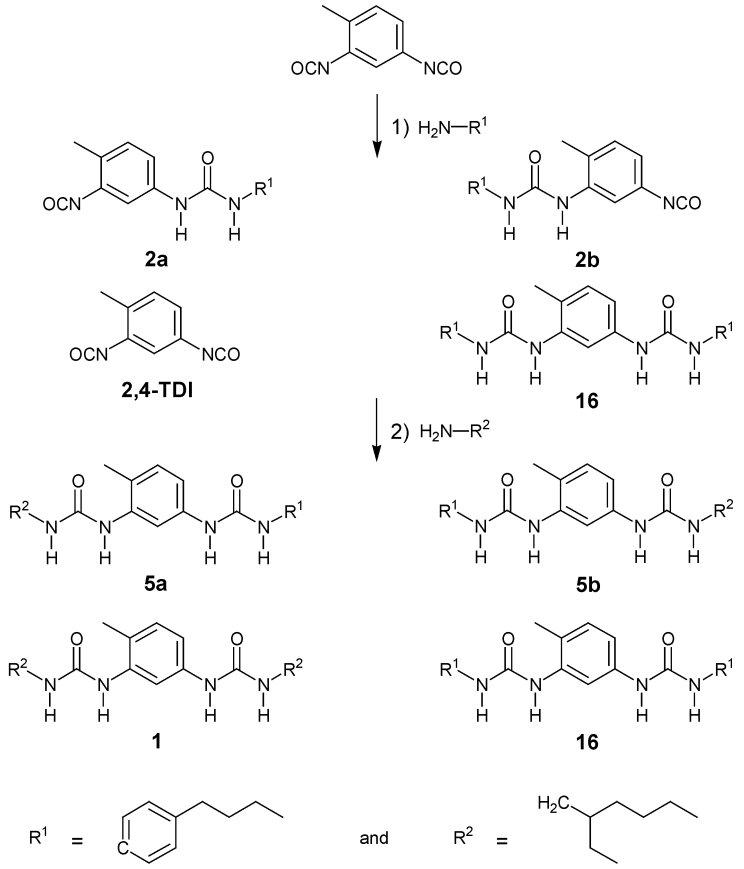
the remaining 2,4-TDI is eliminated before adding EHA. On the contrary, **2** is soluble in THF and no purification is done before the second step. The remaining 2,4-TDI yields **1** during the second step.

Furthermore, the selectivity is slightly lower in dichloromethane than in THF or heptane (see the amount of **16** for each run). This observation may be attributed to the formation of a more viscous reaction mixture in dichloromethane than in THF or heptane, due to the formation of a thick precipitate. Thus, the poorer selectivity could result from inhomogeneity of the reaction medium.

Finally, the **5a**:**5b** ratio is much greater than 1, which confirms the difference of reactivity between the para and ortho isocyanate functions.[8] This ratio depends on the solvent in the order dichloromethane > heptane > THF. This is probably caused by a difference of solubility between **2b** and **2a** rather than by a difference of reactivity of the two isocyanate functions of 2,4-TDI induced by the solvent. Indeed, **2b** may be



Scheme 5 Synthesis of PDMS grafted bis-ureas.



Scheme 6 The four possible products of the reaction of 2,4-TDI with BuA in the first step and EHA in the second step.

more soluble than **2a** and some of it may be eliminated during the filtration in heptane or dichloromethane, but not in THF. This hypothesis is in agreement with the lower yield of the first step in dichloromethane than in heptane.

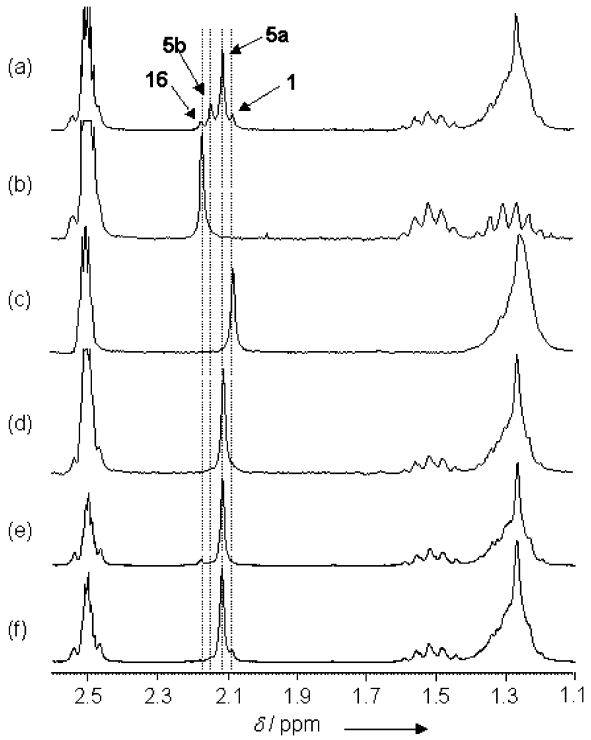


Fig. 1 ^{1}H NMR spectra of the possible products of the reaction described in Scheme 6. Non-selective synthesis as run OC108 (a); symmetrical bis-ureas **16** (b) and **1** (c); non-symmetrical bis-urea **5a** (d); intentional mixtures of **5a** + 5% **16** (e), and **5a** + 5% of **1** (f). The peak at *ca.* 2.1. ppm corresponds to the methyl group on the aromatic ring.

With an excess of 2,4-TDI, the selectivity of the reaction is improved according to the decreasing amount of **16**. Indeed, the excess of 2,4-TDI keeps the **2** : 2,4-TDI ratio low through-

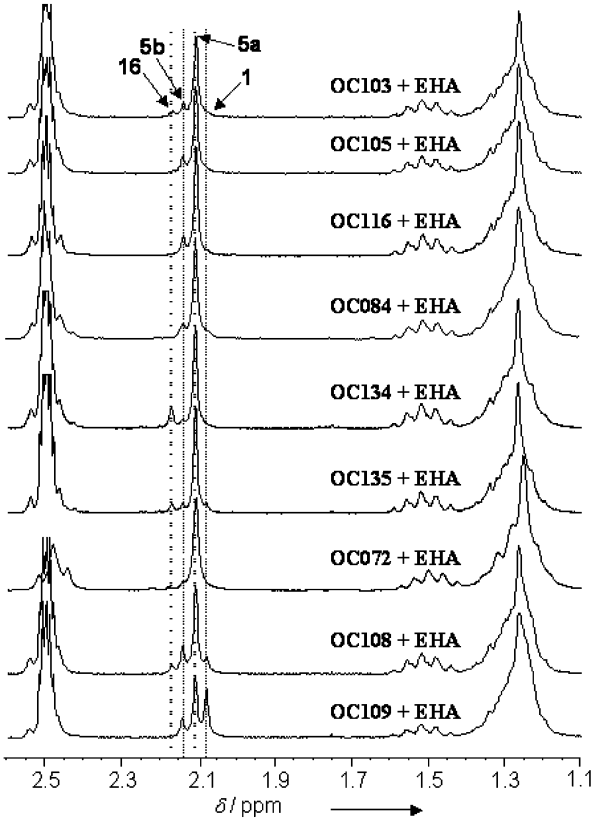


Fig. 2 ^{1}H NMR spectra of the crude product of the second step (Scheme 6), for different reaction conditions of the first step. See Table 1 for the experimental conditions.

Table 1 Evaluation of the selectivity of the synthesis of **2**

Run	Solvent	2,4-TDI : BuA	% Yield[a]	% **16**[b]	% **5b**[b]	% **5a**[b]	% **1**[b]	**5a**/**5b**
OC103	Heptane	1	92	6	11	83	<1	8
OC105	Heptane	1.5	94	1	15	83	1	6
OC116	Heptane	3	95	<1	14	86	<1	6
OC127	Heptane	3	92	<1	8	92	<1	12
OC084	Heptane	5	97	<1	11	89	<1	8
OC134	CH_2Cl_2	1	67	14	2	84	<1	35
OC135	CH_2Cl_2	1.5	70	5	3	90	2	26
OC072	CH_2Cl_2	5	73	<1	<1	>97	<1	>97
OC108	THF	1	n.a.[c]	5	19	59	17	3
OC109	THF	1.5	n.a.[c]	1	14	48	37	3

[a] Product yield for the first step (obtained weight divided by weight of **2** expected if the reaction were fully selective). [b] The amounts of **16**, **5b**, **5a** and **1** at the end of the second step correspond to those of **16**, **2b**, **2a** and 2,4-TDI, respectively, at the end of the first step. [c] Not available because the product of the first step was not purified.

out the reaction and thus favours the selectivity. Here again, the lower selectivity in dichloromethane is confirmed. Indeed, when 1.5 equiv. of 2,4-TDI is used in the first step, almost no **16** is detected in heptane (OC105) or THF (OC109), whereas a significant proportion is formed in dichloromethane (OC135). Nevertheless, full selectivity is reached in heptane and dichloromethane with 3 or 5 equiv. of 2,4-TDI (OC116, OC084, OC072).§

In conclusion, selectivity of the first step is easily reached in either solvent with an excess of 2,4-TDI. Thus, **2** free of **16** can be obtained. Moreover, the use of dichloromethane or heptane is recommended to get rid of the unreacted 2,4-TDI at the end of the reaction. The choice between heptane or dichloromethane depends on the desired mono-isocyanate/mono-urea. Indeed, heptane should be preferred to obtain **2** (mixture of isomers) in yields higher than 90%, whereas dichloromethane is more indicated to obtain almost pure **2a**, but with slightly lower yields (~70%).

2. Synthesis of non-symmetrical bis-ureas and bis-urea functional molecules

Several bis-urea based molecules were synthesised from **2**. First, **2**, synthesised in dichloromethane and containing low amounts of **2b**, was reacted with EHA to obtain almost pure **5a** (Scheme 3). The remaining **5b** was eliminated by recrystallisation in ethyl acetate. It should be highlighted that when **2** containing large amounts of **2b** is used for this reaction, the quantity of **5b** is too large to be eliminated by recrystallisation in ethyl acetate (see Fig. S1 in Electronic supplementary information). Similarly, amino-functional polydimethylsiloxanes were transformed into bis-urea-functional ones (PDMS-*g*-bis-urea) (Scheme 5). Moreover, tetra-ureas (*i.e.*, bis-ureas linked together by an aliphatic or a polymeric spacer) were synthesised from diamines and **2** (Scheme 4). The difficult recrystallisation of tetra-ureas containing an aliphatic spacer explains the poor yields of their synthesis. The characteristics of these new compounds are discussed in Section 4 below.

3. Synthesis of other mono-isocyanates/mono-ureas and non-symmetrical bis-ureas

The synthesis of mono-isocyanate/mono-urea from 2,4-TDI is not limited to the use of BuA. With the analytical technique described above, it was proven that almost pure **3a** is obtained by reacting 1 equiv. of 2,6-diethylaniline with 5 equiv. of 2,4-TDI in dichloromethane at room temperature (Scheme 2). The reaction of this new mono-adduct with EHA and recrystallisation of the final product yielded pure **6a** (Scheme 3).

Finally, *N*-methylaniline, a secondary amine, was used to synthesise a new type of mono-adduct **4** (Scheme 2). The synthesis was performed with 5 equiv. of 2,4-TDI in heptane at 0 °C. Then **4** was either reacted with EHA to obtain **7** or with an amino-functional PDMS to yield the PDMS-*g*-bis-urea **15** (Schemes 3 and 5). As the purification of **4** was more difficult than that of the other mono-adducts, a small quantity of 2,4-TDI remained at the end of the first step. Pure **7** was obtained after column chromatography, precipitation, and recrystallisation. The polymer grafted with **4** underwent limited chain extension reactions because of the presence of traces of 2,4-TDI,[12] but its molecular weight increased only moderately and it was not chemically cross-linked.

4. Characterisation in solution

The solubility of all synthesised molecules was first tested (Table 2).

The aliphatic tetra-ureas **8** to **11** are hardly soluble, even in polar solvents such as THF. The presence of branching in the spacer of **10** does not improve the solubility significantly. Consequently, these compounds were not studied further.

The amino-functional PDMS are viscous oils, whereas the bis-urea modified PDMS **12** to **15** are rubbery solids. However, this dramatic change of behaviour is only caused by a physical cross-linking of the material. Indeed, the PDMS modified by bis-ureas are soluble in THF (a solvent of the polymer backbone and a very good hydrogen-bond competitor as well), which confirms that they are not chemically cross-linked. On the contrary, **12** and **14**, which contain a large amount of bis-urea, swell in heptane, toluene or chloroform, as if they were cross-linked. Indeed, these solvents of the polymer backbone are too weak hydrogen-bond competitors to prevent the self-assembly of bis-ureas into a physical network. As already reported,[13] the physical cross-linking of PDMS by bis-ureas improves dramatically the tensile properties of these materials.

The properties of solutions of **13** in chloroform are described below.

Finally, **5a** and **7** are very soluble at room temperature. Moreover, **5a** forms a gel in toluene at only 1 wt %. The self-assembly of these molecules was characterisized by FTIR spectroscopy and viscosimetry and compared to that of a model symmetrical bis-urea (**1**) whose properties were already reported.[5,6] Bis-urea **1** is a good comparative model since it differs from **5a** by only one moiety (Schemes 1 and 3). Compound **6** has poor solubility and was not studied further.

As already reported,[6] FTIR spectroscopy in chloroform is a powerful tool to quantify the self-association of bis-ureas. Indeed, the vibration frequency of the NH function, ν(NH), depends on whether it is involved in a hydrogen bond or not:

§ In dichloromethane, the elimination of 2,4-TDI is more difficult because of the viscosity of the reaction mixture when 1.5 equiv. are used: a small amount of **1** is formed in the second step of this run. With a larger excess of 2,4-TDI though, more solvent is used and the filtration eliminates all the remaining 2,4-TDI.

Table 2 Solubility tests at room temperature[a]

Name	Compound type	Heptane	Toluene	Chloroform	THF
5a	Bis-urea	I(10)	G(10)	S	S
6a	Bis-urea	I(2)	I(2)	I(2)	I(2)
7	Bis-urea	I(10)	S	S	S
8	Aliphatic tetra-urea	I(5)	I(5)	I(5)	I(5)
9	Aliphatic tetra-urea	I(10)	I(10)	I(10)	I(10)
10	Aliphatic tetra-urea	I(1)	I(1)	I(1)	I(1)
11	Aliphatic tetra-urea	I(1)	I(1)	I(1)	I(1)
12	PDMS tetra-urea	I(10)	SW	SW	S
13	PDMS tetra-urea	S/G(50)	S/G(50)	S	S
14	PDMS-g-bis-urea	SW	SW	SW	S
15	PDMS-g-bis-urea	S	S	S	S
16	Bis-urea	I(1)	I(1)	I(1)	I(1)

[a] I(X): not soluble at X g L^{-1}; G(X): physical gel at X g L^{-1}; SW: swollen (the polymer is in equilibrium with excess solvent); S: soluble at 10 g L^{-1}.

ν(bonded NH) $\sim$3350 cm^{-1} and ν(free NH) $\sim$3430 cm^{-1} (Fig. 3). The quantitative measurement of these bands provides the fraction of chain ends and thus the length of the supramolecular chains.

The evolution of the fraction of free NH functions was plotted *versus* bis-urea concentration in chloroform for **5a**, **7**, and **13** (Fig. 4). The curves reveal that the self-assembly of bis-ureas increases with their concentration in chloroform, as expected. Moreover, the self-assembly of **1**, **5a** and **13** is much stronger than that of a reference mono-urea (*N*-2-ethylhexyl-*N*′-2-methylphenylurea). This was already reported for **1**[6,14] and is due to a pre-organisation of the urea functions by the toluene spacer. Indeed, when one of the urea functions is hydrogen-bonded, the association of the second one is favoured, increasing the overall association strength. Furthermore, the sharp transition between dissociated molecules and almost fully associated ones, observed for the bis-ureas, is characteristic of a strongly cooperative self-assembly.[6]

The comparison of **5a** and **1** shows that the non-symmetrical bis-urea self-assembles much better than the symmetrical one (Fig. 4). This is certainly caused by the presence of the additional aromatic moiety in **5a**, which increases the acidity of the nearest NH,[15,16] without hindering too much the association. However, the cooperativity of the association is not significantly affected by the increased strength of the hydrogen bonds. It is worth mentioning that the symmetrical bis-urea with two aromatic substituents **16** should self-assemble even more strongly than **5a**, but **16** is not soluble in the solvents considered (Table 2). This emphasises the usefulness of non-symmetrical bis-urea **5a**, which combines the solubility of aliphatic bis-ureas with the strong association of aromatic ones.

The PDMS tetra-urea **13** begins to associate at almost the same concentration (10^{-4} mol L^{-1}) as **5a**, which is not surprising since these molecules are composed of very similar bis-ureas. Nevertheless, the cooperativity of the self-assembly of **13** is much lower than that of **5a**. This may be explained by the bulkiness of the macromolecular chain of **13**, which probably hinders the formation of very long supramolecular chains.[17] Moreover, the fact that bis-ureas are linked pair-wise by a macromolecular spacer may add an additional entropic cost to the self-assembly.[18] However, the self-assembly of bis-ureas grafted on a PDMS chain is still very good.

Finally, the behaviour of the bis-urea with only 3 NH functions, **7**, is intermediate between that of the mono-urea and the other bis-ureas.

Beside these qualitative results, a theoretical model can be used to describe the association of bis-ureas (Scheme 7).[6] In this model, K_2 represents the equilibrium constant for the association between two free bis-ureas, whereas K corresponds to the association between a free bis-urea and a supramolecular oligomer containing at least two bis-ureas. With this model, the different bis-ureas can be compared. Indeed, K/K_2 is an evaluation of the cooperativity of the system, whereas K^2/K_2 is the association constant between two oligomers and characterises the strength of the self-assembly.[6]

The values of K_2 and K were determined by fitting this theoretical model to the experimental points for **1**, **5a**, **13**, and the mono-urea (Table 3). The experimental points were not accurate enough to determine precisely K and K_2 for **7**. The values of K/K_2 and K^2/K_2 confirm the previous qualitative observations. In particular, K^2/K_2 is much lower for the mono-

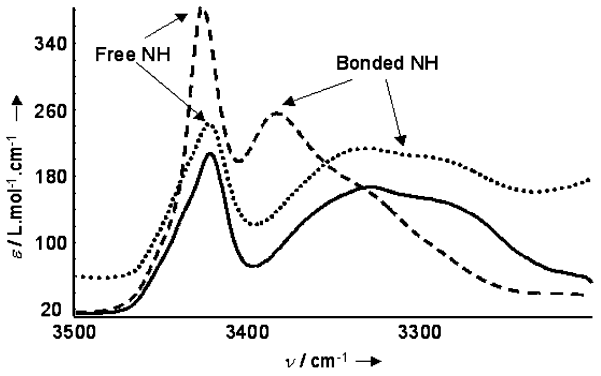


Fig. 3 FTIR spectra of **7** at 4.5×10^{-2} mol L^{-1} (–), **13** at 1.0×10^{-3} mol L^{-1} (. . .), and **5a** at 2.5×10^{-4} mol L^{-1} (—) in $CDCl_3$. These solutions exhibit a free NH fraction of $\sim$60%.

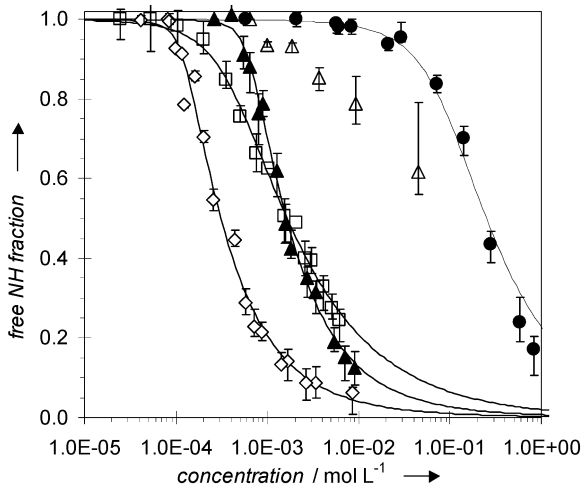
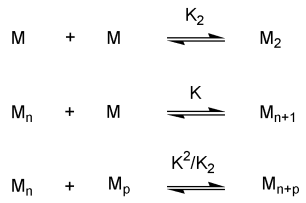


Fig. 4 Evolution of the fraction of free NH function *versus* bis-urea concentration in chloroform. Full curves are obtained by curve fitting with the model described in Scheme 7. See Schemes 1, 3 and 4 for molecular structures. **5a** (-◇-), **1** (-▲-), **13** (-□-), **7** (△), *N*-2-ethylhexyl-*N*′-2-methylphenylurea (●).



Equation 1 - Association equilibria of bis-ureas

M = free bis-urea
M_n = n associated bis-ureas - n > 1
M_p = p associated bis-ureas - p > 1

Scheme 7 Association equilibria of bis-ureas.

Table 3 Association constants (L mol^{-1}) in chloroform, at 20 °C, determined by curve fitting[6]

Compound	K_2	K	K/K_2	K^2/K_2
5a	110 ± 50	7400 ± 500	70 ± 45	5.1 ± 3.7 × 10^5
13	470 ± 20	2200 ± 300	4 ± 1	9.9 ± 2.2 × 10^3
1	21 ± 3	1400 ± 200	70 ± 20	1.0 ± 0.5 × 10^5
Mono-urea	2 ± 1	8 ± 1	4 ± 2	36 ± 10

urea than for the bis-ureas. Moreover, the self-assembly of **13** is much less cooperative than that of the low molecular weight compounds **1** and **5a**.

As the bis-urea concentration in chloroform increases, the self-assembly leads to larger and larger structures. Thus, the measurement of the resulting increase of viscosity of the solution is a good way to estimate the strength of the self-assembly. Viscosimetry measurements are reported on Fig. 5 and show that the viscosity of **5a** is much higher than that of **1** at a given concentration. This difference is in agreement with the much stronger self-assembly of **5a**. The PDMS bis-urea **13** is also more viscous than **1** at a given mass concentration in spite of its low bis-urea content. This may be explained first by the bifunctionality of **13**, which probably leads to the formation of a reversible network, because each bis-urea function is expected to take part in the formation of a multifunctional supramolecular chain. Moreover, the contribution of the macromolecular backbone of **13** is not negligible, as hinted by the evolution of the viscosity of the amino-functional precursor of **13**. Thus, **13** possesses very promising rheological properties, even for low bis-urea concentrations, thanks to its macromolecular structure and its bifunctionnality.

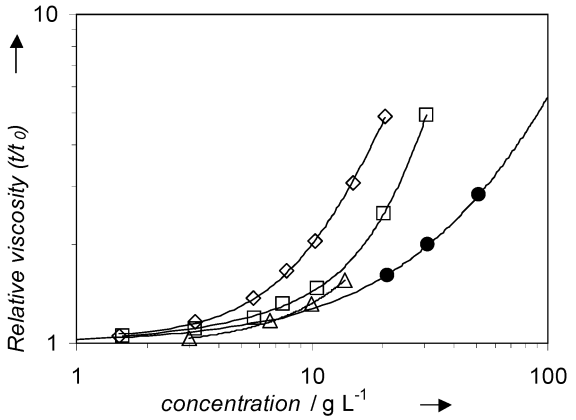


Fig. 5 Relative viscosity of chloroform solutions of **5a** (-◇-), **13** (-□-), **1** (-△-), and of the amino-functional precursor of **13** (-●-) *versus* concentration of the bis-urea at 25 ± 0.1 °C.

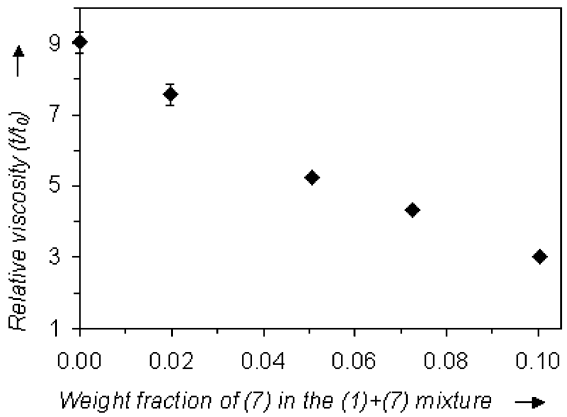


Fig. 6 Relative viscosity of a **7** + **1** solution in toluene *versus* the weight fraction of **7**, at a constant total weight concentration of 0.5 mg g^{-1} and at 25 ± 0.1 °C.

Finally, the bis-urea **7** forms solutions of very low viscosity. This is shown by monitoring the viscosity of a solution of **1** + **7** in toluene as a function of the ratio of **7**, for a constant total concentration (Fig. 6). This curve shows that the viscosity of the solution decreases rapidly when even small amounts of **7** are added. This bis-urea, possessing only 3 NH functions, one of which is sterically hindered, acts as a supramolecular chain stopper.

Conclusion

The selective reaction of an aromatic amine with an excess of 2,4-TDI yielded pure mono-isocyanate/mono-ureas for three different amines. ^{1}H NMR was used to identify the four possible products of the reaction and determine their proportion. With 4-*n*-butylaniline as the first amine, the first step is fully selective in dichloromethane or heptane when an appropriate excess of 2,4-TDI is used. Moreover, the excess of 2,4-TDI can be eliminated easily by filtration. Almost pure **2a** can be obtained in dichloromethane with a yield of about 70%, whereas a **2a** : **2b** mixture (85 : 15 molar ratio) is collected with a higher yield (>90%) in heptane.

The selective synthesis of these mono-isocyanate/mono-ureas is of great interest since it enables the development of interesting new compounds. First, the non-symmetrical bis-urea **5a** combines the solubility of aliphatic bis-ureas with the strong self-assembly of aromatic ones. Consequently, it self-assembles in chloroform more strongly than **1**. On the contrary, **7** self-assembles to a lesser extent than classical bis-ureas, because one of its NH functions is missing. Thus, this compound can be used as a supramolecular chain stopper of bis-ureas.

Moreover, liquid amino-functional PDMS are changed into rubbery solids when modified by bis-ureas, thanks to physical cross-linking.[13] More details on the mechanical properties of these materials will be given shortly.[19]

Furthermore, compound **13**, which consists of two bis-ureas grafted at each end of a PDMS chain, presents very interesting solution properties according to viscosity measurements in chloroform. These properties are related to the very good self-assembly of bis-ureas grafted on this compound, in spite of the bulkiness of the PDMS polymeric chain.

Experimental

Spectroscopic methods

^{1}H NMR spectra were recorded on a Brüker AC200© 200 MHz spectrometer at 20 °C. FTIR spectra were obtained with a Nicolet Avatar 320© spectrometer at 20 °C. Routine spectra were recorded from solutions evaporated on KBr disks. Quan-

titative FTIR was done in solution in KBr cells of 0.1–2.5 cm path length.

Quantitative FTIR spectroscopy

Mother chloroform solutions were prepared and diluted to reach low concentrations. They were prepared at room temperature with stirring for at least one night. After dilution of the mother solutions, daughter solutions were obtained, and stirred for 1 h or longer. Deuterated chloroform ($CDCl_3$) was used instead of hydrogenated chloroform ($CHCl_3$) as the latter absorbs too much in the NH region for diluted solutions. $CDCl_3$ was dried over molecular sieves (4 Å) 2 days before use. The solutions themselves were not dried because bis-ureas are absorbed on molecular sieves.

Capillary viscosimetry

Measurements were performed at 25 ± 0.1 °C with a Cannon–Manning (M108 n °25) semimicro viscometer. Solutions in chloroform (stabilised with amylenes) were filtered on a Millex PVDF filter (0.45 μm) before viscosity measurements, whereas toluene solutions were not filtered because of their high viscosity. No significant difference were observed when $CDCl_3$ was used instead of $CHCl_3$.[6] The toluene mother solution of **1** was prepared 1 week before use and heated 1 day at 50 °C to improve its homogeneity. The toluene mother solution of **7** was prepared 1 day before use at room temperature. Solutions of **1** and **7** at the same weight concentration were mixed to obtain the daughter solutions at different **1**:**7** ratios and constant concentration.

Syntheses

Analytical grade solvents were used and could be dried by refluxing over calcium hydride (dichloromethane, chloroform), or sodium (THF, heptane, toluene, dioxane) for several hours and then distilling.

2,4-Toluene diisocyanate (96% 2,4-TDI + 4% 2,6-TDI), 2-ethylhexylamine (98%), 2-butyl-2-ethyl-1,5-diaminopentane (98%), and 1,10-diaminodecane (97%), from Aldrich, as well as AMS-162, from ABCR, were used as received. 4-*n*Butylaniline (97%), 2,6-diethylaniline (98%), *N*-methylaniline (98%), 1,2-diaminoethane (99%), and 1,3-diaminopropane (99%), were purchased from Aldrich, and distilled before use. The synthesis of **1** was previously reported.[5]

Mono-isocyanate/mono-urea 2. A solution of BuA (13.2 mL, 0.084 mol) in dry dichloromethane (400 mL) was added over 8 h, at room temperature and under nitrogen, to a stirred solution of 2,4-TDI (60 mL, 0.419 mol) in dry dichloromethane (400 mL). The reaction mixture was stirred overnight. The white precipitate formed was then quickly filtered on a fritted funnel, rinsed with dry dichloromethane (3 × 50 mL), and dried under vacuum to afford 19.7 g of a white solid (73%). No further purification was done because of the moisture sensitivity of the product. The purity of the product was checked by ^{1}H NMR and by the two-step method described in Section 1. ^{1}H NMR (200 MHz, [D$_6$]DMSO dried over molecular sieve, 22 °C): δ = 8.73/8.64 (s, 2H, ArN*H*), 7.42 (s, 1H, Ar*H*), 7.34/7.12 [d, ^3J(H,H) = 8 Hz, 4H, Ar*H*], 7.13/7.06 (s, 2H, Ar*H*), 2.5 (t, 2H, ArCH_2), 2.22 (s, 3H, ArCH_3), 1.52 (m, 2H, ArCH$_2$CH_2), 1.31 (m, 2H, ArCH$_2$CH$_2$CH_2), 0.88 [t, ^3J(H,H) = 7 Hz, 3H, CH_3].

When the reaction is performed in dry heptane, the experimental conditions are the same. No purification is done when the reaction is conducted in dry THF. The 2,4-TDI : BuA ratio is adapted for each run, but the concentration of each reagent is unchanged.

Mono-isocyanate/mono-urea 3. The reaction procedure was identical to that of **2** and conducted at room temperature in dry dichloromethane. A white solid (89%) was collected by filtration. ^{1}H NMR (200 MHz, [D$_6$]DMSO dried over molecular sieve, 22 °C): δ = 8.88/7.76 (s, 2H, ArN*H*), 7.42 (s, 1H, Ar*H*), 7.13 (m, 5H, Ar*H*), 2.54 [q, ^3J(H,H) = 7 Hz, 4H, ArCH_2], 2.21 (s, 3H, ArCH_3), 1.12 [t, ^3J(H,H) = 7 Hz, 6H, ArCH$_2$CH_3].

Mono-isocyanate/mono-urea 4. A solution of *N*-methylaniline (6.0 mL, 0.056 mol) in dry heptane (200 mL) was added 2.5 h, at 0 °C and under nitrogen, to a stirred solution of 2,4-TDI (40 mL, 0.279 mol) in dry heptane (270 mL). The reaction mixture was stirred for several hours at 0 °C and allowed to warm up to room temperature overnight. The white precipitate formed was then quickly filtered on a fritted funnel, rinsed with dry heptane (3 × 50 mL), and dried under vacuum to afford 10.1 g of a white solid (64%). No further purification was performed because of the moisture sensitivity of the product. The purity of the product was only checked by the two-step ^{1}H NMR method described in Section 1.

Non-symmetrical bis-ureas: evaluation of the purity of the mono-isocyanate/mono-urea. Pure EHA (0.27 mL, 1.6 × 10^{-3} mol) was added to a stirred solution of **2** (0.5 g, 1.5 × 10^{-3} mol of mono-isocyanate/mono-urea expected) in dry THF (20 mL) in order to convert the remaining isocyanate functions of this product. After standing for one night, the end of the reaction was checked by the absence of the isocyanate band by FTIR (2270 cm^{-1}) and the crude product was collected after elimination of the solvent. ^{1}H NMR of this crude product was realised in order to identify the bis-ureas it contains and deduce the selectivity of the first step. ^{1}H NMR (200 MHz, [D$_6$]DMSO, 22 °C) between 1.1 and 2.6 ppm: δ = 2.5 (t, 2H, ArCH_2 and DMSO), 2.18 (s, 3H, ArCH_3 of **16**), 2.15 (s, 3H, ArCH_3 of **5b**), 2.11 (s, 3H, ArCH_3 of **5a**), 2.08 (s, 3H, ArCH_3 of **1**), 1.52 (m, 2H, ArCH$_2$CH_2), 1.27 (m, 11H, CH + CH_2 + ArCH$_2$CH$_2$CH_2).

Non-symmetrical bis-urea 5a. A solution of EHA (1.06 mL, 6.5 × 10^{-3} mol) in dry dioxane (20 mL) was added over 10 min, at room temperature and under nitrogen, to a stirred solution of **2** (run OC072: dichloromethane, 2,4-TDI : BuA = 5 : 1; 2.0 g, 6.2 × 10^{-3} mol) in dry dioxane (150 mL). A white precipitate appeared rapidly. After stirring overnight, the precipitate was filtered on a fritted funnel, rinsed 3 times with small quantities of dry dioxane, and dried under vacuum to afford 2.1 g of a white solid. The product was then recrystallised in ethyl acetate (final yield = 56%) to get rid of the remaining **5b**. ^{1}H NMR (200 MHz, [D$_6$]DMSO, 22 °C): δ = 8.55/8.38 (s, 2H, ArN*H*), 7.87 [d, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 7.54 (s, 1H, ArN*H*), 7.32 [d, ^3J(H,H) = 8 Hz, 2H, Ar*H*], 7.16 [dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 7.07/6.97 [d, ^3J(H,H) = 8 Hz, 3H, Ar*H*], 6.53 [t, ^3J(H,H) = 6 Hz, 1H, CH$_2$N*H*], 3.06 (m, 2H, NCH_2), 2.5 (t, 2H, ArCH_2), 2.11 (s, 3H, ArCH_3), 1.52 (m, 2H, ArCH$_2$CH_2), 1.27 (m, 11H, CH + CH_2 + ArCH$_2$CH$_2$CH_2), 0.88 [t, ^3J(H,H) = 7 Hz, 9H, CH_3]; ^{13}C-NMR (50 MHz, [D$_6$]DMSO, 22 °C): δ = 155.5/152.6 (*C*=O), 138.6/137.9/137.5/135.5/130.1/ 128.5/119.2/118.1/111.4/109.9 (Ar), 41.5 (N*C*H$_2$), 39.8 (*C*H), 34.3/33.4/30.6/28.6/23.8/22.6/21.8 (*C*H$_2$), 17.3 (Ar*C*H$_3$), 14.0/13.8/10.9 (*C*H$_3$); IR(KBr): ν = 3333/3281 (N–H), 1641 (C=O) cm^{-1}; anal. calcd (%) for $C_{27}H_{40}N_4O_2$ (452.6): C 71.65, H 8.91, N 12.38, O 7.07; found: C 71.22, H 8.98, N 12.29, O 7.62. **5a** contains a little water (~1% by weight), which increases the percentage of O compared to C and N.

Non-symmetrical bis-urea 6. The synthesis is derived from that of **5a** except that the reaction was conducted in dry chloroform and with the mono-isocyanate/mono-urea **3** at a

concentration of 2.3 g L^{-1}. At the end of the reaction, the precipitate was too thin to be filtered. After elimination of most of the solvent, the product was precipitated in heptane, filtered, washed thoroughly with heptane, dried under vacuum, and recrystallised in ethanol (yield = 63%). ^{1}H NMR (200 MHz, [D$_6$]DMSO, 22 °C): δ = 8.62 (s, 1H, ArN*H*), 7.83 [d, ^4J(H,H) = 2 Hz, 1H, Ar-*H*), 7.53/7.47 (s, 2H, ArN*H*), 7.17 [dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 7.10 (m, 3H, Ar*H*), 6.95 [d, ^3J(H,H) = 8 Hz, 1H, Ar*H*], 6.50 [t, ^3J(H,H) = 6 Hz, 1H, CH_2N*H*], 3.06 (m, 2H, NCH_2), 2.59 [q, ^3J(H,H) = 7 Hz, 4H, ArCH_2], 2.10 (s, 3H, ArCH_3), 1.27 (m, 9H, C*H* + CH_2), 1.13 [t, ^3J(H,H) = 7 Hz, 6H, ArCH$_2$CH_3], 0.88 (m, 6H, CH_3); anal. calcd (%) for $C_{27}H_{40}N_4O_2$ (452.6): C 71.65, H 8.91, N 12.38, O 7.07; found: C 71.40, H 8.97, N 12.32, O 7.70. **6** contains a little water (~1% by weight), which increases the percentage of O compared to C and N.

Non-symmetrical bis-urea 7. The synthesis is derived from that of **5a**, except that the mono-isocyanate/mono-urea used was **4** and that the reaction was conducted in dry THF. The crude product was collected by evaporation of the solvent, and then purified by silica gel column chromatography with chloroform–ethanol (96 : 4 v/v) as the eluent, precipitated from a concentrated chloroform solution in heptane, and recrystallised in an heptane–cyclohexane (78 : 22 v/v) mixture. A white product was obtained with a final yield of 11%. ^{1}H NMR (200 MHz, [D$_6$]DMSO, 22 °C): δ = 7.97 (s, 1H, ArN*H*), 7.79 [d, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 7.50 (s, 1H, ArN*H*), 7.32 (m, 5H, Ar*H*), 7.07 [dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 6.94 [d, ^3J(H,H) = 8 Hz, 1H, Ar*H*], 6.47 [t, ^3J(H,H) = 6 Hz, 1H, CH_2N*H*], 3.25 (s, 3H, NCH_3), 3.03 (m, 2H, NCH_2), 2.10 (s, 3H, ArCH_3), 1.25 (m, 9H, C*H* + CH_2), 0.86 (m, 6H, CH_3); ^{13}C NMR (50 MHz, [D$_6$]DMSO, 22 °C): δ = 155.3/154.8 (*C*=O), 144.3/138.0/129.4/129.2/126.2/ 125.6/120.3/113.9/112.6 (Ar), 41.6 (N*C*H$_2$), 39.3 (*C*H), 37.4 (N*C*H$_3$), 30.5/28.5/23.7/22.5 (*C*H$_2$), 17.3 (Ar*C*H$_3$), 14.0/10.8 (*C*H$_3$); anal. calcd (%) for $C_{24}H_{34}N_4O_2$ (410.6): C 70.21, H 8.35, N 13.65, O 7.79; found: C 69.82, H 8.35, N 14.05, O 8.03.

Tetra-urea 11. A solution of 1,10-diaminodecane (1.20 g, 6.98 × 10^{-3} mol) in dry THF (240 mL) was slowly added, at room temperature and under nitrogen, to a stirred solution of **2** (run OC084: heptane, 2,4-TDI : BuA ratio = 5 : 1; 4.51g, 13.95 × 10^{-3} mol) in dry THF (180 mL). An off-white solid precipitated quickly. After one night, FTIR spectroscopy revealed the absence of remaining isocyanate functions (2270 cm^{-1}). The precipitate was then filtered on a Buchner, rinsed with THF and dried under vacuum to give 5.4 g of a yellowish solid. The recrystallisation of this crude product in DMF at 80 °C led to a white product (17%). ^{1}H NMR (200 MHz, [D$_6$]DMSO, 22 °C): δ = 8.52/8.38 (s, 4H, ArN*H*), 7.85 (s, 2H, Ar*H*), 7.50 (s, 2H, ArN*H*), 7.32 [d, ^3J(H,H) = 8 Hz, 4H, Ar*H*], 7.11 [dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 2H, Ar*H*], 7.07/6,97 [d, ^3J(H,H) = 8 Hz, 6H, Ar*H*], 6.53 (m, 2H, CH_2N*H*), 3.1 (m, 4H, NCH_2), 2.5 (t, 4H, ArCH_2), 2.10 (s, 6H, ArCH_3), 1.48 (m, 4H, ArCH$_2$CH_2), 1.29 (m, 20H, CH_2 + ArCH$_2$CH$_2$CH_2), 0.88 [t, ^3J(H,H) = 7 Hz, 6H, CH_3); anal. calcd (%) for $C_{48}H_{66}N_8O_4$ (819.1): C 70.38, H 8.12, N 13.68, O 7.81; found: C 70.01, H 8.20, N 13.61, O 8.54. **11** contains a little water (~1% by weight), which increases the percentage of O compared to C and N.

Tetra-ureas 8, 9, 10. The synthesis of these tetra-ureas is derived from that of **11**.

***Compound* 8. 8** was recrystallised in DMF–AcOEt (50 : 50 v/v) at 80 °C (yield = 10%). No ^{1}H NMR was done because of the poor solubility of this product. Anal. calcd (%) for $C_{40}H_{50}N_8O_4$ (706.9): C 67.96, H 7.13, N 15.85, O 9.05; found: C 67.41, H 7.08, N 16.08, O 9.44.

***Compound* 9. 9** was recrystallised in DMF–AcOEt (50/ : 50 v/v) at 80 °C (10%). ^{1}H NMR (200 MHz, [D$_6$]DMSO, 22 °C): δ = 8.51/8.39 (s, 4H, ArN*H*), 7.85 [d, ^4J(H,H) = 2 Hz, 2H, Ar*H*], 7.61 (s, 2H, ArN*H*), 7.32 [d, ^3J(H,H) = 8 Hz, 4H, Ar*H*], 7.14 [dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 2H, Ar*H*], 7.07/6.98 [d, ^3J(H,H) = 8 Hz, 6H, Ar*H*], 6.61 [t, ^3J(H,H) = 6 Hz, 2H, CH_2N*H*], 3.16 (m, 4H, NCH_2), 2.5 (t, 4H, ArCH_2), 2.12 (s, 6H, ArCH_3), 1.59 (m, 2H, CH$_2$CH_2CH$_2$), 1.48 (m, 4H, ArCH$_2$CH_2), 1.31 (m, 4H, ArCH$_2$CH$_2$CH_2), 0.88 [t, ^3J(H,H) = 7 Hz, 6H, CH_3]; anal. calcd (%) for $C_{41}H_{52}N_8O_4$ (720.9): C 68.31, H 7.27, N 15.54, O 8.88; found: C 67.83, H 7.08, N 15.44, O 9.07.

***Compound* 10. 10** was collected by evaporation of THF instead of filtration because the precipitate was too thin to be filtered. Moreover, the reaction took 1 week instead of overnight. The compound was recrystallised in DMF–AcOEt (17 : 83 v/v) at 80 °C (yield 21%). ^{1}H NMR (200 MHz, [D$_6$]DMSO, 22 °C): δ = 8.51/8.37 (s, 4H, ArN*H*), 7.86/7.83 [d, ^4J(H,H) = 2 Hz, 2H, Ar*H*], 7.62/7.52 (s, 2H, ArN*H*), 7.32 [d, ^3J(H,H) = 8 Hz, 4H, Ar*H*], 7.18/7.15 [dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2.0 Hz, 2H, Ar*H*], 7.06/6.98 [d, ^3J(H,H) = 8 Hz, 6H, Ar*H*], 6.58/6.40 [t, ^3J(H,H) = 6 Hz, 2H, CH_2N*H*], 3.07/3.00 (m, 4H, NCH_2), 2.5 (t, 4H, ArCH_2), 2.13/2.10 (s, 6H, ArCH_3), 1.55 (m, 4H, ArCH$_2$CH_2), 1.31 (m, 16H, CH_2 + ArCH$_2$CH$_2$CH_2), 0.88/0.80 [t, ^3J(H,H) = 7 Hz, 12H, CH_3]; anal. calcd (%) for $C_{49}H_{68}N_8O_4$ (833.1): C 70.64, H 8.23, N 13.45, O 7.68; found: C 70.59, H 8.23, N 13.67, O 7.92.

Bis-urea grafted PDMS 14. The content of amine functions of PDMS-*g*-NH_2 was determined by ^{1}H NMR (200 MHz, $CDCl_3$, 22 °C). Indeed, the peak at 2.65 ppm corresponds to 2*n* protons, whereas the peak at 0.06 ppm corresponds to 6*m* + 3*n* protons if the chain ends are neglected (Scheme 5). Therefore, the ratio *m*/*n* can easily be determined.

A solution of the amino-functional PDMS precursor (AMS-162, 35.0 g, 19.8 × 10^{-3} molar equivalent of NH_2 functions) in dry THF (300 mL) was slowly added, at room temperature and under nitrogen, to a stirred solution of **2** (run OC127: heptane, 2,4-TDI : BuA ratio = 3 : 1;7.66 g, 23.7 × 10^{-3} mol) in dry THF (300 mL). After 1 week, the reaction mixture was concentrated down to about 200 mL by evaporation of the solvent and precipitated in 2 L of methanol. The precipitate was then filtered on a n° 2 fritted funnel, washed thoroughly with methanol and dried under vacuum to give 31.5 g (76% yield) of an off-white rubbery solid. ^{1}H NMR {200 MHz, $CDCl_3$–[D$_6$]DMSO (85 : 15 v/v), 22 °C}: δ = 8.14/8.03 (s, 2H, ArN*H*), 7.66 (s, 1H, Ar*H*), 7.26 (s, 1H, ArN*H*), 7.22 (m, 3H, Ar*H*), 6.97 [d, ^3J(H,H) = 8 Hz, 2H, Ar*H*], 6.90 [d, ^3J(H,H) = 8 Hz, 1H, Ar*H*], 6.10 (t, 1H, CH_2N*H*), 3.08 (m, 2H, NCH_2), 2.46 (t, 2H, ArCH_2), 2.08 (s, 3H, ArCH_3), 1.49 (m, 4H, CH$_2$CH_2CH$_2$ + ArCH$_2$CH_2), 1.24 (m, 2H, ArCH$_2$CH$_2$CH_2), 0.84 [t, ^3J(H,H) = 7 Hz, 3H, CH_3], 0.48 (m, 2H, SiCH_2), 0.01 (s, 139H, SiCH_3); IR(KBr): ν = 3318 (N–H), 1640 (C=O) cm^{-1}; anal. calcd (%): C 38.9, H 7.9, N 2.7; found: C 38.53, H 7.92, N 2.72.

PDMS-spaced tetra-ureas (12, 13) and other bis-urea grafted PDMS (15). They were synthesised and purified in the same way as **14**.

12. Molar ratio **2** : diamine = 4.4 (yield = 54%), ^{1}H NMR {200 MHz, $CDCl_3$–[D$_6$]DMSO (85 : 15 v/v), 22 °C}: δ = 8.09/7.99 (s, 2H, ArN*H*), 7.63 [d, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 7.26 (s, 1H, ArN*H*), 7.22/7.14 (m, 3H, Ar*H*), 6.97 [d, ^3J(H,H) = 8 Hz, 2H, Ar*H*], 6.90 [d, ^3J(H,H) = 8 Hz, 1H, Ar*H*], 6.05 [t, ^3J(H,H) = 6 Hz, 1H, CH_2N*H*], 3.10 (m, 2H, NCH_2), 2.46 [t, ^3J(H,H) = 7 Hz, 2H, ArCH_2], 2.07 (s, 3H, ArCH_3), 1.48

(m, 4H, $CH_2CH_2CH_2$ + $ArCH_2CH_2$), 1.26 (m, 2H, $ArCH_2CH_2CH_2$), 0.84 [t, ^3J(H,H) = 7 Hz, 3H, CH_3], 0.49 (m, 2H, $SiCH_2$), 0.00 (s, 146H, $SiCH_3$); IR(KBr): ν = 3304 (N–H), 1638 (C═O) cm^{-1}; anal. calcd (%): C 38.5, H 7.9, N 2.6; found: C 39.11, H 8.14, N 2.73.

13. Molar ratio **2**:diamine = 6.6 (yield = 86%), ^{1}H NMR {200 MHz, $CDCl_3$–[D_6]DMSO (85:15 v/v), 22 °C}: δ = 8.07/7.94 (s, 2H, ArN*H*), 7.62 [d, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 7.35 (s, 1H, ArN*H*), 7.27/6.97 (m, 6H, Ar*H*), 5.92 [t, ^3J(H,H) = 6 Hz, 1H, CH_2NH], 3.09 (m, 2H, NCH_2), 2.45 (t, 2H, $ArCH_2$), 2.09 (s, 3H, $ArCH_3$), 1.47 (m, 4H, $CH_2CH_2CH_2$ + $ArCH_2CH_2$), 1.25 (m, 2H, $ArCH_2CH_2CH_2$), 0.82 [t, ^3J(H,H) = 7 Hz, 3H, CH_3], 0.48 (m, 2H, $SiCH_2$), −0.01 (s, 1160H, $SiCH_3$); IR(KBr): ν = 3303 (N–H), 1638 (C═O) cm^{-1}; anal. calcd (%): C 33.3, H 8.1, N 0.4; found: C 33.28, H 8.15, N 0.43.

15. Molar ratio **2**:amine = 1.2 (yield = 69%), ^{1}H NMR {200 MHz, $CDCl_3$–[D_6]DMSO (85:15 v/v), 22 °C}: δ = 7.39/7.24 (m, 8H, Ar*H* + ArN*H*), 6.89 [d, ^3J(H,H) = 8 Hz, 1H, Ar*H*], 6.32 (s, 1H, ArN*H*), 6.10 (t, 1H, CH_2NH), 3.22 (m, 3H, NCH_3), 3.04 (m, 2H, NCH_2), 2.18 (s, 3H, $ArCH_3$), 1.43 (m, 2H, $CH_2CH_2CH_2$), 0.44 (m, 2H, $SiCH_2$), 0.00 (s, 141H, $SiCH_3$); IR(KBr): ν = 3429/3346/3290 (N–H), 1637 (C═O) cm^{-1}; anal. calcd (%): C 37.7, H 7.8, N 2.7; found: C 37.33, H 7.92, N 2.56.

Symmetrical bis-urea 16. This symmetrical bis-urea could have been obtained directly by reacting 2,4-TDI with 2 equiv. of BuA; but the synthesis described here consists in reacting **2** with BuA. A solution of BuA (0.22 mL, 1.4×10^{-3} mol) in dry THF (10 mL) was added over 10 min, at room temperature and under nitrogen, to a stirred solution of **2** (run OC072: dichloromethane, 2,4-TDI:BuA = 5:1; 0.220 g, 6.8×10^{-4} mol) in dry THF (20 mL). A white precipitate appeared more than 3 h after addition of the amine. After 11 days at room temperature, the reaction was complete according to the absence of isocyanate functions (2270 cm^{-1} in FTIR spectroscopy). The precipitate was filtered on a fritted funnel, rinsed 3 times with small quantities of THF, and dried under vacuum to afford a white solid (70%). It was not recrystallised because of its poor solubility. ^{1}H NMR (200 MHz, [D_6]DMSO, 22 °C): δ = 8,96/8.61/8.42 (s, 3H, ArN*H*), 7.92 [d, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 7.84 (s, 1H, ArN*H*), 7.37/7.32 [d, ^3J(H,H) = 8 Hz, 4H, Ar*H*], 7.19 [dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H, Ar*H*], 7.09/7.07 [d, ^3J(H,H) = 8 Hz, 4H, Ar*H*], 7.03 (m, 1H, Ar*H*), 2.5 (t, 4H, $ArCH_2$), 2.17 (s, 3H, $ArCH_3$), 1.52 (m, 4H, $ArCH_2CH_2$), 1.29 (m, 4H, $ArCH_2CH_2CH_2$), 0.89 [t, ^3J(H,H) = 7 Hz, 6H, CH_3].

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