



Self-assembly in solution of a reversible comb-shaped supramolecular polymer

François Boué, Sandrine Pensec, Nicolas Nouvela, Audrey Guilleman,
Costantino Creton, Laurent Bouteiller

► To cite this version:

François Boué, Sandrine Pensec, Nicolas Nouvela, Audrey Guilleman, Costantino Creton, et al.. Self-assembly in solution of a reversible comb-shaped supramolecular polymer. *International Journal of Biological Macromolecules*, 2010, 43, pp.2529-2534. 10.1021/ma901709e . hal-00482118v1

HAL Id: hal-00482118

<https://hal.science/hal-00482118v1>

Submitted on 9 May 2010 (v1), last revised 13 May 2010 (v2)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Self-assembly in solution of a reversible comb-shaped supramolecular polymer

Sandrine Pensec^a, Nicolas Nouvel^a, Audrey Guilleman^a, Costantino Creton^b, François Boué^c, Laurent Bouteiller^{a}*

^a UPMC Université Paris 06, UMR 7610, Chimie des Polymères, F-75005 Paris, France, and CNRS, UMR 7610, Chimie des Polymères, F-75005 Paris, France

^b Physico-chimie des Polymères et des Milieux Dispersés, UMR 7615, UPMC-CNRS-ESPCI, 10 rue Vauquelin 75231 Paris cedex 05, France

^c Laboratoire Léon Brillouin, UMR 12 CNRS-CEA, 91191 Gif-sur-Yvette Cedex, France

* Corresponding author. E-mail: laurent.bouteiller@upmc.fr

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT. We report a single step synthesis of a polyisobutene with a bis-urea moiety in the middle of the chain. In low polarity solvents, this polymer self-assembles by hydrogen bonding to form a comb-shaped polymer with a central hydrogen bonded backbone and polyisobutene arms. The comb backbone can be reversibly broken, and consequently, its length can be tuned by changing the solvent, the concentration or the temperature. Moreover, we have proved that the bulkiness of the side-chains have a strong influence on both the self-assembly pattern and the length of the backbone. Finally, the density of arms can be reduced, by simply mixing with a low molar mass bis-urea.

Introduction

Supramolecular polymers are chains of small molecules held together through reversible non-covalent interactions.¹⁻³ The dynamic character of such weak interactions is responsible for the appearance of new properties, as compared to those of usual covalent polymers. For example, these materials can display thermoreversible polymer-like properties (such as visco-elasticity), or even form self-healing elastomers.⁴

It is well known in the field of macromolecular science that the architecture of a polymer can have a strong effect on its properties. Therefore, there is a strong incentive to design and investigate the properties of supramolecular polymers with various architectures, such as macrocyclic,⁵⁻¹⁰ star-shaped,¹¹⁻¹³ hyperbranched,¹⁴ or reversibly cross-linked.^{4,15-18} In this respect, comb-shaped supramolecular polymers¹⁹ were among the first supramolecular polymers to be described and their original properties have been well appreciated.^{20,21} However, all these comb-shaped supramolecular polymers consist of a covalent backbone decorated with side-chains that are reversibly linked to the backbone (Figure 1a); the reverse situation, where the backbone itself is dynamic (Figure 1b) has not been reported previously.

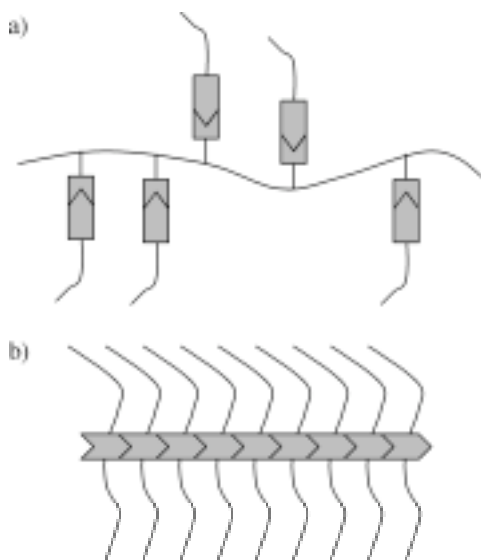


Figure 1. Schematic structure of a comb-shaped supramolecular polymer with a covalent (a) or a dynamic (b) backbone.

To build such a comb-shaped supramolecular polymer with a dynamic backbone, we chose the bis-urea synthon as self-assembling unit, because of its strong self-association and its straightforward synthetic accessibility. Moreover, we have previously reported that bis-urea based low molar mass compound

(**EHUT**, Figure 2) self-assembles in non-polar solvents into two distinct dynamic supramolecular polymer structures.²² Depending on solvent, concentration and temperature, either long hydrogen bonded filaments with a single molecule in the cross-section, or even longer and more rigid tubes with three molecules in the cross-section are formed (Figure 3a). This competition between two different self-assembled structures opens the possibility to design responsive systems.

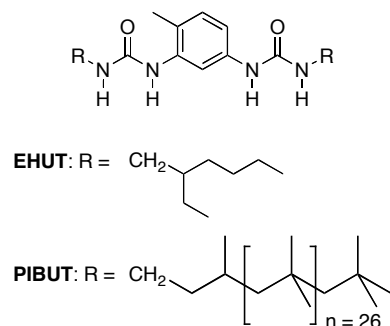


Figure 2. Structure of bis-ureas.

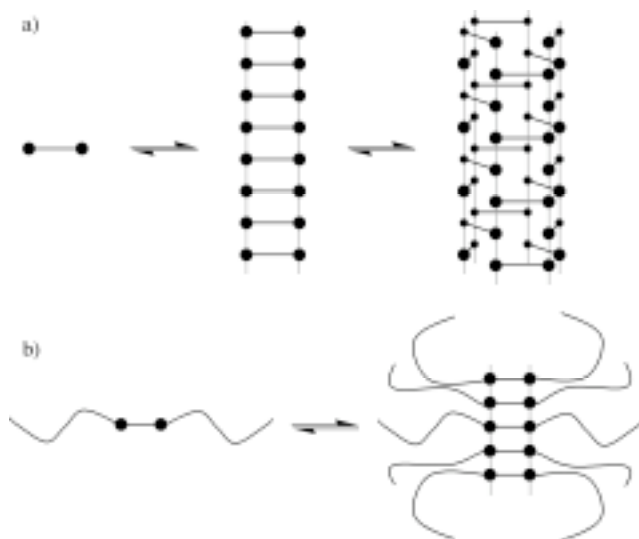


Figure 3. Schematic supramolecular arrangements for **EHUT** (a) and **PIBUT** (b). Hydrogen bonds are represented by dotted lines connecting the urea functions. For more detailed **EHUT** models, see reference 23.

Polyisobutene, which was often used in the context of hydrogen bonded supramolecular assemblies,²⁴⁻²⁶ was chosen as the polymer side-chain because of its good solubility and absence of interfering hydrogen

bonding groups. Therefore, we report in the present article the characterization of solutions of macromolecular bis-urea **PIBUT** (Figure 2).

Experimental Section

Synthesis. The synthesis of **EHUT** was described previously.²⁷ Non functional polyisobutene **PIB** ($M_n = 2800$ g/mol, $M_w/M_n = ??$) was obtained from Aldrich. Synthesis of 2,4-bis-(polyisobuteneureido)toluene **PIBUT**: 2,4-toluenediisocyanate (98% from Aldrich) (3.5 mL, 24.5 mmol) was added, at room temperature and under nitrogen to a stirred solution of amino functional polyisobutylene (Kerocom PIBA, 65% solution in hydrocarbon, from BASF) (150 g) in dry THF (90 mL). After 24h, the reaction mixture was precipitated under vigorous stirring into 1L of ethyl acetate. A viscous oil decanted. After 24h, the upper phase was eliminated and the product was dried under vacuum for one month, to give a rubbery solid **PIBUT** (47.5 g, 59% yield). ¹H NMR (200MHz, CDCl₃/d₆-DMSO (90/10 v/v)) see Supporting Information: δ (ppm) = 7.73 (s, 1H, Ar-NH), δ = 7.35 (s, 1H, Ar-H), δ = 7.06 (s, 1H, Ar-H), δ = 6.93 (s, 1H, Ar-H), δ = 6.80 (s, 1H, Ar-NH), δ = 5.73 (s, 1H, CH₂-NH), δ = 5.47 (s, 1H, CH₂-NH), δ = 2.99 (m, 4H, CH₂-NH), δ = 1.95 (s, 3H, Ar-CH₃), δ = 1.5-0.5 (m, 515H, CH₂-CH(CH₃)-CH₂ and (-C(CH₃)₂-CH₂)_n and -C(CH₃)₃). $M_{n,NMR} = 3430$ g/mol. ¹³C NMR (75MHz, CDCl₃/d₆-DMSO (90/10 v/v)): δ (ppm) = 155.2 (C=O), δ = 137.7/137.0/129.5/119.5/112.1/110.7 (Ar), δ = 58.7 (-C(CH₃)₂-CH₂)_n, δ = 57.2 (CH₂-CH(CH₃)-CH₂), δ = 37.1 (-C(CH₃)₂-CH₂)_n, δ = 34.8 (N-CH₂-CH₂), δ = 31.7 (-C(CH₃)₃), δ = 31.6 (-C(CH₃)₃), δ = 30.4 (-C(CH₃)₂-CH₂)_n, δ = 25.7 (CH₂-CH(CH₃)-CH₂), δ = 22.0 (CH₂-CH(CH₃)-CH₂), δ = 16.6 (Ar-CH₃). SEC (THF, polystyrene calibration): $M_n = 2700$ g/mol, $M_w/M_n = 1.3$. MALDI-TOF (dithranol, Na⁺): $M_{exp(n=9)} = 1493.24$ g/mol, $M_{th(n=9)} = 1493.44$ g/mol. DSC (2°C/min, N₂): $T_g = -73^\circ\text{C}$, $T_m = 52^\circ\text{C}$.

Viscometry. Solvents were used as received. Solutions were prepared by shaking at room temperature for several hours, and filtered (0.45 μ m). Measurements were performed with an automatic Anton-Paar AMVn viscometer (capillary internal diameter 1.8 mm; ball diameter 1.5 mm), tilted at an angle of 20°, and repeated 6 times.

IR spectroscopy. Infrared spectra were recorded on a Nicolet Avatar 320 spectrometer in a KBr cell of 0.1 cm path length. The temperature was controlled with a heating device (P/N21525) from Specac.

Consecutive measurements were separated by at least 10 minutes, to allow for thermal equilibration. Thermal expansion of the solutions was not corrected.

SANS. Measurements were made at the LLB (Saclay, France) on the Paxy instrument, at three distance-wavelength combinations to cover the $3 \cdot 10^{-3}$ to $0.3 \text{ \AA}^{-1}$ q-range, where the scattering vector q is defined as usual, assuming elastic scattering, as $q=(4\pi/\lambda)\sin(\theta/2)$, where θ is the angle between incident and scattered beam. Sample diaphragm was 7.6mm. Collimation was achieved by a diaphragm of 22mm for a sample – detector distance of 1.5m, or 16mm for a sample – detector distance of 3.2 and 6.7m. Data were corrected for the empty cell signal and the solute and solvent incoherent background. A light water standard was used to normalize the scattered intensities to cm^{-1} units.

ITC. Chloroform (99% Acros, stabilized with amylene) was used as received. Solutions were prepared by shaking at room temperature for several hours. Heats of dissociation were measured using a MicroCal VP-ITC titration microcalorimeter.²⁸ The sample cell (1.435 cm^3) was filled with chloroform. A relatively concentrated bis-urea solution in the same solvent was placed in a 0.295 cm^3 continuously stirred (270rpm) syringe. A first $2\mu\text{L}$ 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 ($3\mu\text{L}$) were automatically injected into the sample cell every 200s, until the syringe was empty.

DSC. Heptane (99% Carlo Erba) was used as received. Thermograms were measured using a N-DSC III instrument from CSC.^{28b} The reference cell was filled with pure solvent and the sample cell (0.3 mL) with the bis-urea solution. The capillary cells were not capped, and a constant pressure of $6 \cdot 10^5 \text{ Pa}$ was applied. A baseline scan (solvent in both reference and sample cells) was systematically performed in identical conditions and subtracted from the sample scan. Transition temperature (T^{**}) was measured as the average of heating and cooling scans, at a scan rate of $1^\circ\text{C}/\text{min}$.

Results and Discussion

1. Synthesis. The bis-urea **PIBUT** was obtained by reacting an excess of amino-functional polyisobutene with 2,4-toluenediisocyanate. After purification by precipitation, the structure of the product was identified by ^1H and ^{13}C NMR spectroscopy. Size exclusion chromatography (SEC) showed a

monomodal distribution with a relatively low polydispersity index ($I_p = 1.3$), proving that the excess of amino-functional polyisobutene has been washed off (Figure 4). The degree of polymerization was calculated from NMR signals, using the integration ratio between methylene protons of the repeat unit at 0.93 ppm and an aromatic proton at 7.35 ppm. The total degree of polymerization was found to be 50 (ie $n = 25$), corresponding to $M_n = 3430\text{g/mol}$. The structure of **PIBUT** was also confirmed by the agreement between experimental molar masses measured by MALDI-TOF mass spectrometry and the theoretical molar mass.

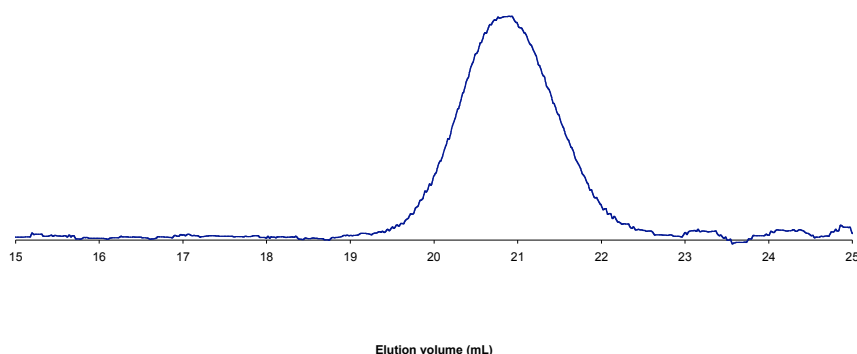


Figure 4. SEC trace (THF, refractive index detection) for **PIBUT**. UV, PIB-NH₂ ??

2. Viscosity of solutions. Whether **PIBUT** self-assembles in solution can be qualitatively probed through the influence of solvent on the viscosity of **PIBUT** solutions. Figure 5 shows that the viscosity of **PIBUT** solutions increases significantly in the order tetrahydrofuran < chloroform < toluene < heptane. In contrast, solutions of **PIB** (a non hydrogen bonded polyisobutene of similar molar mass) have roughly the same viscosity, whatever the solvent. This shows that the variation of viscosity for **PIBUT** solutions is not related to any potential difference in polyisobutene backbone solvation, but rather to the influence of solvent on the strength of intermolecular hydrogen bond. The similar viscosity of **PIBUT** and **PIB** in tetrahydrofuran, means that **PIBUT** does not form any supramolecular assembly in this hydrogen bonding solvent. However, in a less competitive solvent such as chloroform, hydrogen bonds between urea

functions can occur, as confirmed by FTIR spectroscopy (see below). Moreover, decreasing the polarity (from chloroform to toluene and to heptane) strengthens hydrogen bonds and increases the viscosity.

Furthermore, it is of interest to compare the viscosity of **PIBUT** solutions to the viscosity of the low molar mass bis-urea **EHUT**. In tetrahydrofuran, where self-assembly is negligible, **PIBUT** is more viscous than **EHUT**, due to its one order of magnitude larger molar mass. In hydrocarbon solvents however, the ranking is reversed: **PIBUT** forms viscous solutions, whereas **EHUT** forms viscoelastic gels due to the entanglement of very long hydrogen bonded assemblies.^{27,29,30} The comparatively much stronger effect of the solvent on **EHUT** viscosity than on **PIBUT** viscosity is an indication that the supramolecular assemblies formed are significantly different.

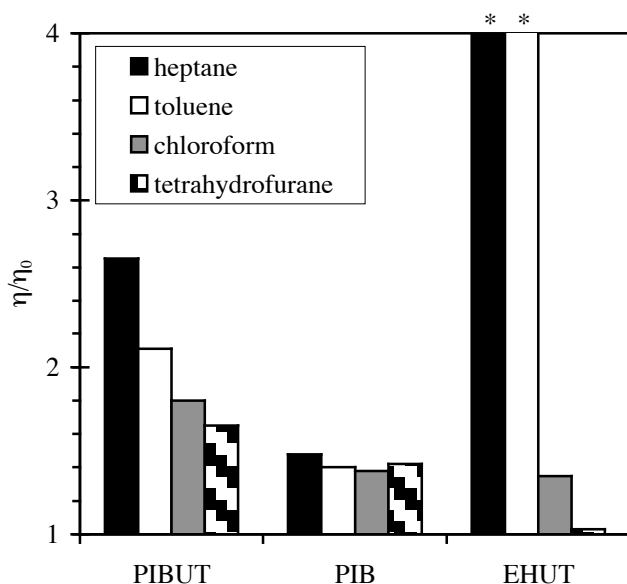


Figure 5. Relative viscosity (η/η_0) measured at 25 °C, for solutions of **EHUT** (24mM, 10g/L), **PIB** (24mM, 67g/L) and **PIBUT** (24mM, 82g/L) in several solvents. * The viscosity of **EHUT** solutions in heptane and toluene is much higher ($\eta/\eta_0 \gg 100$).³¹

3. Characterization of the macromolecular structure. The structure of the assembly formed by **PIBUT** was further characterized by SANS in d_8 -toluene solution. Figure 6 shows that the scattered intensity reaches a plateau value at low q , which means that the scattering objects are of limited size. At high q , the usual q^{-2} dependence for Gaussian chains is found, but in the intermediate q range, a decrease

stronger than q^{-2} is present and can be emphasized in a Kratky representation (inset of Figure 6). This maximum in Kratky representation is characteristic for branched structures. Therefore, a quantitative fit of the data was attempted with the form factor of a Gaussian comb.³² Four parameters are necessary to describe such a comb: its molar mass (M), its radius of gyration (R_g), the number of arms per comb (f), and the relative extension of the backbone (λ). In the present case, the number of arms is directly linked to the comb molar mass, so that only three independent parameters were adjusted to fit the data (see details in Supporting Information). Figure 6 shows that an excellent fit is obtained with the following parameter values: $M = 30000\text{g/mol}$ (and thus $f = 17$ branches per comb); $R_g = 71\text{\AA}$; and $\lambda = 0.15$. A fit was also attempted with the form factor for a Gaussian star, but the fit is not as good (see Supporting Information). Therefore, at this concentration, **PIBUT** can be considered to form comb shaped supramolecular polymers in solution. The relatively small size of the comb (on average 8.5 **PIBUT** per comb) is in part due to the low concentration of the experiment (11g/L, 3.2mM).

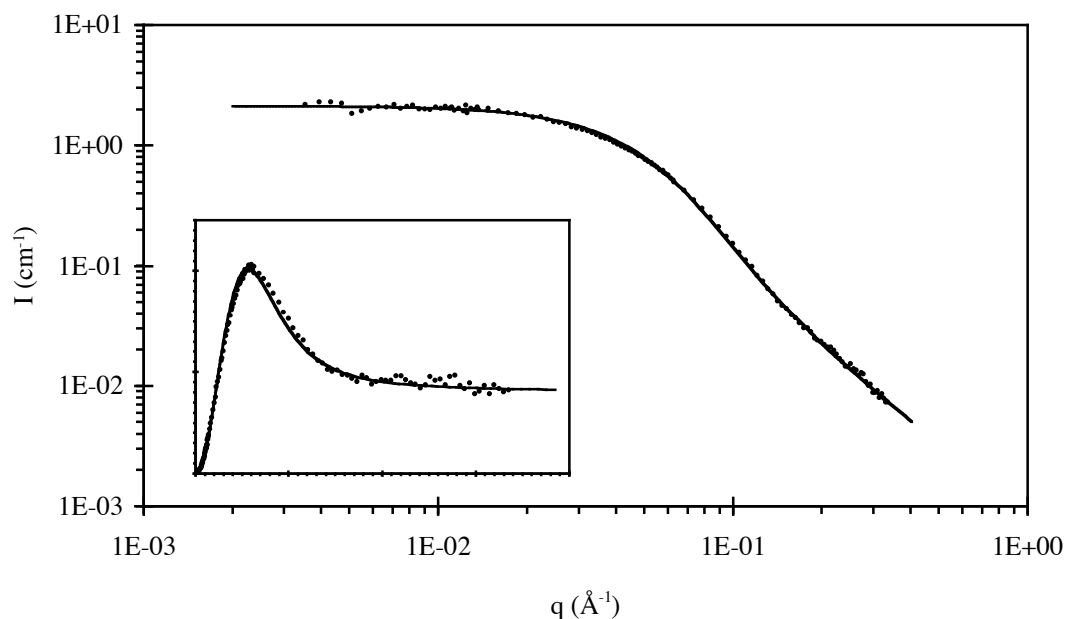


Figure 6. SANS intensity (I) versus scattering vector (q) for a solution of **PIBUT** in d_8 -toluene at 11g/L (3.2mM) and 22°C. The inset shows the same data in a q^2I versus q linear plot. The plain curve is a fit according to a model for comb-shaped polymers (see text and Supporting Information).

These SANS data give us the overall shape of the assemblies, but not the local structure of the comb backbone. Based on previous data on **EHUT** and related bis-ureas,^{22b,c} it is known that two different supramolecular arrangements can be envisaged: either hydrogen bonded filaments with a single molecule in the cross-section, or thicker and more rigid tubes with three molecules in the cross-section (Figure 3a). It was previously shown that FTIR spectroscopy can be used to discriminate between the two supramolecular structures,^{22b} because the shape of the hydrogen bonded N-H vibration band is related to the exact hydrogen bonding pattern of the urea groups. Figure 7 shows the values of the ratio characterizing this band shape: a high value (c.a. 1.3) is attributed to the thick tubular structure, whereas a low value (c.a. 1.1) is attributed to the thin filament structure. Apparently, the supramolecular structure formed by **PIBUT** does not depend on the solvent nature: in all solvents tested, the same thin filament structure is obtained. This is in sharp contrast to the behavior of low molar mass bis-ureas such as **EHUT**. The relative instability of the thick tubular structure for **PIBUT** is probably due to a steric reason, because for a given backbone length, three times as many side-chains have to be accommodated in the tubular structure compared to the filament structure.

Therefore, a reasonable model for the self-assembly of **PIBUT** in low polarity solvents is depicted in Figure 3b: comb-shaped objects are formed with a backbone made of a single filament of bis-urea moieties, and with polyisobutene side-chains.

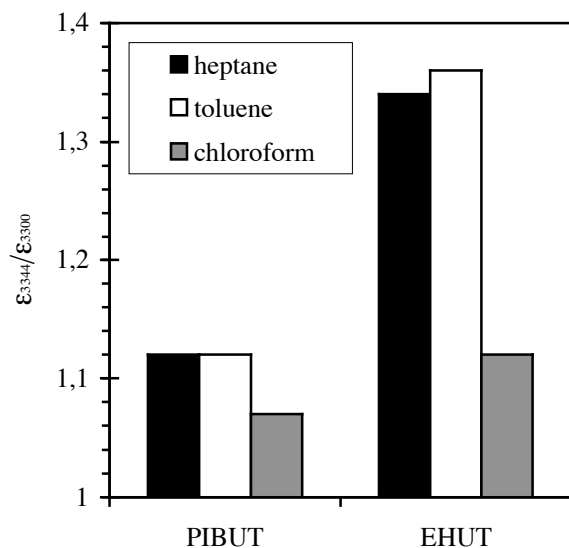


Figure 7. Ratio of FTIR absorbances at 3344 and 3300 cm^{-1} for 12mM solutions of **EHUT** or **PIBUT** (25°C).

4. Macromolecular effect on association strength. Due to the reversibility of hydrogen bonds, the average length of these comb backbones can be expected to depend on parameters such as the solvent, the concentration and the temperature. Moreover, the steric bulk of the polyisobutene side-chains can be expected to be responsible for a weaker association than in the case of a low molar mass analog. The extent of this effect was studied by FTIR spectroscopy and isothermal titration calorimetry (ITC). Chloroform was chosen as the solvent, because in this solvent, both **EHUT** and **PIBUT** self-assemble into filaments with the same structure. Thus, any difference observed should be ascribed to a difference in association strength. Figure 8 shows the FTIR spectra of **EHUT** and **PIBUT** at the same molar concentration in chloroform. In both cases, the hydrogen bonded N-H vibration band ($3340\text{--}3280\text{cm}^{-1}$) is the main band, but a weak free N-H vibration band ($3450\text{--}3430\text{cm}^{-1}$) can be detected. The intensity of this band is larger for **PIBUT** than for **EHUT** meaning that hydrogen bonding of the bis-urea moiety in **PIBUT** is indeed weaker than for **EHUT**. To quantitatively describe this effect over a large concentration range, it is useful to consider an association model describing the relative stability of monomer, dimer and all possible oligomers. The two-constant association model shown on Figure 9 was shown to adequately describe the

assembly behavior of **EHUT** in chloroform.³¹ Moreover, the association constants in this model were shown to be accessible through an ITC experiment, when a relatively concentrated solution is diluted, and the corresponding heat of dissociation is measured.^{28a} Figure 10 shows such an enthalpogram: the dissociation of **PIBUT** occurs over a much broader concentration range than the dissociation of **EHUT**, which means that the formation of **PIBUT** supramolecular polymers is much less cooperative. Both curves can be fitted by the association model of Figure 9. The parameter values derived from the fit (Table 1) show that the dimerization step is not significantly affected by the bulk of the **PIBUT** side-chains, but that the subsequent steps are disfavored. This increased sensitivity to steric crowding for longer oligomers is not surprising and is the reason for the reduced cooperativity of **PIBUT** self-assembly. The knowledge of the association constants makes it possible to compute the molar mass of the comb-shaped supramolecular polymer over the whole concentration range (Figure 11). Figure 11 shows that the formation of the **PIBUT** combs occurs only above 10^{-3} mol/L in chloroform and that their growth is more sluggish than for **EHUT** supramolecular polymers. However, high molar masses are nevertheless reached at reasonable concentrations.

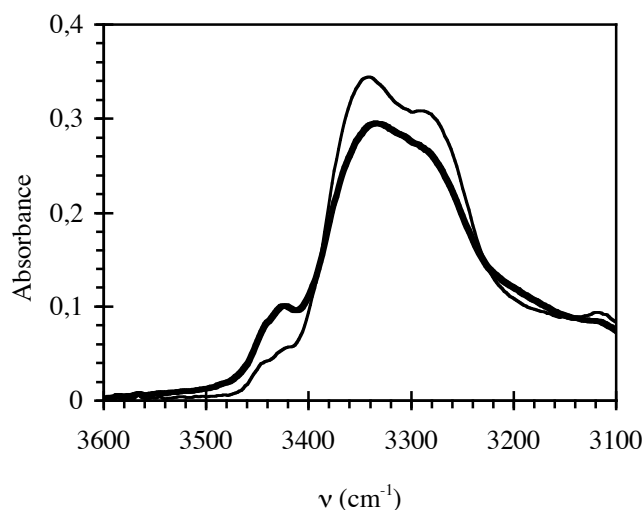


Figure 8. FTIR spectra for 12mM solutions of **EHUT** (plain) or **PIBUT** (bold) in chloroform (25°C).

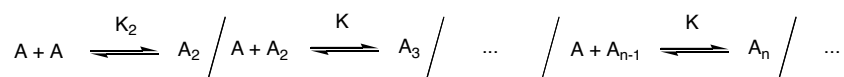


Figure 9. Association scheme describing the formation of a supramolecular polymer (A = monomer, A_n = oligomer of degree of polymerization n).

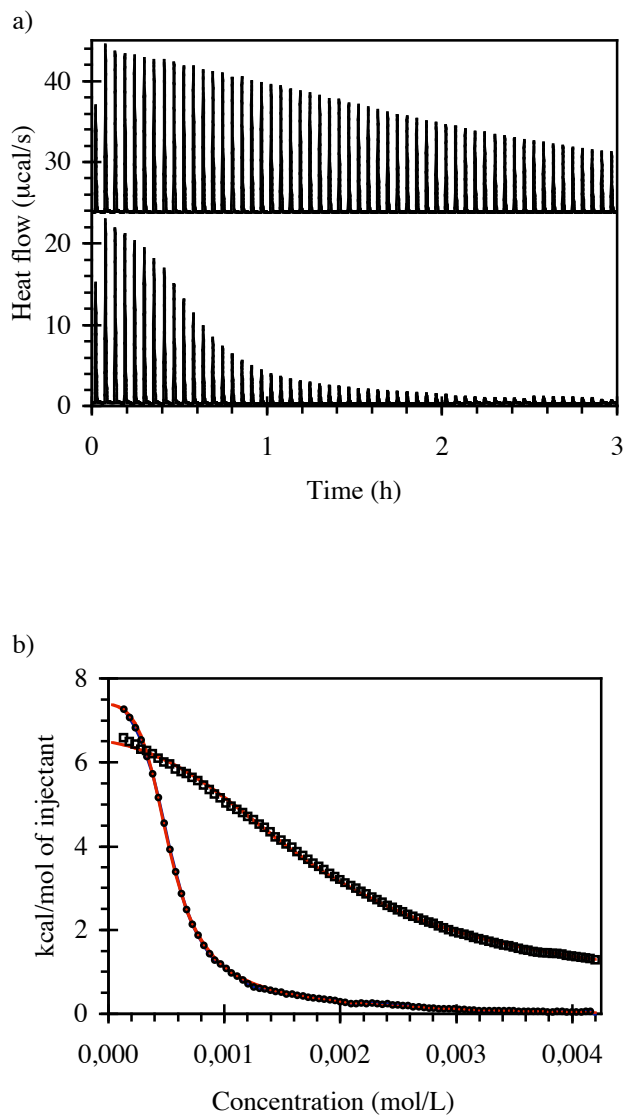


Figure 10. (a) Heat effect produced by injecting 3- μL aliquots of a 24mM chloroform solution of **PIBUT** (upper curve) or **EHUT** (lower curve) into chloroform (20°C). (b) Corresponding enthalpograms; the plain curves are the fits obtained with the model of Fig. 9 and the parameter values of Table 1.

Table 1 Values for the parameters of the association scheme in Fig. 9, deduced from the ITC data of Fig. 10.

	ΔH_{assoc}	K_2	K
	(kJ/mol)	(L/mol)	(L/mol)
EHUT	-35	58	1700
PIBUT	-35	50	390

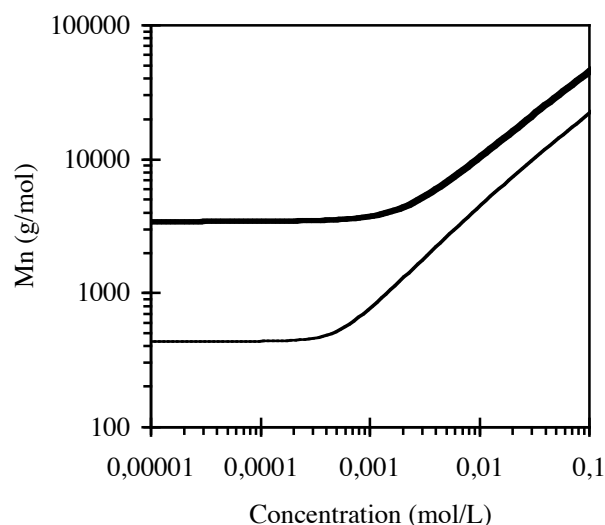


Figure 11. Calculated number average molar mass for **EHUT** (plain curve) or **PIBUT** (bold curve) supramolecular polymer solutions in chloroform (20°C).

5. Comb-shaped copolymers. The presence of the same associating bis-urea moiety in **PIBUT** and **EHUT** makes it potentially straightforward to form copolymers: simply mixing two solutions should afford a (probably statistical) copolymer.³³ In the present case, comb-shaped copolymers with an adjustable number of arms should be obtained. To check this possibility, heptane was chosen as solvent because the association is stronger than in the other more polar solvents. Moreover, the influence of temperature was monitored, because in heptane, **EHUT** self-assembles into filaments (above 75°C) or tubes (below 75°C), thus enabling to probe the possible copolymerization between **EHUT** and **PIBUT**, either in the filament or in the tube form. Figure 12 shows the result of variable temperature FTIR measurements on solutions of

different compositions. The **EHUT** solution shows the expected transition between the low temperature tube and high temperature filament forms. The **PIBUT** solution shows no transition in the same temperature range, showing that only the filament form is stable, even down to -62°C . However, the equimolar mixture of the two solutions shows a transition temperature close to room temperature. To confirm this result and improve the precision of the transition temperature measurements, DSC experiments were performed on solutions of various compositions (Figure 13). The DSC results are in perfect agreement with the FTIR data. The fact that the transition temperature is affected by the composition proves that the two bis-ureas interact together and form some mixed assemblies, because if **EHUT** and **PIBUT** did not interact at all, then the transition temperature of **EHUT** would remain constant.³⁴ Moreover, the fact that the transition temperature decreases when **PIBUT** is added, means that **PIBUT** interacts more favorably with the filament form of **EHUT** than with the tube form of **EHUT**. Thus, it seems reasonable to expect that comb-shaped copolymers with a thin filament backbone structure and an adjustable proportion of arms are formed at composition and temperature values corresponding to the region lying above the curve in Figure 13. However, the situation is less clear in the region lying below the curve: we have no indication that **PIBUT** interacts with the tube form of **EHUT**. Therefore, the two components do not necessarily form mixed tubes. It is possible that in this region, tubes composed mainly of **EHUT** coexist with filaments composed mainly of **PIBUT**. This situation would explain why the step of the transition for the 50/50 mixture is about half that for **EHUT** (Figure 12). However, further experiments will be needed to clarify this last point.

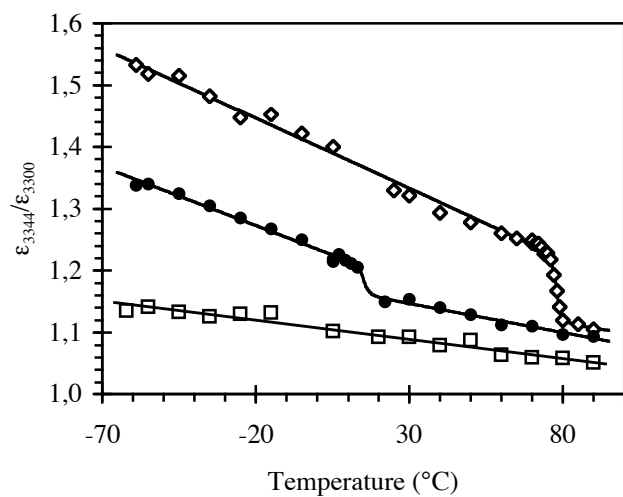


Figure 12. Ratio of absorbances at 3344 and 3300cm⁻¹ for 12mM heptane solutions of **EHUT** (◇), **PIBUT** (□), or their equimolar mixture (●).

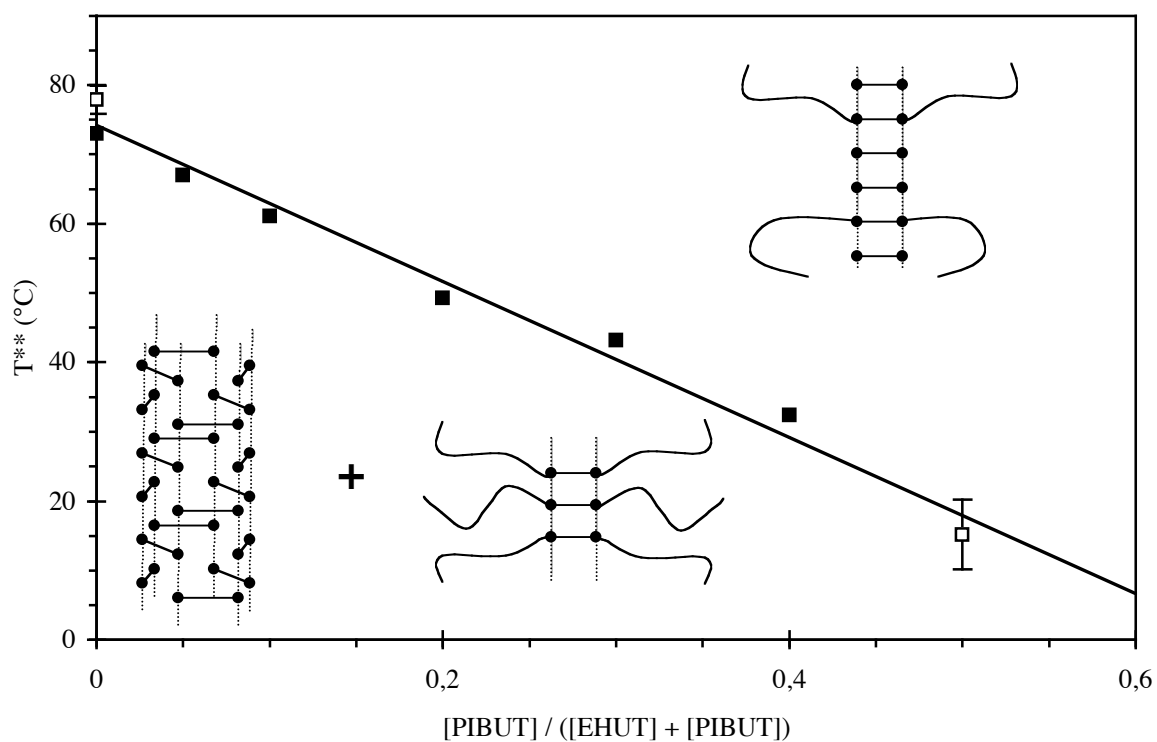


Figure 13. Transition temperature between tubes and filaments for **EHUT / PIBUT** mixtures, measured by FTIR (□) or DSC (■). (12mM solutions in heptane).

Conclusion

We report the synthesis of a polyisobutene with a single bis-urea moiety in the middle of the chain. In low polarity solvents, this polymer self-assembles by hydrogen bonding to form a comb-shaped polymer with a central backbone, that can be reversibly broken. The length of the comb backbone can therefore be tuned by changing the solvent, the concentration or the temperature. Moreover, we have proved that the bulkiness of the side-chains have a strong influence on both the self-assembly pattern and the length of the backbone. Finally, the density of arms can be reduced, by simply mixing with a low molar mass bis-urea. We are currently studying the bulk properties of this new dynamic comb-shaped polymer.

Acknowledgements. We warmly thank A. Lange and BASF company for the gift of a Kerocom PIBA sample. C. Ng Pak Leung and L. Liejour are acknowledged for their contribution to this project.

Supporting Information Available. Additional NMR and SANS data.

References and Notes

- (1) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, 101, 4071.
- (2) Ciferri, A. *Supramolecular Polymers*. New York, Marcel Dekker Inc.; 2005.
- (3) (a) Binder, W. H.; Zirbs R. *Adv. Polym. Sci.* **2007**, 207, 1. (b) Bouteiller, L. *Adv. Polym. Sci.* **2007**, 207, 79.
- (4) Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. *Nature* **2008**, 451, 977.
- (5) Ercolani, G.; Mandolini, L.; Mencarelli, P.; Roelens, S. *J. Am. Chem. Soc.* **1993**, 115, 3901.
- (6) Yamaguchi, N.; Gibson, H. W. *Chem. Commun.* **1999**, 789.

- (7) Abed, S.; Boileau, S.; Bouteiller, L. *Macromolecules* **2000**, 33, 8479.
- (8) ten Cate, A. T.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, 126, 3801.
- (9) Scherman, O. A.; Ligthart, G. B. W. L.; Sijbesma, R. P.; Meijer, E. W. *Angew. Chem. Int. Ed.* **2006**, 45, 2072.
- (10) Ohkawa, H.; Takayama, A.; Nakajima, S.; Nishide, H. *Org. Lett.* **2006**, 8, 2225.
- (11) Huang, F.; Nagvekar, D. S.; Slebodnik, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2005**, 127, 484.
- (12) Todd, E. M.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2007**, 129, 14534.
- (13) Bernard, J.; Lortie, F.; Fenet, B. *Macromol. Rapid Commun.* **2009**, 30, 83.
- (14) Miyawaki, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *Tetrahedron* **2008**, 64, 8355.
- (15) Lange, R. F. M.; van Gurp, M.; Meijer, E. W. *J. Polym. Sci. A, Polym. Chem.* **1999**, 37, 3657.
- (16) Berl, V.; Schmutz, M.; Krische, M. J.; Khoury, R. G.; Lehn, J.-M. *Chem. Eur. J.* **2002**, 8, 1227.
- (17) (a) Colombani, O.; Bouteiller, L. *New J. Chem.* **2004**, 28, 1373. (b) Colombani, O.; Barioz, C.; Bouteiller, L.; Chanéac, C.; Fompérie, L.; Lortie, F.; Montès, H. *Macromolecules* **2005**, 38, 1752.
- (18) Yount, W. C.; Loveless, D. M.; Craig, S. L. *Angew. Chem. Int. Ed.* **2005**, 44, 2746.
- (19) (a) Kato, T.; Fréchet, J.-M. *Macromolecules* **1989**, 22, 3818. (b) Kato, T.; Fréchet, J.-M. *Macromolecules* **1990**, 23, 360. (c) Kato, T.; Mizoshita, N.; Kanie, K. *Macromol. Rapid Commun.* **2001**, 22, 797.
- (20) (a) Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Mäkelä, T.; Serimaa, R.; ten Brinke, G.; Ikkala O. *Science* **1998**, 280, 557. (b) Ikkala O.; ten Brinke, G. *Chem. Commun.* **2004**, 2131. (c) ten Brinke, G.; Ruokolainen, J.; Ikkala O. *Adv. Polym. Sci.* **2007**, 207, 113.

- (21) Hammond, M. R.; Mezzenga, R. *Soft Matter* **2008**, 4, 952.
- (22) (a) Boileau, S.; Bouteiller, L.; Lauprêtre, F.; Lortie, F. *New J. Chem.* **2000**, 24, 845. (b) Bouteiller, L.; Colombani, O.; Lortie, F.; Terech, P. *J. Am. Chem. Soc.* **2005**, 127, 8893. (c) Pinault, T.; Isare, B.; Bouteiller, L. *Chem. Phys. Chem.* **2006**, 7, 816.
- (23) (a) Shikata, T.; Nishida, T.; Isare, B.; Linares, M.; Lazzaroni, R.; Bouteiller, L. *J. Phys. Chem. B* **2008**, 112, 8459. (b) Vonau, F.; Suhr, D.; Aubel, D.; Bouteiller, L.; Reiter, G.; Simon, L. *Phys. Rev. Lett.* **2005**, 94, 066103.
- (24) (a) Mueller, M.; Dardin, A.; Seidel, U.; Balsamo, V.; Ivan, B.; Spiess, H. W.; Stadler, R. *Macromolecules* **1996**, 29, 2577. (b) Schirle, M.; Hoffmann, I.; Pieper, T.; Kilian, H. G.; Stadler, R. *Polym. Bull.* **1996**, 36, 95.
- (25) Fang, Z.; Wang, S.; Wang, S.Q.; Kennedy, J.P. *J. Appl. Polym. Sci.* **2003**, 88, 1516.
- (26) (a) Binder, W. H.; Kunz, M. J.; Ingolic, E. *J. Polym. Sci. A, Polym. Chem.* **2003**, 42, 162. (b) Binder, W. H.; Kunz, M. J.; Kluger, C.; Hayn, G.; Saf, R. *Macromolecules* **2004**, 37, 1749. (c) Binder, W. H.; Bernstorff, S.; Kluger, C.; Petraru, L.; Kunz, M. J. *Adv. Mat.* **2005**, 17, 2824. (d) Binder, W. H.; Petraru, L.; Roth, T.; Groh, P. W.; Palfi, V.; Keki, S.; Ivan, B. *Adv. Funct. Mat.* **2007**, 17, 1317.
- (27) Lortie, F.; Boileau, S.; Bouteiller, L.; Chassenieux, C.; Demé, B.; Ducouret, G.; Jalabert, M.; Lauprêtre, F.; Terech, P. *Langmuir* **2002**, 18, 7218.
- (28) (a) Arnaud, A.; Bouteiller, L. *Langmuir* **2004**, 20, 6858. (b) Bellot, M.; Bouteiller, L. *Langmuir* **2008**, 24, 14176.
- (29) (a) van der Gucht, J.; Besseling, N. A. M.; Knoben, W.; Bouteiller, L.; Cohen Stuart, M. A. *Phys. Rev. E* **2003**, 67, 051106. (b) Knoben, W.; Besseling, N. A. M.; Bouteiller, L.; Cohen Stuart, M. A. *Phys. Chem. Chem. Phys.* **2005**, 7, 2390. (c) Knoben, W.; Besseling, N. A. M.; Cohen Stuart, M. A. *Phys. Rev. Lett.* **2006**, 97, 068301.

- (30) Ducouret, G.; Chassenieux, C.; Martins, S.; Lequeux, F.; Bouteiller, L. *J. Coll. Interface Sci.* **2007**, 310, 624.
- (31) Simic, V.; Bouteiller, L.; Jalabert, M. *J. Am. Chem. Soc.* **2003**, 125, 13148.
- (32) Casassa, E. F.; Berry, G. C. *J. Polym. Sci. A2* **1966**, 4, 881.
- (33) (a) Isare, B.; Bouteiller, L.; Ducouret, G.; Lequeux, F. *Supramol. Chem.* **2009**, 21, 416. (b) Isare, B.; Linares, M.; Lazzaroni, R.; Bouteiller, L. *J. Phys. Chem. B* **2009**, 113, 3360.
- (34) The influence of concentration on the transition temperature of pure **EHUT** solutions has been shown to be negligible in this concentration range.^{28b}

Self-assembly in solution of a reversible comb-shaped supramolecular polymer

*Sandrine Pensec, Nicolas Nouvel, Audrey Guilleman, Costantino Creton, François Boué, Laurent
Bouteiller*