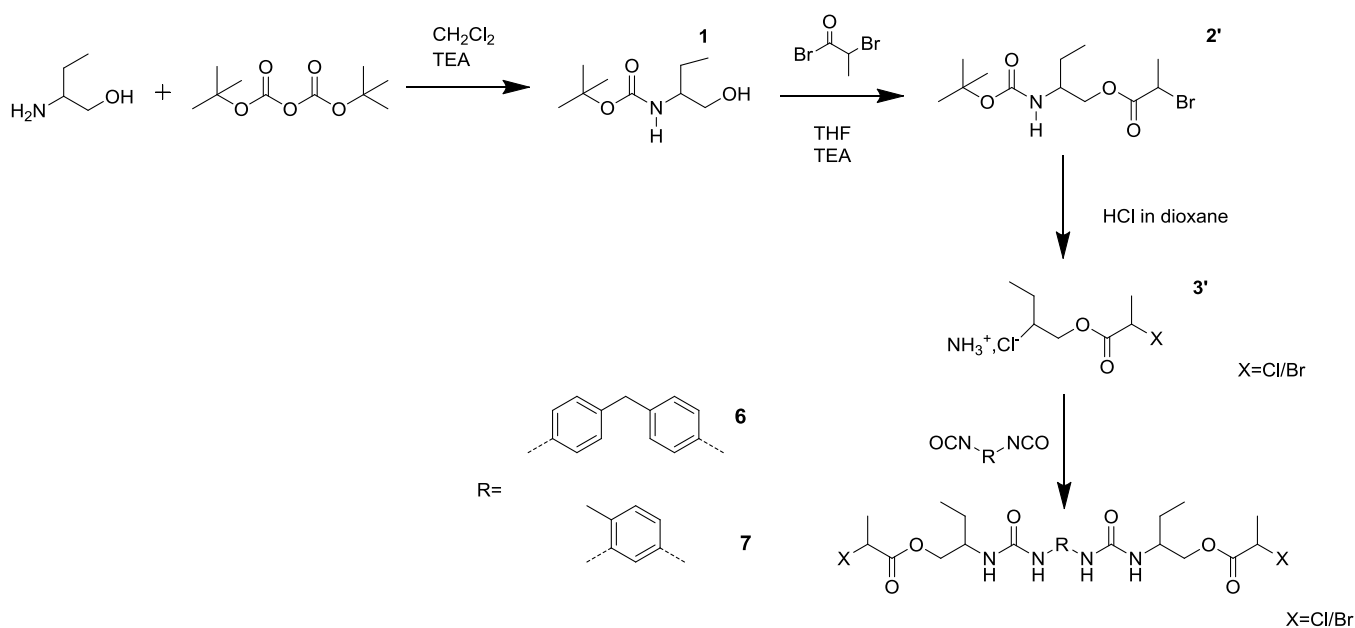


# Versatile Synthesis of Reversible Comb-Shaped Supramolecular Polymers

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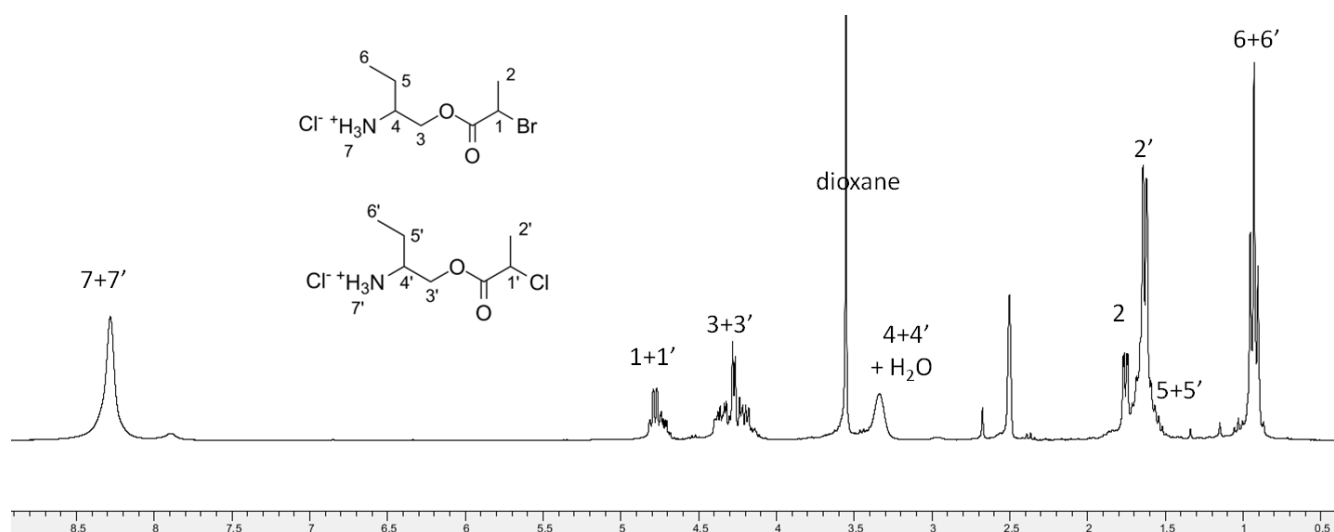
## Supporting Information

### Synthesis of the MDI bisurea, tolyl bisurea and trisurea initiators.



**Fig. S1:** Synthesis of the tolyl and MDI bisureas initiators

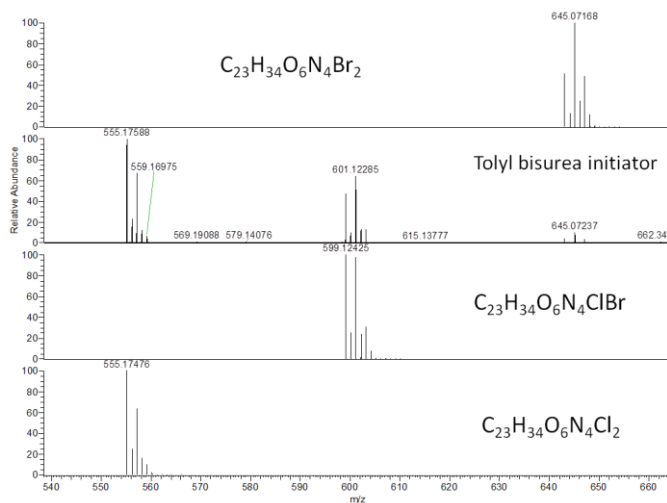
The synthesis of the MDI and tolyl bisureas is similar to the xylyl one (Figure S1). In fact the first step is the same. For the second step, bromopropionyl bromide is used instead of chloropropionyl chloride. The third step is identical to the one for the xylyl bisurea. The NMR of the ammonium **3'** after step 3 showed the presence of two different compounds. A compound with a terminal bromine and another one with a terminal chlorine, as shown by  $^1\text{H}$  NMR with the presence of two doublets at 1.6 and 1.7 ppm (Figure S2).



**Fig. S2:** <sup>1</sup>H NMR spectrum of the ammonium 3' in d<sub>6</sub>-DMSO.

This exchange from Br to Cl probably happens during the deprotection step with HCl.

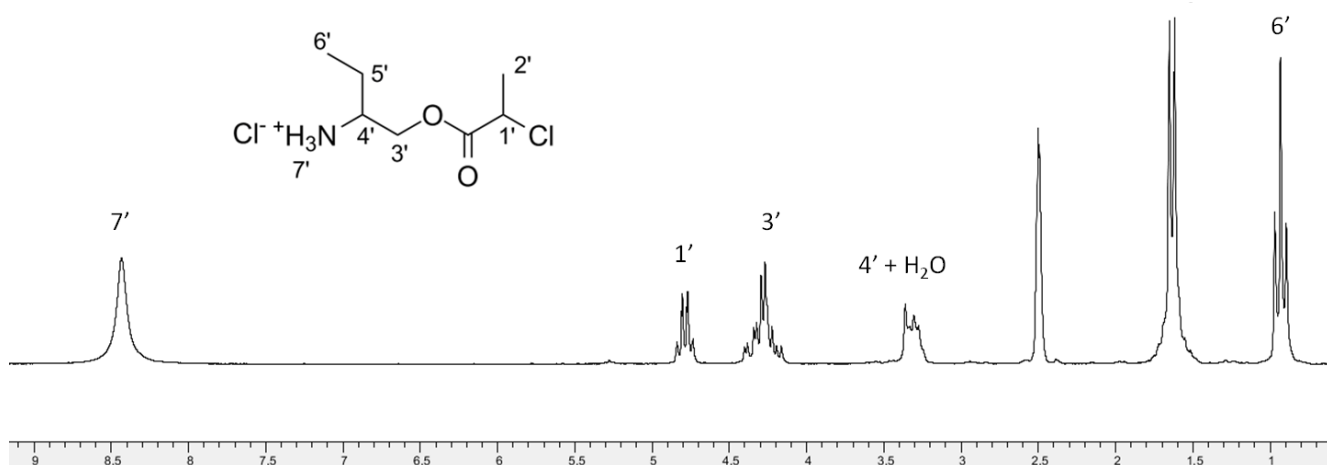
Consequently, the synthesized bisureas 6 and 7 are a mixture of three compounds as confirmed by the HRMS analysis (Figure S3). A compound with two chlorine atoms, one with two bromine atoms and one with a bromine and a chlorine atom. The exact proportion of each compound depended on the actual experiment.



**Fig. S3:** HRMS spectrum of the tolyl bisurea initiator 7

To avoid this exchange, the synthesis of the xylyl bisurea 5 (Experimental section) and of the trisurea initiator 8 were made from an ammonium prepared with chloropropionylchloride instead of bromopropionylbromide as described in the manuscript. The <sup>1</sup>H NMR of the ammonium (Figure S4) shows the presence of the chlorinated compound only as expected. The HRMS of the xylyl bisurea and of the trisurea confirmed the presence of only

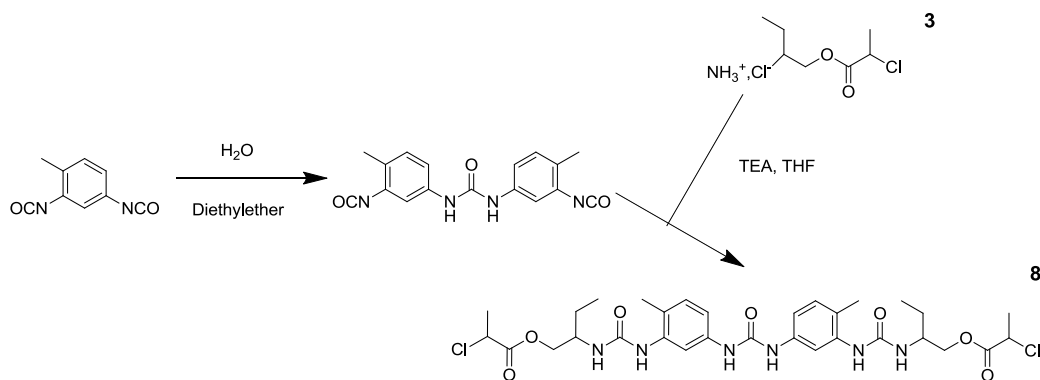
one fully chlorinated compound.



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**Fig. S4:** <sup>1</sup>H NMR spectrum of the ammonium **3** in d<sub>6</sub>-DMSO.

The ATRP polymerizations were conducted with CuBr for the MDI and the tolyl bisureas initiators. For the xylyl bisurea and the trisurea initiators, CuCl was usually used. However some polymerizations with the xylyl bisurea were done with CuBr instead of CuCl. In all cases, a good control of the polymerization was observed.



**Fig. S5:** Synthesis of the trisurea initiator **8**.

### Synthesis of 2'

**1** (27.24 g, 144 mmol) was dissolved in 200 ml of anhydrous THF in a round-bottom flask under argon. Triethylamine (144 mmol, 14.57 g) was added with a syringe. The solution was cooled to 0°C in an ice bath. Then a solution of 2-bromopropionylbromide (144 mmol, 31.08 g) in 50 mL of anhydrous THF was added dropwise in one hour in the flask cooled with an ice bath. The solution was allowed to reach room temperature and stirred overnight. The mixture was filtered and the solvent removed under reduced pressure. This product was dissolved in diethyl ether and washed 3 times with distilled water. The organic layer was collected and dried with MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The resulting product is a yellow oil (38 g, 81 %).

<sup>1</sup>H NMR (200 MHz, DMSO) δ (ppm): 0.83 (t, 3H, CH<sub>3</sub>-CH<sub>2</sub>), 1.14-1.50 (m, 9H+2H, C(CH<sub>3</sub>)<sub>3</sub> + CH<sub>2</sub>-CH<sub>3</sub>), 1.7 (d, 3H, CH-CH<sub>3</sub>), 3.53-3.6 (m, 1H, CH-CH<sub>2</sub>), 3.88-4.1 (m, 2H, O-CH<sub>2</sub>), 4.57-4.68 (m, 1H, CH-CH<sub>3</sub>), 6.78 (d, 1H, NH).

<sup>13</sup>C NMR (50 MHz, DMSO) δ(ppm): 10.54 (CH<sub>3</sub>-CH<sub>2</sub>), 22.25 (CH<sub>3</sub>-CH), 24.13 (CH<sub>3</sub>-CH<sub>2</sub>), 28.81 (C(CH<sub>3</sub>)<sub>3</sub>), 40.41 (CH-Br), 51.07 (CH-NH), 67.47 (CH<sub>2</sub>-OCO), 78.25 (C(CH<sub>3</sub>)<sub>3</sub>), 156.50 (NH-CO), 170.32 (CO-O)

### Synthesis of 3'

**2'** (117 mmol, 38 g) is placed in a round-bottom flask with an ice bath under argon. HCl 4M in dioxane (333 mmol, 88 mL), is added with a syringe. The solution was allowed to reach room temperature and stirred overnight. Then dioxane was evaporated under reduced pressure. The crude product was purified by recrystallization in a mixture (toluene/cyclohexane : 70/30). The product **3'** is obtained (19.8 g, 65 %).

<sup>1</sup>H NMR (200 MHz, DMSO) δ (ppm): 0.93 (t, 3H, CH<sub>3</sub>-CH<sub>2</sub>), 1.50-1.7 (m, 3H+2H, CH-CH<sub>3</sub> + CH<sub>3</sub>-CH<sub>2</sub>), 3.37 (m, 1H, CH-NH<sub>3</sub><sup>+</sup>), 4.14-4.28 (m, 2H, O-CH<sub>2</sub>), 4.72-4.79 (m, 1H, CH-Br), 8.4 (d, 3H, NH<sub>3</sub><sup>+</sup>).

<sup>13</sup>C NMR (50 MHz, DMSO) δ(ppm): 7.4 (CH<sub>3</sub>-CH<sub>2</sub>), 21.39 (CH<sub>3</sub>-CH), 22.61 (CH<sub>3</sub>-CH<sub>2</sub>), 49.8 (CH-Br), 53.05 (CH-NH<sub>3</sub><sup>+</sup>), 64.7 (CH<sub>2</sub>-OCO), 169.93 (CO-O).

### Synthesis of 6

A solution of **3'** (19 mmol, 5 g) in 20 mL of anhydrous dichloromethane and triethylamine (19 mmol, 2.64 mL) were added dropwise to a solution of 4,4'-diphenylmethylenediisocyanate (9 mmol, 1.9 mL) in 50 mL of anhydrous dichloromethane.

The reaction was followed by infrared spectroscopy until the disappearance of the NCO band at 2270 cm<sup>-1</sup>.

When the reaction was over, the mixture was washed with water. The organic layer was dried and evaporated under reduced pressure. The product was then purified by gel chromatography with an eluant (dichloromethane/ethylacetate: 60/40). A white solid is obtained (2.04 g, 33 %)

**<sup>1</sup>H NMR** (200 MHz, DMSO)  $\delta$  (ppm): 0.90 (t, 6H,  $CH_3-CH_2$ ), 1.30-1.7 (m, 6H+4H,  $CH-CH_3 + CH_3-CH_2$ ), 3.8 (m, 2H+2H,  $CH-NH+Ph-CH_2-Ph$ ), 4.1 (m, 4H,  $CH_2-O$ ), 4.72 (m, 2H,  $CH-Br/Cl$ ), 6.03 (m, 2H,  $CH-NH-CO$ ), 7.06 (d, 4H,  $H-Ph$ ), 8.35 (s, 2H,  $CO-NH-Ph$ ).

**<sup>13</sup>C NMR** (50 MHz, DMSO)  $\delta$ (ppm): 10.54 ( $CH_3-CH_2$ ), 21.63 ( $CH_3-CH$ ), 24.77 ( $CH_3-CH_2$ ), 40.1 ( $Ph-CH_2-Ph$ ), 49.99 ( $CH-Cl/Br$ ), 53.21 ( $CH-NH$ ), 67.73 ( $CH_2-OCO$ ), 118.32 ( $Ph-H$ ); 129.01 ( $Ph-H$ ), 134.66 ( $Ph-CH_2$ ), 138.89 ( $Ph-NH$ ), 155.82 ( $NH-CO-NH$ ), 170.34 ( $CO-O$ ).

**ESI m/z** [ $M^+Na^+$ ]  $C_{29}H_{38}O_6N_4Br_2$  calculated 721.1 measured 721.1.  
 $C_{29}H_{38}O_6N_4BrCl$  calculated 677.2 measured 677.2.  
 $C_{29}H_{38}O_6N_4Cl_2$  calculated 631.2 measured 631.3.

### Synthesis of 7

A solution of **3'** (19 mmol, 5 g) in 20 mL of anhydrous dichloromethane and triethylamine (19 mmol, 2.64 mL) were added dropwise to a solution of 2,4-toluenediisocyanate (9 mmol, 1.27 mL) in 50 mL of anhydrous dichloromethane. The reaction was followed by infrared spectroscopy until the disappearance of the NCO band at 2270  $cm^{-1}$ .

When the reaction was over, the mixture was washed with water. The organic layer was dried and evaporated under reduced pressure. The product was then purified by precipitation in cyclohexane. A white solid is obtained (3.1 g, 56 %)

**<sup>1</sup>H NMR** (200 MHz, DMSO)  $\delta$  (ppm): 0.90 (t, 6H,  $CH_3-CH_2$ ), 1.30-1.7 (m, 6H+4H,  $CH-CH_3 + CH_3-CH_2$ ), 2.07 (s, 3H,  $Ph-CH_3$ ), 3.8 (m, 2H,  $CH-NH$ ), 4.1 (m, 4H,  $CH_2-O$ ), 4.72 (m, 2H,  $CH-Br/Cl$ ), 5.94 (m, 1H,  $CH-NH-CO$ ), 6.51 (m, 1H,  $CH-NH-CO$ ), 6.92 (d, 1H,  $H-Ph$ ), 7.10 (d, 1H,  $H-Ph$ ), 7.57 (s, 1H,  $CO-NH-Ph$ ), 7.73 (s, 1H,  $Ph-H$ ), 8.35 (s, 1H,  $CO-NH-Ph-CH_3$ ).

**<sup>13</sup>C NMR** (50 MHz, DMSO)  $\delta$ (ppm): 10.78 ( $CH_3-CH_2$ ), 17.20 ( $Ph-CH_3$ ), 22.18 ( $CH_3-CH$ ), 24.46 ( $CH_3-CH_2$ ), 46.62 ( $CH-Cl/Br$ ), 49.95 ( $CH-NH$ ), 67.15 ( $CH_2-OCO$ ), 110.47 ( $Ph-H$ ); 119.93 ( $Ph-H$ ), 119.66 ( $Ph-CH_3$ ), 130.58 ( $Ph-H$ ), 138.56 ( $Ph-NH$ ), 138.87 ( $Ph-NH$ ), 155.24 ( $NH-CO-NH$ ), 170.34 ( $CO-O$ ).

**HRMS m/z** [ $M^+Na^+$ ]  $C_{23}H_{34}O_6N_4Br_2$  calculated 645.07168 measured 645.07237  
 $C_{23}H_{34}O_6N_4BrCl$  calculated 599.1245 measured 601.12285  
 $C_{23}H_{34}O_6N_4Cl_2$  calculated 555.17467 measured 555.17588

### Synthesis of 8

A small amount of water (14.4 mmol, 0.260 mL) was mixed in 100 mL of anhydrous diethylether. This mixture was added in a solution of 2,4-toluenediisocyanate (33.2 mmol, 4.74 mL) in 30 mL of anhydrous diethylether at 30 mL/h. A white precipitate was formed. The reaction was stirred over night. The white solid was filtered and dried. The diisocyanate is obtained (1.93 g, 42 %). The product is not characterized because of his water sensitivity.

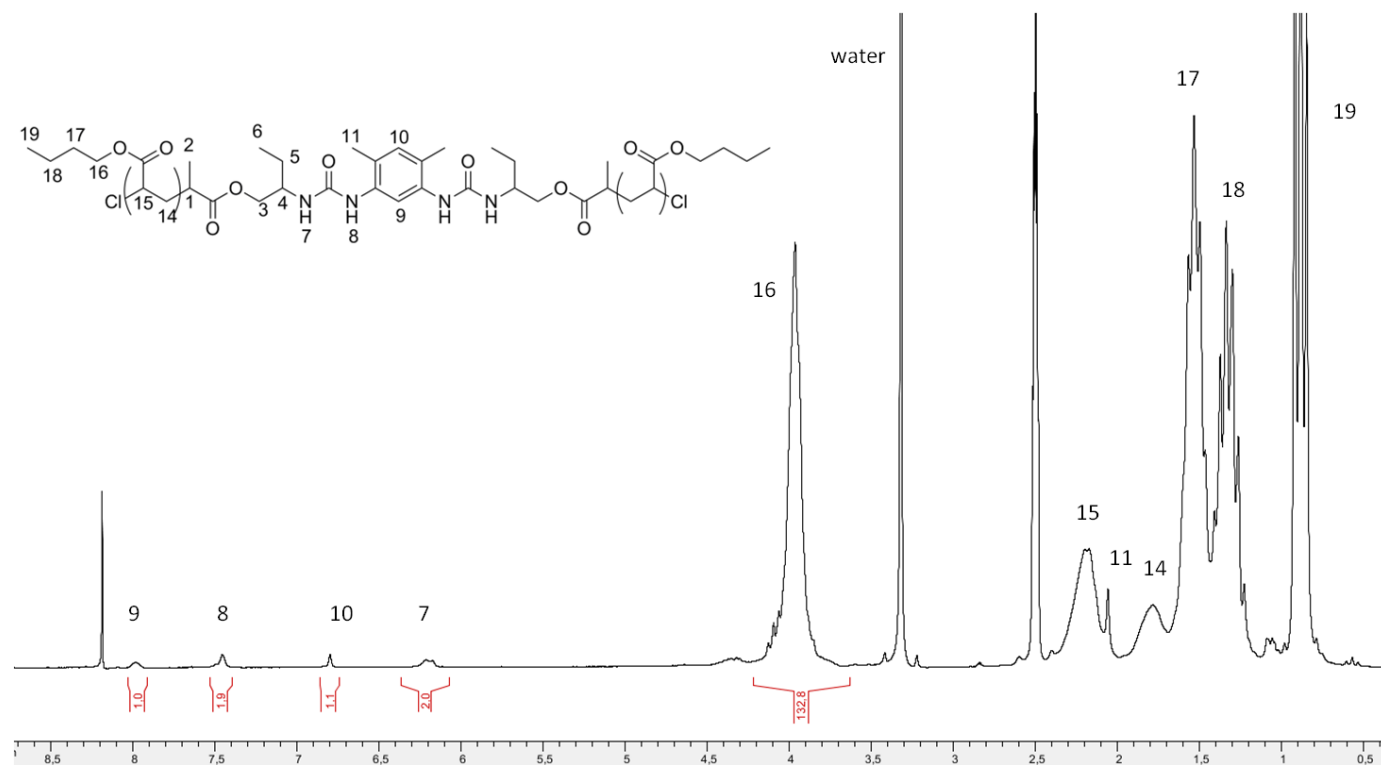
A solution of **3** (6.3 mmol, 1.36 g) in 20 mL of THF and triethylamine (6.3 mmol, 0.88 mL) were added dropwise to a solution of the diisocyanate synthesized previously (3 mmol, 0.96 g) in 100 mL of anhydrous THF.

The reaction was followed by infrared spectroscopy until the disappearance of the NCO band at 2270  $\text{cm}^{-1}$ . When the reaction was over, a gel was formed. It was precipitated in 500 mL of water. The solid was filtered and recrystallized in methanol. A white solid is obtained (1 g, 50 %)

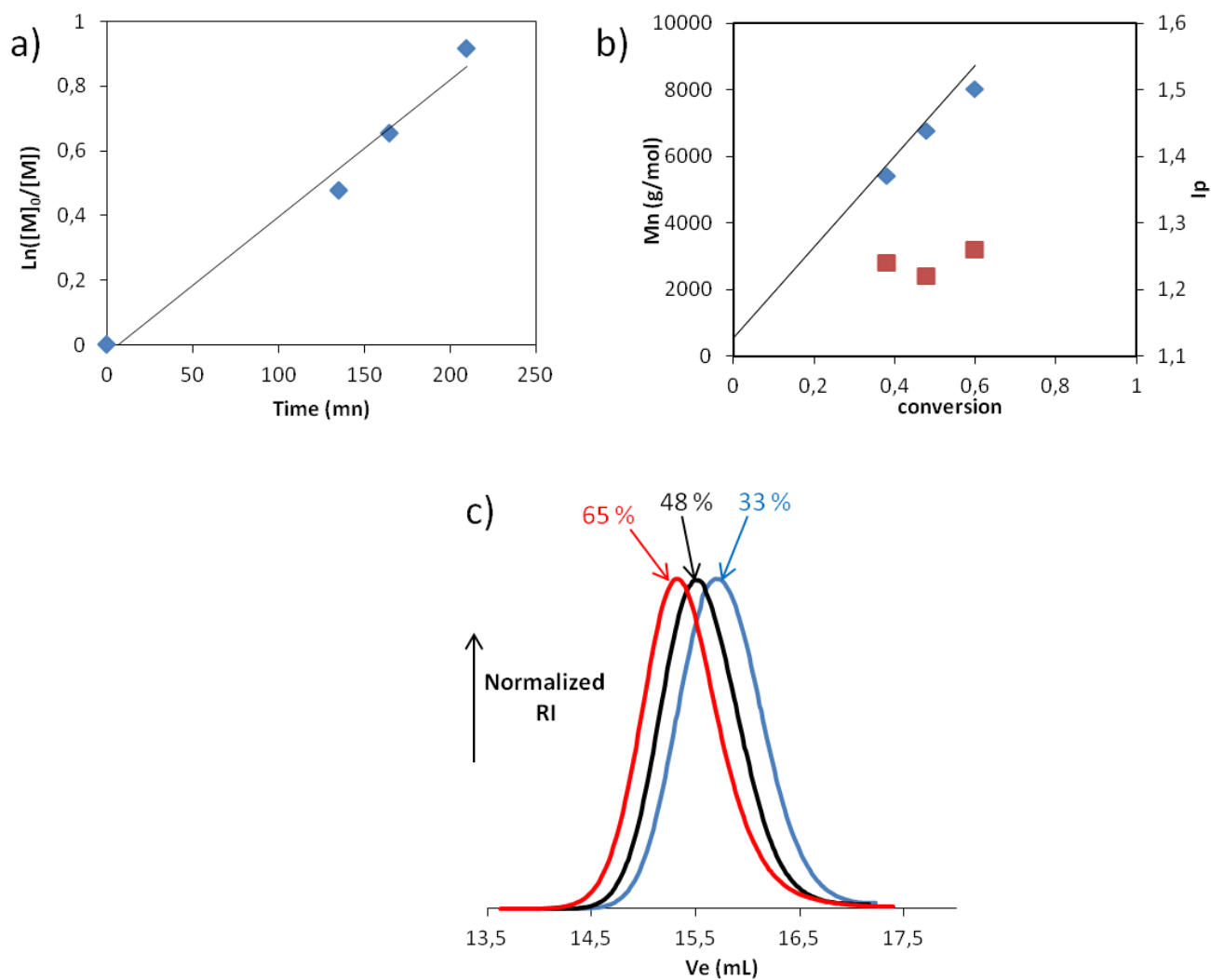
**$^1\text{H}$  NMR** (200 MHz, DMSO)  $\delta$  (ppm): 0.90 (t, 6H,  $\text{CH}_3\text{-CH}_2$ ), 1.30-1.6 (m, 6H+4H,  $\text{CH-CH}_3 + \text{CH}_3\text{-CH}_2$ ), 2.12 (s, 6H,  $\text{Ph-CH}_3$ ), 3.8 (m, 2H,  $\text{CH-NH}$ ), 4.1 (m, 4H,  $\text{CH}_2\text{-O}$ ), 4.72 (m, 2H,  $\text{CH-Cl}$ ), 6.56 (m, 2H,  $\text{CH-NH-CO}$ ), 6.97 (d, 2H,  $\text{H-Ph}$ ), 7.15 (d, 2H,  $\text{H-Ph}$ ), 7.62 (s, 2H,  $\text{CO-NH-Ph}$ ), 7.84 (s, 2H,  $\text{Ph-H}$ ), 8.40 (s, 2H,  $\text{CO-NH-Ph}$ ).

**$^{13}\text{C}$  NMR** (50 MHz, DMSO)  $\delta$ (ppm): 10.78 ( $\text{CH}_3\text{-CH}_2$ ), 17.20 ( $\text{Ph-CH}_3$ ), 22.18 ( $\text{CH}_3\text{-CH}$ ), 24.46 ( $\text{CH}_3\text{-CH}_2$ ), 49.75 ( $\text{CH-Cl}$ ), 53.40 ( $\text{CH-NH}$ ), 67.65 ( $\text{CH}_2\text{-OCO}$ ), 110.47 ( $\text{Ph-H}$ ); 112.15 ( $\text{Ph-H}$ ), 119.66 ( $\text{Ph-CH}_3$ ), 130.58 ( $\text{Ph-H}$ ), 138.56 ( $\text{Ph-NH}$ ), 138.87 ( $\text{Ph-NH}$ ), 155.24 ( $\text{NH-CO-NH}$ ), 170.34 ( $\text{CO-O}$ ).

**HRMS**  $m/z$  [ $\text{M}^+\text{Na}^+$ ]  $\text{C}_{31}\text{H}_{42}\text{O}_7\text{N}_6\text{Cl}_2$  calculated 703.23842 measured 703.24005.



**Fig. S6:**  $^1\text{H}$  NMR of the xyllyl bisurea polybutylacrylate CF151 in a mixture  $\text{d}_6\text{-DMSO/CDCl}_3$



**Fig. S7:** Kinetic study of the polymerization of 2-ethylhexylacrylate by ATRP initiated by tolyl bisurea 6 in 10% DMF at 80°C with M/I/CuCl/PMDETA : 86/1/1/1.

### Fit of the SANS data.

#### Polyacrylates with MDI, tolyl or xylyl bisurea stickers:

The scattered intensity was compared to the form factor for Gaussian chains. The following expression was considered:

$$I(q) = (\rho - \rho_{\text{solv}})^2 \Phi V \frac{2(e^{-x} - 1 + x)}{x^2} \quad \text{with } x = (qR_g)^2 \text{ and } V = \frac{M}{dN_A}$$

where  $\rho = 6.72 \cdot 10^9 \text{ cm}^{-3}$  and  $\rho_{\text{solv}} = 5.66 \cdot 10^{10} \text{ cm}^{-3}$  are the scattering length densities of PnBA and toluene-D<sub>8</sub>, respectively,  $\Phi$  is the volume fraction of the polymer,  $V$  the molecular volume of a chain,  $R_g$  its radius of gyration,  $M$  its molar mass,  $d$  the density of PnBA,  $N_A$  the Avogadro number and  $q$  the wave vector.

The fitted curves shown on Figure 10 were obtained by adjusting the values for  $M$  and  $R_g$ . The values obtained (Table S1) indicate that, at this concentration, the polymers are essentially present as free chains.

Table S1: Parameters deduced from the fit of the SANS data with equation (1)

Sample	Sticker	$M_n$ NMR <sup>a</sup> (g/mol)	$M_{n,\text{SEC (RI)}}$ <sup>b</sup> (g/mol)	$M_{w,\text{SEC (RI)}}$ <sup>b</sup> (g/mol)	$M^c$ (g/mol)	$R_g^c$ (Å)
CF50	Tolyl bisurea	7500	7300	8500	8800	26
CF62	MDI bisurea	8400	8500	9800	8900	26
CF151	Xylyl bisurea	8800	8500	10500	12600	32

<sup>a</sup> Calculated by <sup>1</sup>H NMR <sup>b</sup> Evaluated by SEC in THF using polystyrene standards <sup>c</sup> From the SANS data, after fitting with equation (1)