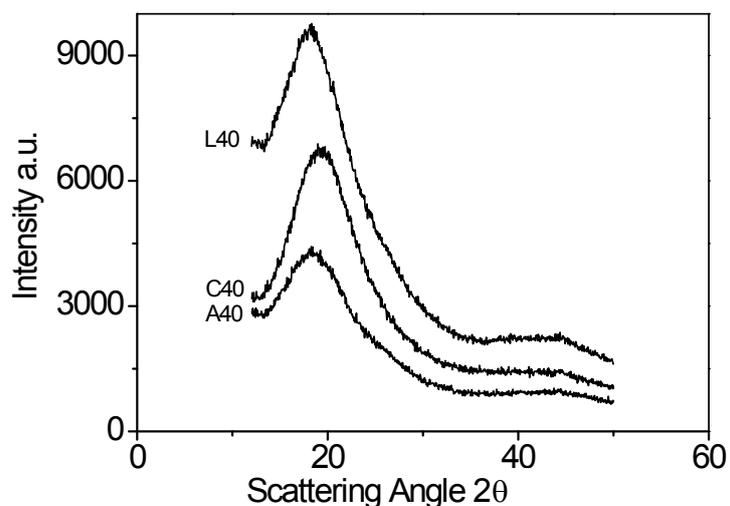


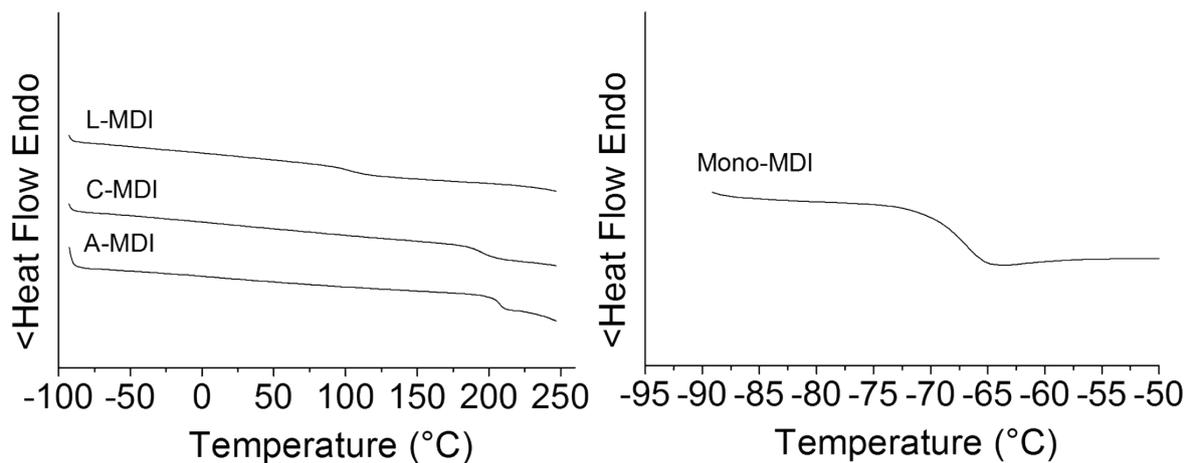
## Supplementary Information

### Novel synthesis of polyurea nanoparticles via spontaneous nanoprecipitation.

Pietro Locatelli<sup>1</sup>, Steve Wouters<sup>2</sup>, Chris Lindsay<sup>2</sup>, SLM Schroeder<sup>3</sup>, John H. Hobdell<sup>2</sup> and Alberto Saiani<sup>1\*</sup>



**Figure ESI 1:** Wide-angle X-ray scattered intensity vs. scattering angle,  $\theta$ , obtained for L40, C40 and A40 samples. WAXS experiments were performed using a Philips X'Pert-APD (PW3011/10) camera equipped with a Cu ( $K\alpha'$  0.154 nm) anode X-Ray tube, operating at 40 mA and 45 kV. The detector used was a PW3011/10 (Miniprop. small window) sealed Xe proportional detector. The experiments were carried out at room temperature using an angular range of 10 to 50 °, and a scanning step of 0.05 °.



**Figure ESI 2:** . DSC graphs obtained at  $10\text{ }^{\circ}\text{C min}^{-1}$  for L-MDI, C-MDI, A-MDI and Mono-MDI reference compounds.

Samples	Experimental values			Theoretical values		
	C%	N%	O%	C%	N%	O%
L-MDI	79.6%	10.7%	9.7%	73.1%	15.4%	11.5%
C-MDI	83.8%	8.8%	7.4%	79.3%	13.8%	6.9%
A-MDI	88.4%	4.8%	6.8%	80%	9%	4.7%
Mono-MDI	77.6%	0.7%	21.7%	74.3%	1.4%	24.3%
L-40	74%	2.3%	23.7%	73.9%	13.6%	12.5%
C-40	73.2%	4.7%	22.1%	76.9%	12%	11.1%
A-40	75.5%	0.4%	24.1%	84.7%	8%	7.3%

**Table ESI 1:** Measured (by XPS) and theoretical (from known bulk compositions) elemental composition of reference compounds and PNP samples.

Samples	C 1s					O 1s		
	<u>C</u> -C/ <u>C</u> -H	C=C	<u>C</u> -N	<u>C</u> -O	N-( <u>C</u> =O)-N	C- <u>O</u>	N-(C= <u>O</u> )-N Shake-up	
L-MDI	17.1%	47.4%	19.9%	8.8%	6.8%	38.4%	61.6%	
<i>Theoretical values</i>	4.8%	57.2%	19%	9.5%	9.5%	33.3%	66.7%	
C-MDI	49.9%	29.5%	14.9%	-	5.7%	-	9.1%	90.9
<i>Theoretical values</i>	33.3%	44.4%	14.8%	-	7.5%	-	100%	
A-MDI	32.1%	62.1%	3.5%	-	2.3%	-	9.1%	90.9%
<i>Theoretical values</i>	16.3%	69.8%	9.3%	-	4.6%	-	100%	
Mono-MDI	41.6%	-		57.2%	1.2%	98.4%	-	1.6%
<i>Theoretical values</i>	40.5%	8.1%		50%	1.4%	97.2%	-	2.8%

**Table ESI 2:** Measured (from fitting of C 1s and O 1s spectra) and theoretical (from known sample bulk compositions) molar composition of the different species contributing to the C 1s and O 1s spectra of the reference compounds (see text for more details)

Samples	C 1s				O 1s	
	<u>C-C/C-H</u>	C=C	<u>C-N/C-O</u>	N-( <u>C=O</u> )-N	C- <u>O</u>	N-(C= <u>O</u> )-N
L-MDI	<i>285.0</i>	284.5	286.5	288.8	532.6	531.5
C-MDI	<i>285.0</i>	284.4	286.7	288.8	532.7	531.6
A-MDI	<i>285.0</i>	284.4	286.6	288.8	532.7	531.4

**Table ESI 3:** Binding energies obtained from the fitting analysis of the C 1s and O 1s spectra of the PNP samples (values in italics indicate fixed peak positions used to calibrate the binding energy scale of the spectra).

Samples	T <sub>g</sub> (°C)	ΔC <sub>p</sub> J(g°C) <sup>-1</sup>
L-MDI	102.6±0.2	0.14±0.03
C-MDI	194.6±0.6	0.18±0.01
A-MDI	204.7±0.5	0.27±0.01
Mono-MDI	-67.0±0.2	0.703±0.002

**Table ESI 4:** T<sub>g</sub>s and associated ΔC<sub>p</sub>s obtained for the reference compounds. (See figure ESI 2 for corresponding DSC curves)