

## Supporting Information

### Preparation of highly uniform and crosslinked polyurea microspheres through precipitation copolymerization of isophorone diisocyanate with diethylenetriamine and property and structure characterization of the polyurea

Jinjin Xu, Hui Han, Ling Zhang, Xiaoli Zhu, Xubao Jiang and Xiang Zheng Kong\*

**1. Polymerization of IPDI and DETA**, in H<sub>2</sub>O-acetone with H<sub>2</sub>O/acetone at 30/70 and 2 wt% of monomer concentration, was conducted with varied reciprocating shaking rates. SEM pictures are given in Fig S1. The results showed that all the microspheres were quite highly monodisperse, regardless of shaking rate.

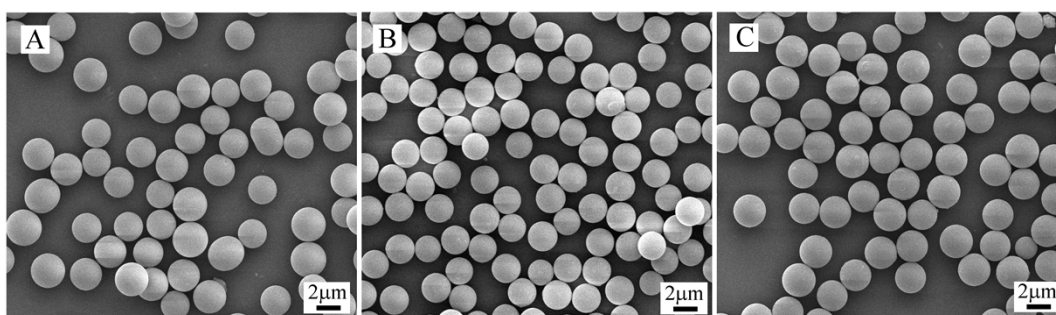


Fig. S1 SEM pictures of the PU microspheres prepared by copolymerization of IPDI and DETA in H<sub>2</sub>O-acetone with H<sub>2</sub>O/acetone at 30/70 and 2 wt% of monomer concentration with varied reciprocating shaking rates (A, 40 osc./min; B, 80 osc./min; C, 120 osc./min)

**2. Scheme of chemical process for preparation of crosslinked PU microspheres** through copolymerization of IPDI and DETA (Fig. S2). It is reported and well accepted that, for a given isocyanate group, the reactive activity of the hydrogen atoms of a secondary amine was higher than those in a primary amine.

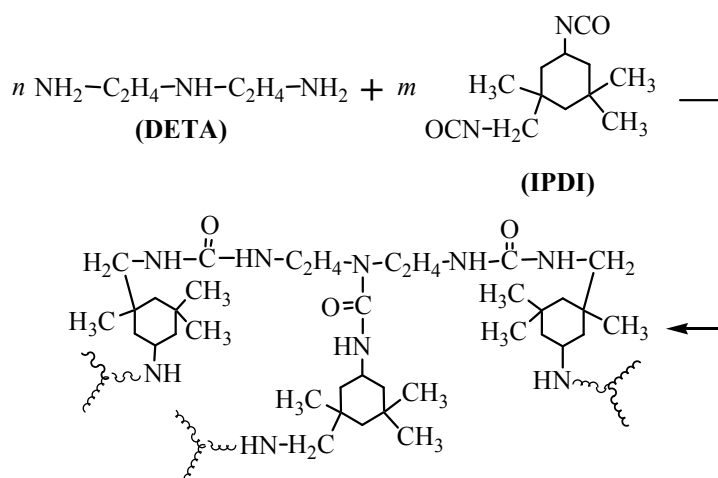


Fig. S2 Schematic presentation of copolymerization of IPDI with DETA.

### 3. Thermal properties of PU microspheres by TGA test

PU of linear polymer (prepared by IPDI reaction with water) and crosslinked PU (by copolymerization of IPDI with DETA at DETA/IPDI molar ratio of 2/3) were subjected to TGA test. The curves are given in Fig. S3 here below.

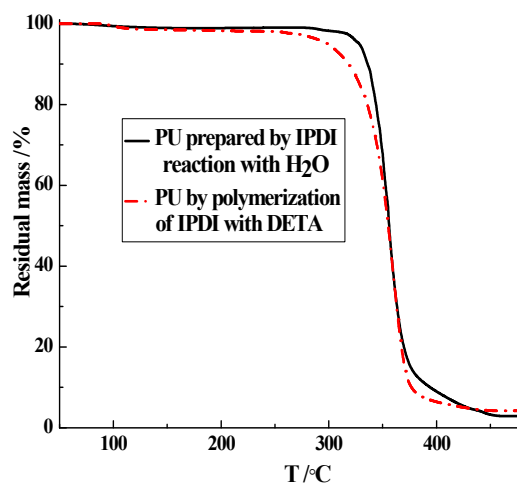


Fig. S3 TGA curves of the PU microspheres prepared with (Dash-dotted line) and without DETA (solid line)

### 4. Theoretical calculation of NH<sub>x</sub>/CH<sub>x</sub> in a polyurea and their estimation from FTIR spectra.

Table S1 Theoretical calculation of NH<sub>x</sub>/CH<sub>x</sub> in polyurea prepared with H<sub>2</sub>O and IPDI or with DETA/IPDI of different molar ratios

DETA / IPDI	H <sub>2</sub> O / IPDI	2 / 3	2 / 9	2 / 15	2 / 30
NH <sub>x</sub> (x=1, 2)/NCO in monomers	0	1.00	0.33	0.20	0.10
Number of NH <sub>x</sub> (x=1, 2) in PU	2	10	22	34	64
Number of CH <sub>x</sub> (x=1,2,3) in PU	8	32	80	128	248
Theoretical NH <sub>x</sub> /CH <sub>x</sub> in PU	0.2500	0.3125	0.2750	0.2656	0.2581

It is to point out that the theoretical NH<sub>x</sub>/CH<sub>x</sub> in PU was obtained based on the composition of DETA and IPDI and their relative amounts used in PU synthesis. To count the number of CH<sub>x</sub>, one IPDI molecule possesses 3 methyls, 4 methylenes and 1 methine; and one DETA molecule possesses only 2 methylene. The number and structure of all these groups keep unchanged in the polymerization because these groups are not involved in the polymer formation. With regard to NH<sub>x</sub> in PU, one

source is from DETA. Note that its secondary amine (-R-NH-R-, R being -CH<sub>2</sub>CH<sub>2</sub>-) turns to urea with the nitrogen atom attached by two ethylene groups without NH bond [-R<sub>2</sub>N-CO-NH-]; -NH bond can be formed only when the two primary amines in DETA are reacted with NCO (yielding urea, -R-NH-CO-NH-). This is to say that one DETA molecule can produce only two -NH<sub>x</sub> groups. Another source to deliver -NH<sub>x</sub> is by the reactions of -NCO: one urea NH is formed if it reacts with amine, and one primary amine is formed if it reacts with water. This means that one NCO will yield only one NH<sub>x</sub> (x=1 or 2) regardless of its reaction.

Based on this analysis, and assuming that all DETA and IPDI are full reacted, one can easily calculate the ratio of NH<sub>x</sub>/CH<sub>x</sub> in a PU synthesized with known amounts of DETA and IPDI. This ratio for different PU is given in Table S1 as theoretical NH<sub>x</sub>/CH<sub>x</sub>.

To estimate this same ratio (NH<sub>x</sub>/CH<sub>x</sub>) from FTIR spectra, the absorption peak at 3360 cm<sup>-1</sup>, assigned to stretching vibration of NH, and the peak at 2953 cm<sup>-1</sup>, assigned to stretching vibration of C-H in -CH<sub>3</sub>, were chosen (see Fig. S4). This large and asymmetric peak at 3360 cm<sup>-1</sup> are in fact composed of several peaks, owing to -NH- and -NH<sub>2</sub> in different chemical environments (aliphatic primary and secondary amines, -NH in urea group, for instance). The peak at 2953 cm<sup>-1</sup> was overlapped with that at 2907 cm<sup>-1</sup> (assigned to C-H in -CH<sub>2</sub>-). These zone comprehends in fact also a group of peaks (2800 cm<sup>-1</sup> to 2953 cm<sup>-1</sup>), owing to absorption of C-H in different form of -CH<sub>x</sub> in different chemical environments.

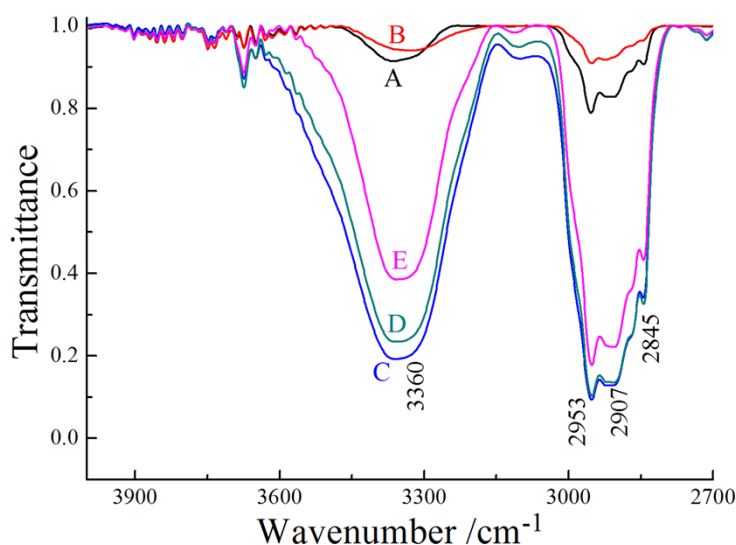


Fig. S4. Enlarged FTIR spectra of PU prepared by reaction of IPDI with water (A) and with DETA at different DETA/IPDI molar ratio (B, 2/3; C, 2/9; D, 2/15; E, 1/15)

It is known that, through FTIR, the most reliable estimation for the composition of a substance is by its peak area when a peak is well separated and symmetric. Because the peaks at 2953 cm<sup>-1</sup> and 2907 cm<sup>-1</sup> were seriously overlapped, estimations of NH<sub>x</sub> and CH<sub>x</sub> were first conducted from the heights of the assigned peaks, i.e. the peak at 3360 cm<sup>-1</sup> for NH<sub>x</sub> and that at 2950 cm<sup>-1</sup> for CH<sub>x</sub>. The ratios of the peak heights (Height 1/Height 2 in Table S2), assumingly representing that of NH<sub>x</sub>/CH<sub>x</sub> in PU, are listed in

Table S2.

Table S2 Experimental NHx/CHx in PU estimated from FTIR peak height (3360 cm<sup>-1</sup> for NHx and 2953 cm<sup>-1</sup> for CHx) and theoretical NHx/CHx based on the amounts of DETA and IPDI used in the precipitation polymerization

DETA — IPDI	NHx — NCO	Peak height 1 <sup>a</sup>	Peak height 2 <sup>b</sup>	Height 1 <sup>c</sup> — Height 2 <sup>d</sup>	Theoretical NHx/CHx
IPDI-H <sub>2</sub> O	0	0.0863	0.2107	0.4096	0.2500
2/3	1/1	0.0603	0.0908	0.6641	0.3125
2/9	1/3	0.8079	0.9035	0.8942	0.2750
2/15	1/5	0.7659	0.8962	0.8545	0.2656
2/30	1/10	0.6150	0.8222	0.7480	0.2581

<sup>a</sup> Peak height of NHx at 3360 cm<sup>-1</sup>; <sup>b</sup> Peak height of CHx at 2953 cm<sup>-1</sup>.

For the purpose of reference, the experimental NHx/CHx ratios were also estimated through calculation of peak areas for the relevant peaks instead of peak heights. Since the peaks, particularly those of CHx from 2800 cm<sup>-1</sup> to 2960 cm<sup>-1</sup>, comprehends a group of small peaks, a simulated peak separation using a software (Origin 8.1) was necessary prior to the integration of peak areas. The results are given in Table S3 for reference. In comparison to the theoretical value (NHx/CHx), these data are more biased than those obtained from peak height. This may be an indication that the results on PU composition estimation from peak heights are more reliable than those from peak areas when the peaks are overlapped.

Table S3 Experimental NHx/CHx in PU estimated from FTIR peak area (3360 cm<sup>-1</sup> for NHx and 2953 cm<sup>-1</sup> for CHx) and theoretical NHx/CHx based on the amounts of DETA and IPDI used in the precipitation polymerization

DETA — IPDI	NHx — NCO	Peak area 1 <sup>a</sup>	Peak area (2) <sup>b</sup>	Area 1 <sup>a</sup> — Area 2 <sup>b</sup>	Theoretical NHx/CHx
IPDI-H <sub>2</sub> O	0	11.5378	23.5783	0.4893	0.2500
2/3	1/1	9.7490	10.1835	0.9573	0.3125
2/9	1/3	210.1229	143.5853	1.4634	0.2750
2/15	1/5	193.9108	142.0253	1.3653	0.2656
2/30	1/10	122.2022	119.1943	1.0252	0.2581

<sup>a</sup> Peak area of NHx at 3360 cm<sup>-1</sup>; <sup>b</sup> Peak area of CHx at 2907 cm<sup>-1</sup> and 2953 cm<sup>-1</sup>.