Electronic Supplementary Information For

Advantages and Limitations of Diisocyanates for Intramolecular Collapse

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1. Kinetic results

Table S1 GPC data for cross-linking of P(MA-*co*-HEA) at 20 ^{o}C.

Time (h)	$^{a}M_n$ (kDa)	^{a}PDI	$^{a}[\eta]$ (mL/g)	$^{a}R_h$ (nm)
0	99.0	1.20	37.3	8.35
8	103.4	1.19	31.1	8.14
18	106.5	1.17	29.7	7.93
24	109.2	1.16	27.0	7.86
32	117.7	1.13	25.8	7.53
48	121.9	1.11	25.7	7.51

^{a} Determined by SEC with triple-detectors (RI, MALS, and VI detectors) in THF at 30 ^{o}C.

Table S2 GPC data for cross-linking of P(MA-*co*-HEA) at 60 ^{o}C.

Time (h)	$^{a}M_n$ (kDa)	^{a}PDI	$^{a}[\eta]$ (mL/g)	$^{a}R_h$ (nm)
0	99.0	1.20	37.3	8.35
20 min	102.8	1.21	34.6	8.25
40 min	106.8	1.21	31.8	8.02
1	108.3	1.18	29.0	7.92
2	110.2	1.13	26.8	7.76
3	119.3	1.10	26.0	7.57
6	121.2	1.10	25.5	7.50

^{a} Determined by SEC with triple-detectors (RI, MALS, and VI detectors) in THF at 30 ^{o}C.

A second batch of linear P(MA-*co*-HEA) copolymer (named as P(MA-*co*-HEA)’), with M_n = 102.9 kDa and PDI = 1.22 was used for further study of kinetics vs. temperature. The molar fraction of HEA in P(MA-*co*-HEA)’ is 17.3 mol% (from ^{1}H NMR spectroscopy). SCPNs$_{15}$’ was prepared at room temperature (20 ^{o}C), 30 ^{o}C, 40 ^{o}C and 60 ^{o}C respectively to examine the intramolecular collapse kinetics in more detail. Table S3-S6 and Figure S1-S4 summarizes the data from these reactions.

Activation energy (E_a = 53.0 kJ mol^{-1}) was calculated from kinetic rate constant using an Arrhenius plot (Figure S5). The rate constants were determined from $\ln(R_h/R_0)$ versus time (Fig. 2 in manuscript).

Table S3 GPC data for cross-linking of P(MA-*co*-HEA)' at 20 ^{o}C.

Time (h)	$^{a}M_{n}$ (kDa)	^{a}PDI	$^{a}[\eta]$ (mL/g)	$^{a}R_{h}$ (nm)
0	102.9	1.22	38.80	9.00
3	104.2	1.22	35.12	8.87
7	107.5	1.22	33.14	8.62
18	111.3	1.20	31.01	8.45
24	117.8	1.20	29.21	8.31
30	119.7	1.19	27.06	8.17
42	120.5	1.18	26.55	8.10

^{a}Determined by SEC with triple-detectors (RI, MALS, and VI detectors) in THF at 30 ^{o}C.

Table S4 GPC data for cross-linking of P(MA-*co*-HEA)' at 30 ^{o}C.

Time (h)	$^{a}M_{n}$ (kDa)	^{a}PDI	$^{a}[\eta]$ (mL/g)	$^{a}R_{h}$ (nm)
0	102.9	1.22	38.80	9.00
2	105.1	1.22	34.24	8.80
5	108.3	1.21	31.44	8.59
8	114.1	1.21	29.09	8.43
18	118.3	1.20	27.32	8.20
22	120.7	1.19	25.89	8.09
25	121.0	1.19	25.55	8.05

^{a}Determined by SEC with triple-detectors (RI, MALS, and VI detectors) in THF at 30 ^{o}C.

Table S5 GPC data for cross-linking of P(MA-*co*-HEA)' at 40 ^{o}C.

Time (h)	$^{a}M_{n}$ (kDa)	^{a}PDI	$^{a}[\eta]$ (mL/g)	$^{a}R_{h}$ (nm)
0	102.9	1.22	38.80	9.00
1	104.6	1.22	37.00	8.84
2	109.7	1.21	34.23	8.68
3	112.1	1.21	32.48	8.54
4	114.7	1.21	30.26	8.42
6	116.2	1.20	28.14	8.32
9	118.8	1.18	26.61	8.18
12	119.7	1.18	24.88	8.02
15	120.1	1.18	24.57	8.01

^{a}Determined by SEC with triple-detectors (RI, MALS, and VI detectors) in THF at 30 ^{o}C.

Table S6 GPC data for cross-linking of P(MA-*co*-HEA)' at 60 ^{o}C.

Time (h)	$^{a}M_n$ (kDa)	^{a}PDI	$^{a}[\eta]$ (mL/g)	$^{a}R_h$ (nm)
0	102.9	1.22	38.80	9.00
20 min	106.5	1.22	36.12	8.82
40 min	110.3	1.21	33.59	8.60
1 h	114.1	1.20	30.68	8.46
1.5 h	116.7	1.20	28.32	8.35
2 h	118.2	1.19	26.57	8.16
3 h	120.3	1.18	24.45	7.94
4 h	120.8	1.18	24.03	7.89
6 h	120.9	1.17	24.00	7.86

^{b}Determined by SEC with triple-detectors (RI, MALS, and VI detectors) in THF at 30 ^{o}C.

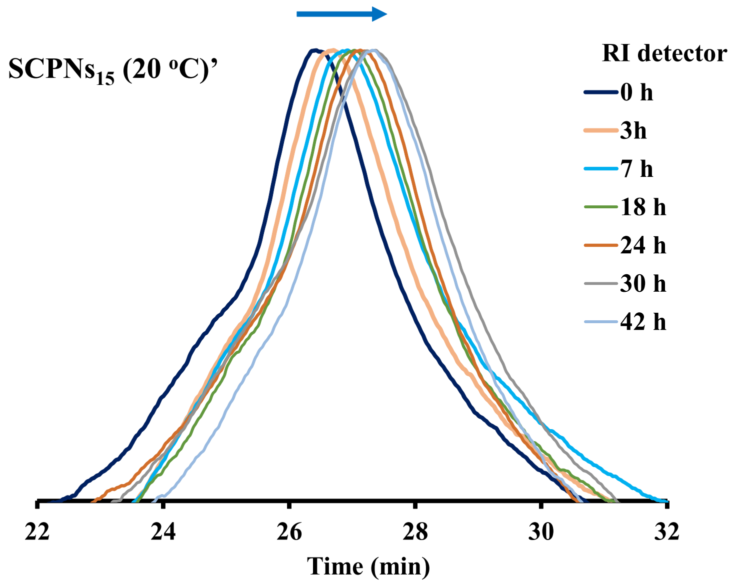

Figure S1. GPC traces as a function of time for P(MA-*co*-HEA)' intramolecular collapse at 20 ^{o}C.

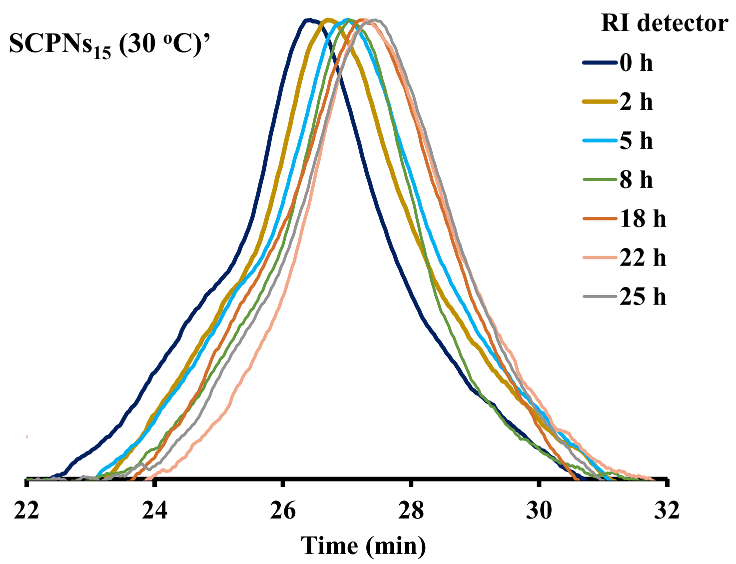

Figure S2. GPC traces as a function of time for P(MA-*co*-HEA)' intramolecular collapse at 30 ^{o}C.

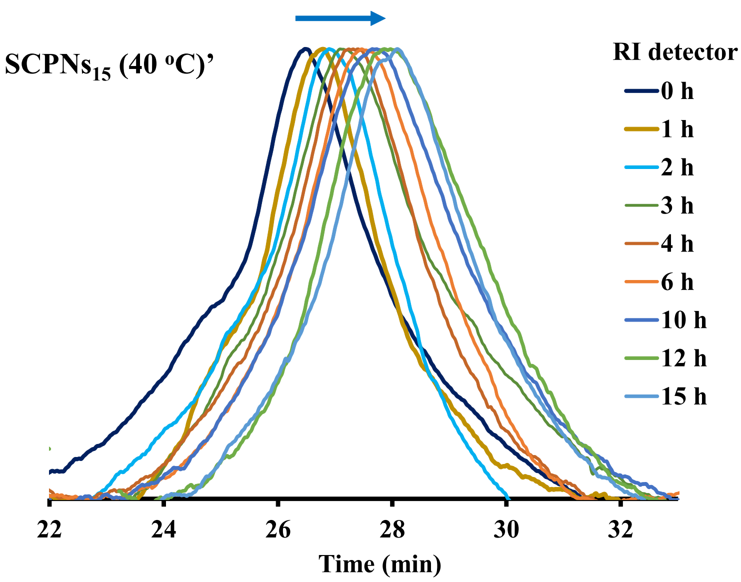

Figure S3. GPC traces as a function of time for P(MA-*co*-HEA)' intramolecular collapse at 40 ^{o}C.

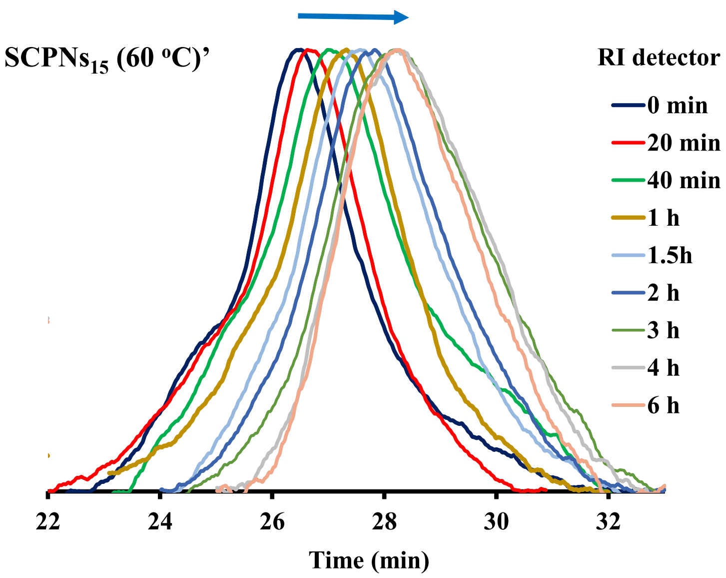

Figure S4 GPC traces as a function of time for P(MA-*co*-HEA)' intramolecular collapse at 60 ^{o}C.

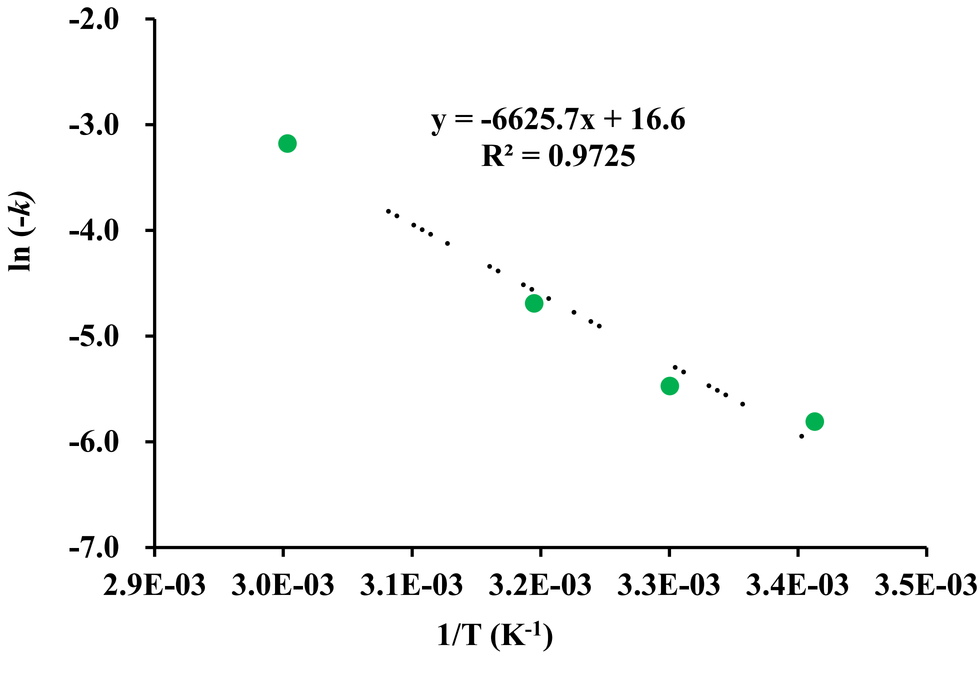

Figure S5. Arrhenius plot for P(MA-*co*-HEA)' intramolecular collapse.

2. Calculations of Actual Cross-link Parameters from ^{1}H-NMR

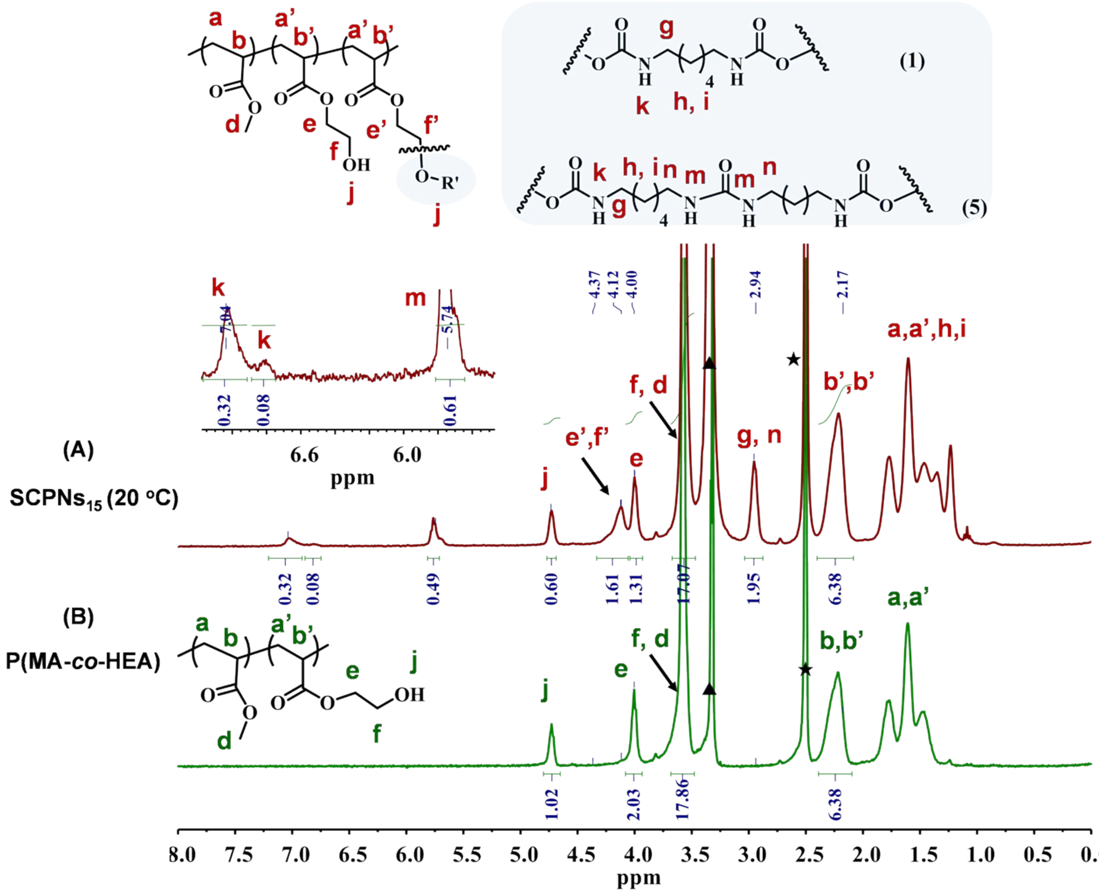

Figure S6. (A) ^{1}H-NMR of SCPNs$_{15}$ (20 °C) in DMSO-d_6. (B) ^{1}H-NMR of P(MA-*co*-HEA) in DMSO-d_6.

Based on the ratio between methylene *e* (connected to ester in HEMA) and methines *b* and *b'* in the main chain, equation (1) was used to calculate the molar percentage of HEA monomer in the linear copolymer:

$$HEA\ mol\% = \frac{I_e/2}{I_{b,b'}} \times 100 \qquad (1)$$

Using Figure S6 as an example, the ratio of HEA in P(MA-*co*-HEA) copolymer is 15.7 mol%.

The crosslink density was calculated from the ration between methylenes e' and f', which shift in HEAs only when reacted with isocyanate to main chain methines *b* and *b'*:

$$cross-link\ density\ mol\% = \frac{I_e'f'/4}{I_{b,b'}} \times 100 \qquad (2)$$

Using Figure S6 as an example, the actual cross-link density in $SCPNs_{15}$ (20 ^{o}C) is 6.3 mol%.

Urethane/Urea ration was calculated by comparing the Urea and Urethane N-H peaks (k and m), following equation (3):

$$n(urethane)/n(urea) = \frac{[I_k/(I_k + I_m/2)] \times 100}{[I_m/2/(I_k + I_m/2)] \times 100} \quad (3)$$

Using Figure S6 as an example, the actual urethane/urea molar ratio in $SCPNs_{15}$ (20 ^{o}C) is 56.7/43.3.

Table S7. Characteristics of P(MA-*co*-HEA) and corresponding [a]SCPNs

Sample	[b]M_n (th) (kDa)	[c]M_n (exp) (kDa)	[c]PDI	[c]$[\eta]$ (mL/g)	[c]R_h (nm)	[d]Yield (wt%)	[e]Cross-link density (mol%)	[f]urethane /urea	[g]T_g (^{o}C)
P(MA-*co*-HEA)		99.0	1.20	37.3	8.35				13.5
$SCPNs_1$	99.9	99.8	1.15	36.5	8.30	94.3	0.47	70.0/30.0	13.9
$SCPNs_3$	103.1	104.0	1.13	33.7	8.07	95.2	1.88	62.3/37.7	15.7
$SCPNs_5$	105.2	107.8	1.12	30.1	7.80	95.6	2.35	63.9/36.1	16.7
$SCPNs_{10}$	109.4	111.9	1.12	28.2	7.62	94.7	3.08	54.4/45.6	21.2
$SCPNs_{15}$	114.7	120.8	1.12	25.5	7.50	95.7	4.41	44.4/55.6	21.9

[a]Reaction temperature: 60 ^{o}C. [b]Theoretical M_n of SCPNs samples. [c]Determined by GPC in THF at 30 ^{o}C. [d]Yield of SCPNs synthesized from P(MA-*co*-HEA). [e]Determined by ^1H NMR according to equation (2). [f]Determined by ^1H NMR according to equation (3). [g]Determined by DSC.

Theoretical M_n was calculated assuming 100% conversion:

1) For each cross-linking reaction 100 mg of P(MA-*co*-HEA) was used, which means 1 mmol of polymer chains was present in the reaction.

2) Assuming 100% conversion, all the HDI added is summed to the original 100 mg of polymer, and the overall weight is divided by the number of chains (1 mmol).

3. NMR spectra

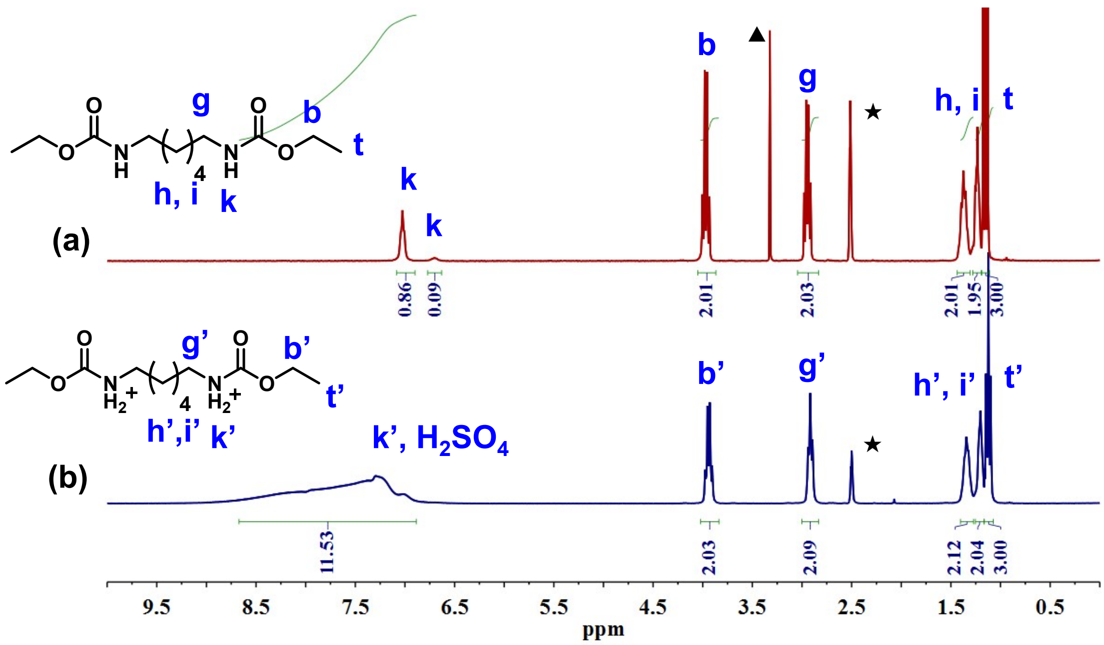

Figure S7. (a) ^{1}H NMR spectrum of model urethane compound DMSO-d_6. (b) ^{1}H NMR spectrum of model urethane compound upon addition of one drop H_2SO_4 in DMSO-d_6. ▲H_2O, *DMSO-d_5

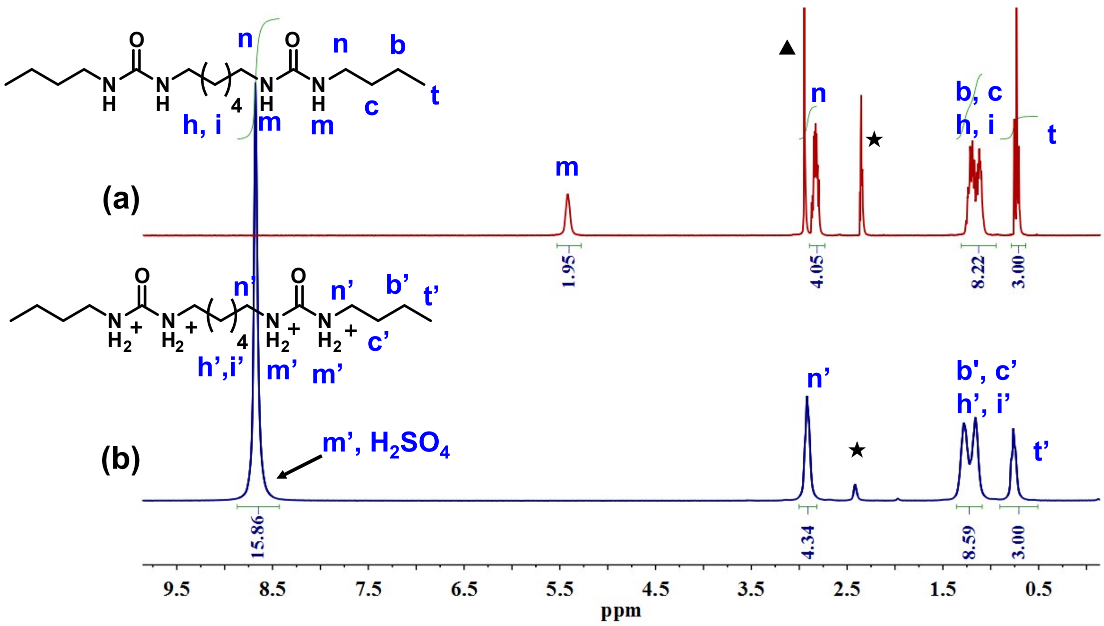

Figure S8. (a) ^{1}H NMR spectrum of model urea compound in DMSO-d_6. (b) ^{1}H NMR spectrum of model urea compound upon addition of one drop H_2SO_4 in DMSO-d_6. ▲H_2O, *DMSO-d_5

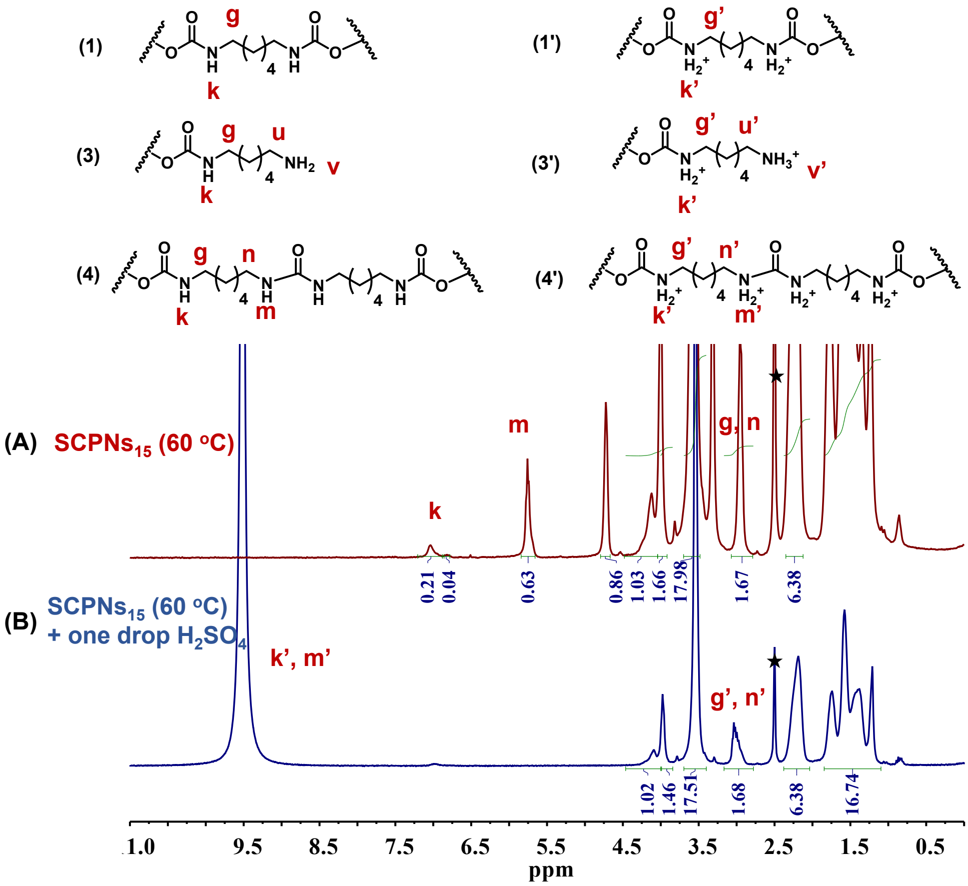

Figure S9. (A) ^{1}H NMR spectrum SCPNs$_{15}$ (60 ^{o}C) in DMSO-d_6. (B) ^{1}H NMR spectrum of SCPNs$_{15}$ (60 ^{o}C) upon addition of one drop H_2SO_4 in DMSO-d_6, ★DMSO-d_5.

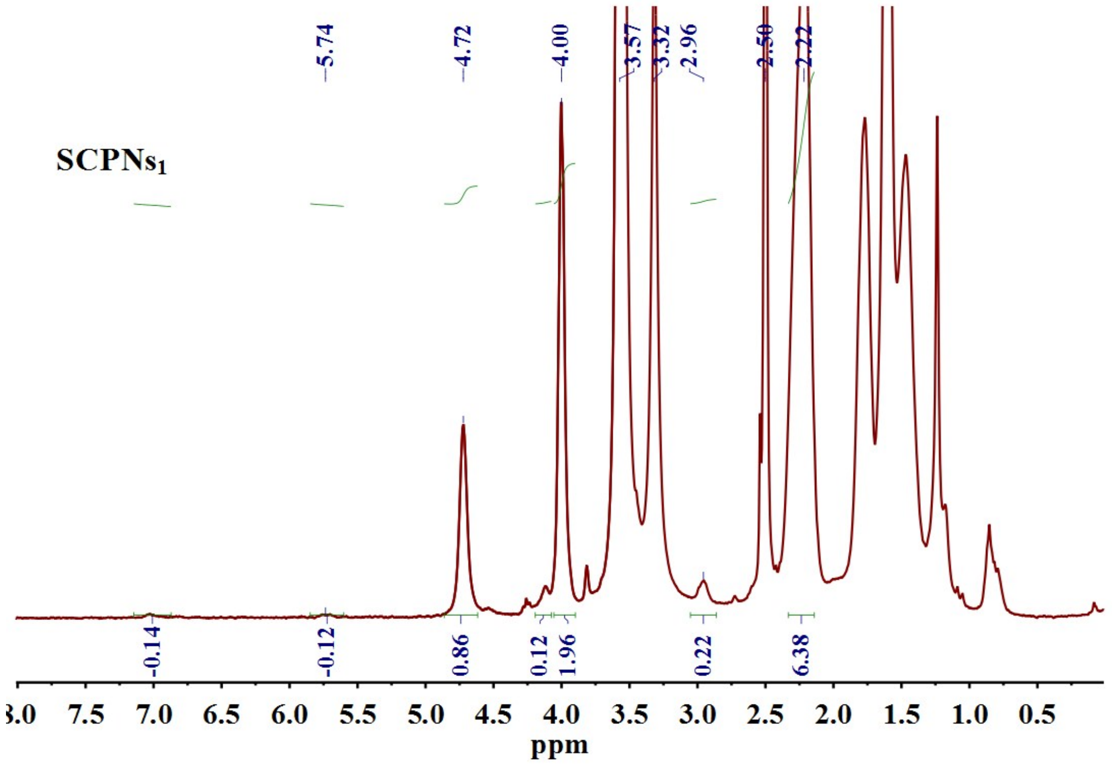

Figure S10. ^{1}H-NMR of $SCPNs_1$ in DMSO-d_6

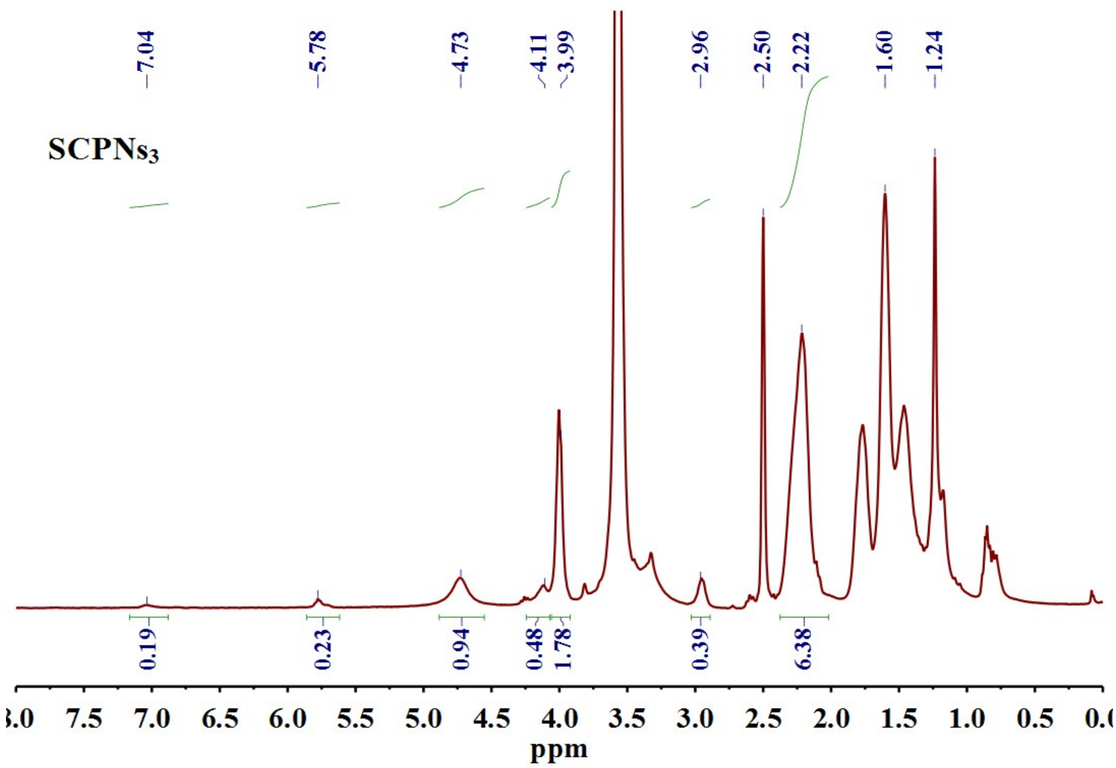

Figure S11. ^{1}H-NMR of $SCPNs_3$in DMSO-d_6

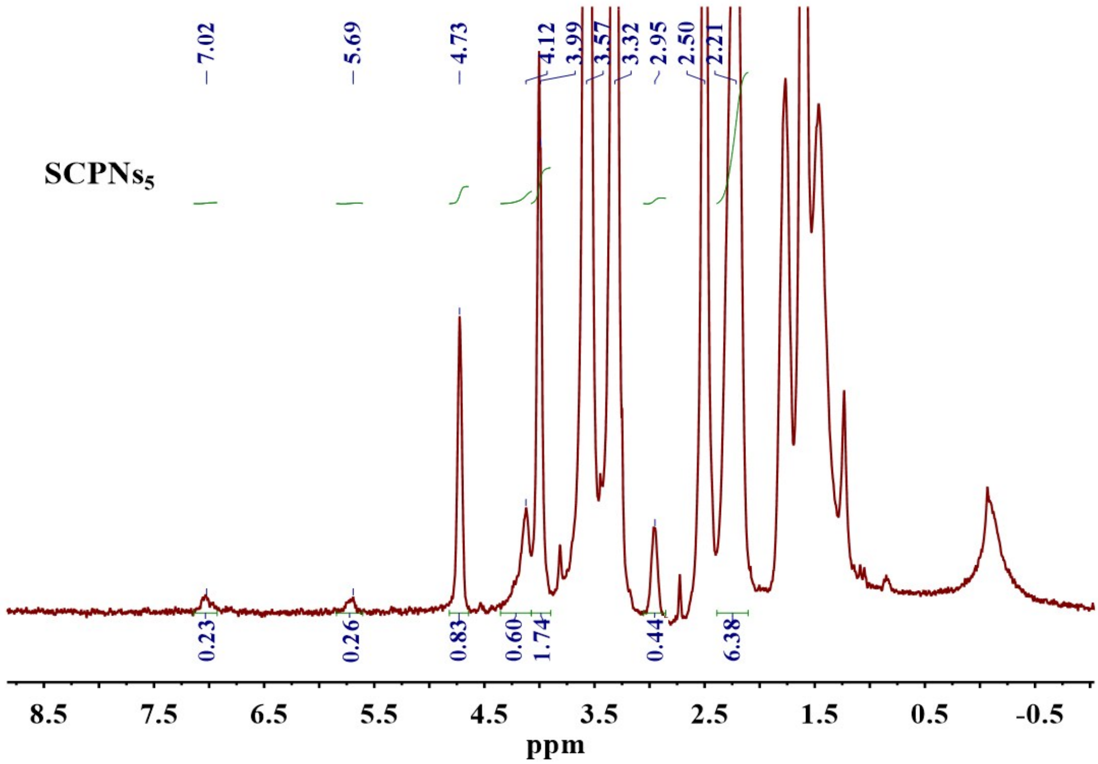

Figure S12. ^{1}H-NMR of $SCPNs_5$ in DMSO-d_6

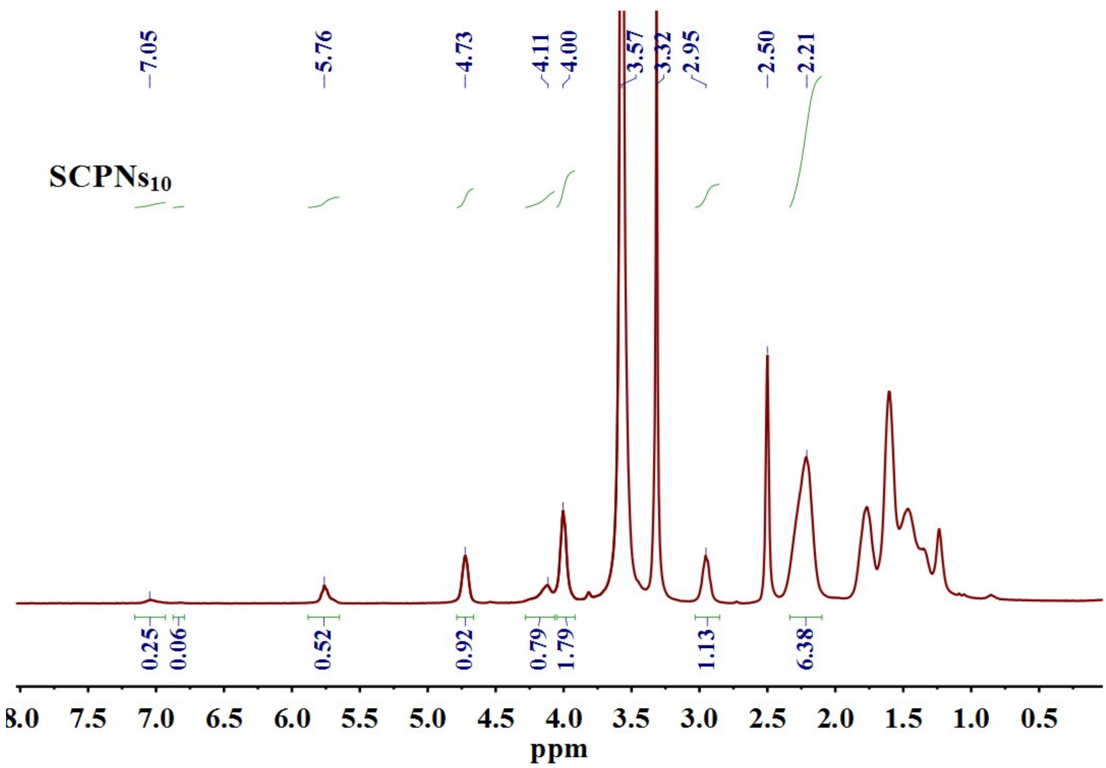

Figure S13. ^{1}H-NMR of $SCPNs_{10}$ in DMSO-d_6