Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

for

Studying the activity of the MacMillan catalyst embedded within hydrophobic crosslinked polymeric nanostructures

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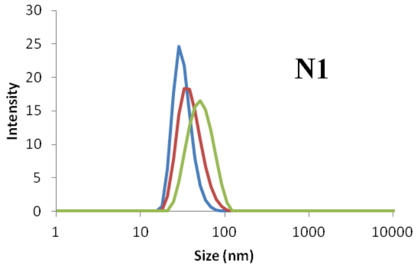
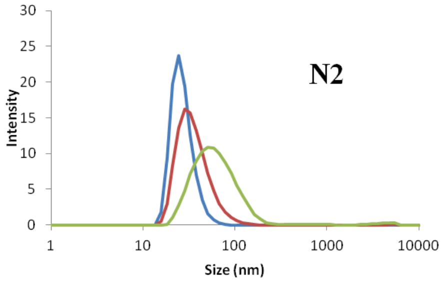
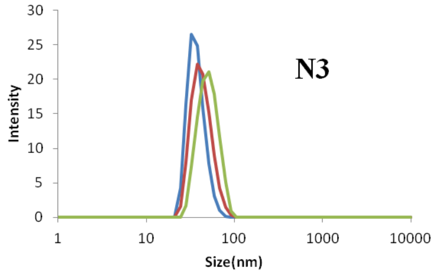
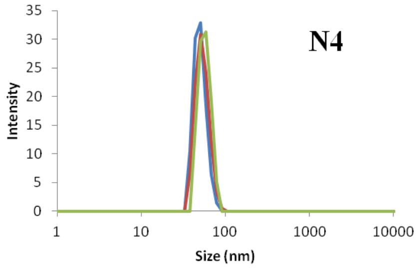
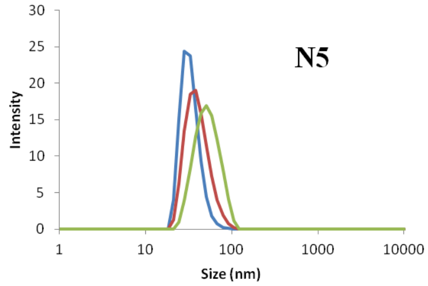
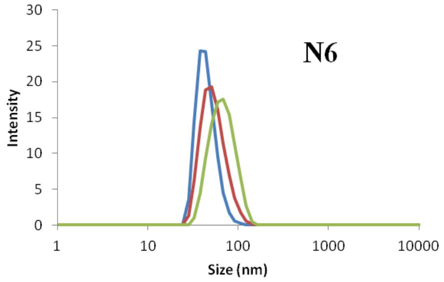


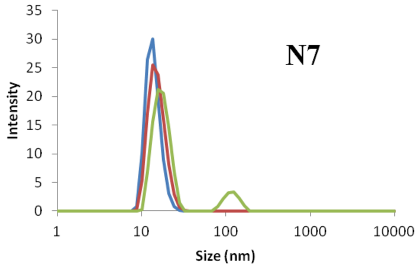


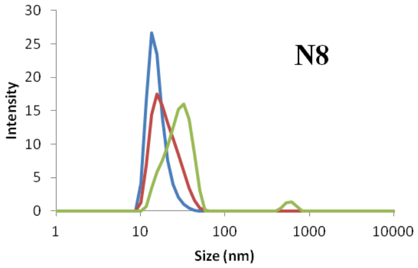












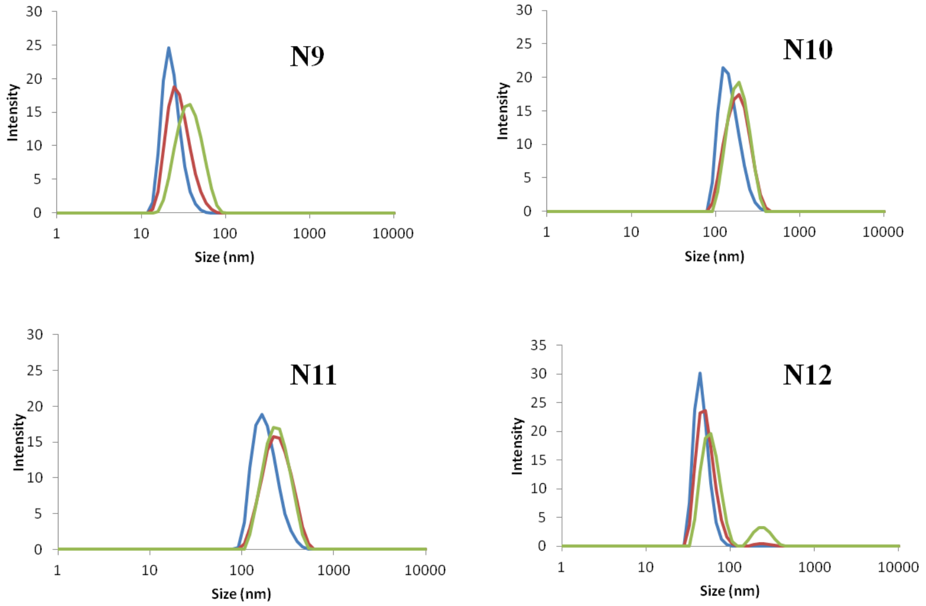
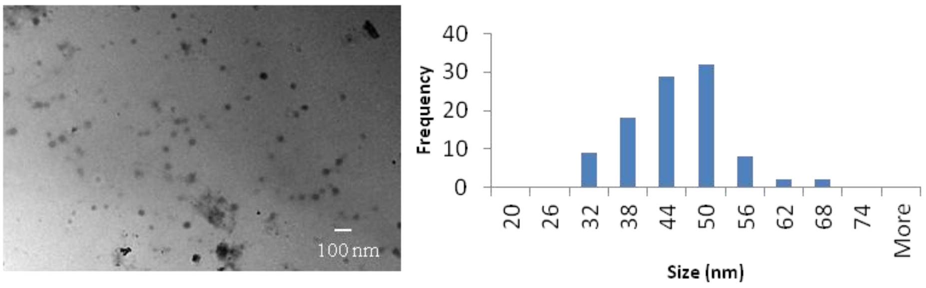
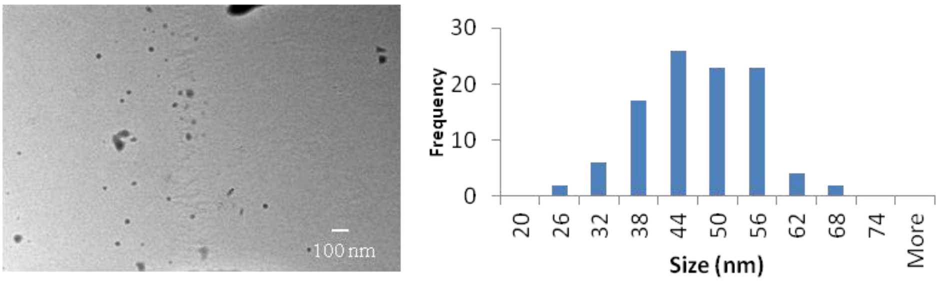


Figure S1. DLS trace of **N1–N12** showing intensity (green line), volume (red line) and number (blue line) distributions. All traces show good overlap and in the majority of cases relatively low dispersity (*ca.* 0.1).

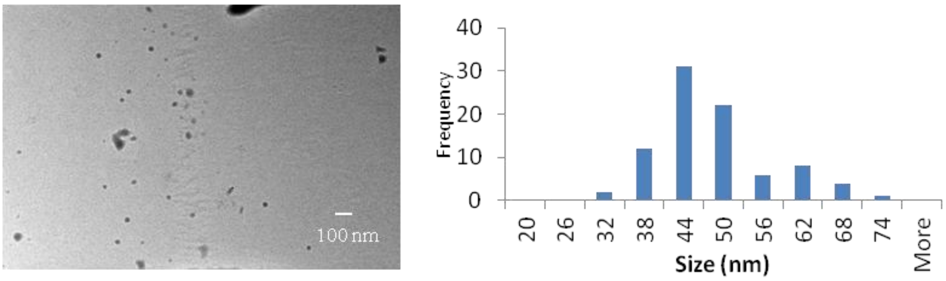
N1



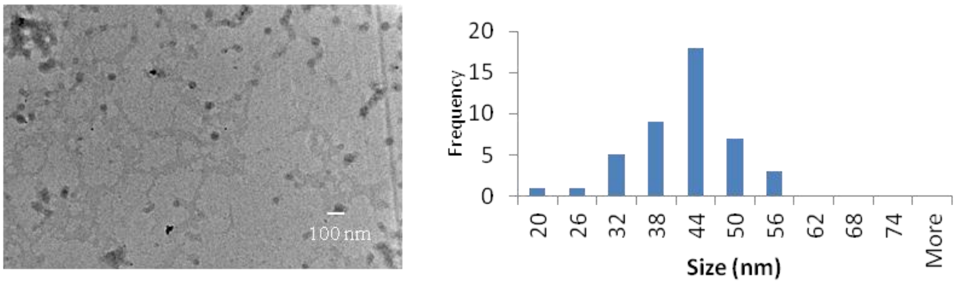
N2



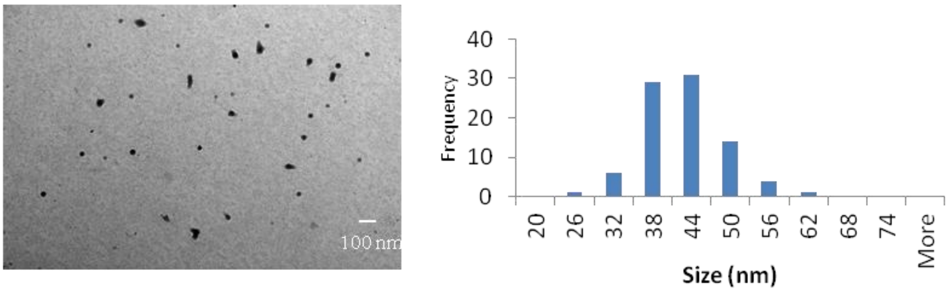
N3


100 nm
Frequency
40
30
20
10
0
20
26
32
38
44
50
56
62
68
74
More
Size (nm)

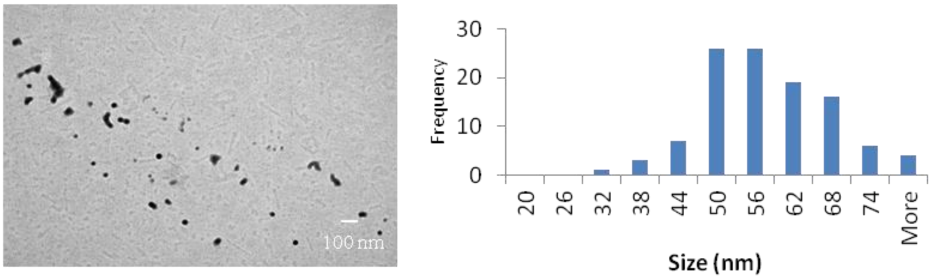
N4


100 nm
Frequency
20
15
10
5
0
20
26
32
38
44
50
56
62
68
74
More
Size (nm)

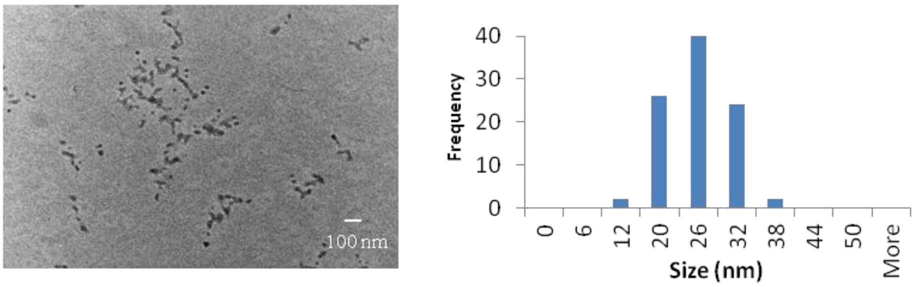
N5


100 nm
Frequency
40
30
20
10
0
20
26
32
38
44
50
56
62
68
74
More
Size (nm)

N6


100 nm
Frequency
30
20
10
0
20
26
32
38
44
50
56
62
68
74
More
Size (nm)

N7


100 nm
Frequency
40
30
20
10
0
0
6
12
20
26
32
38
44
50
More
Size (nm)

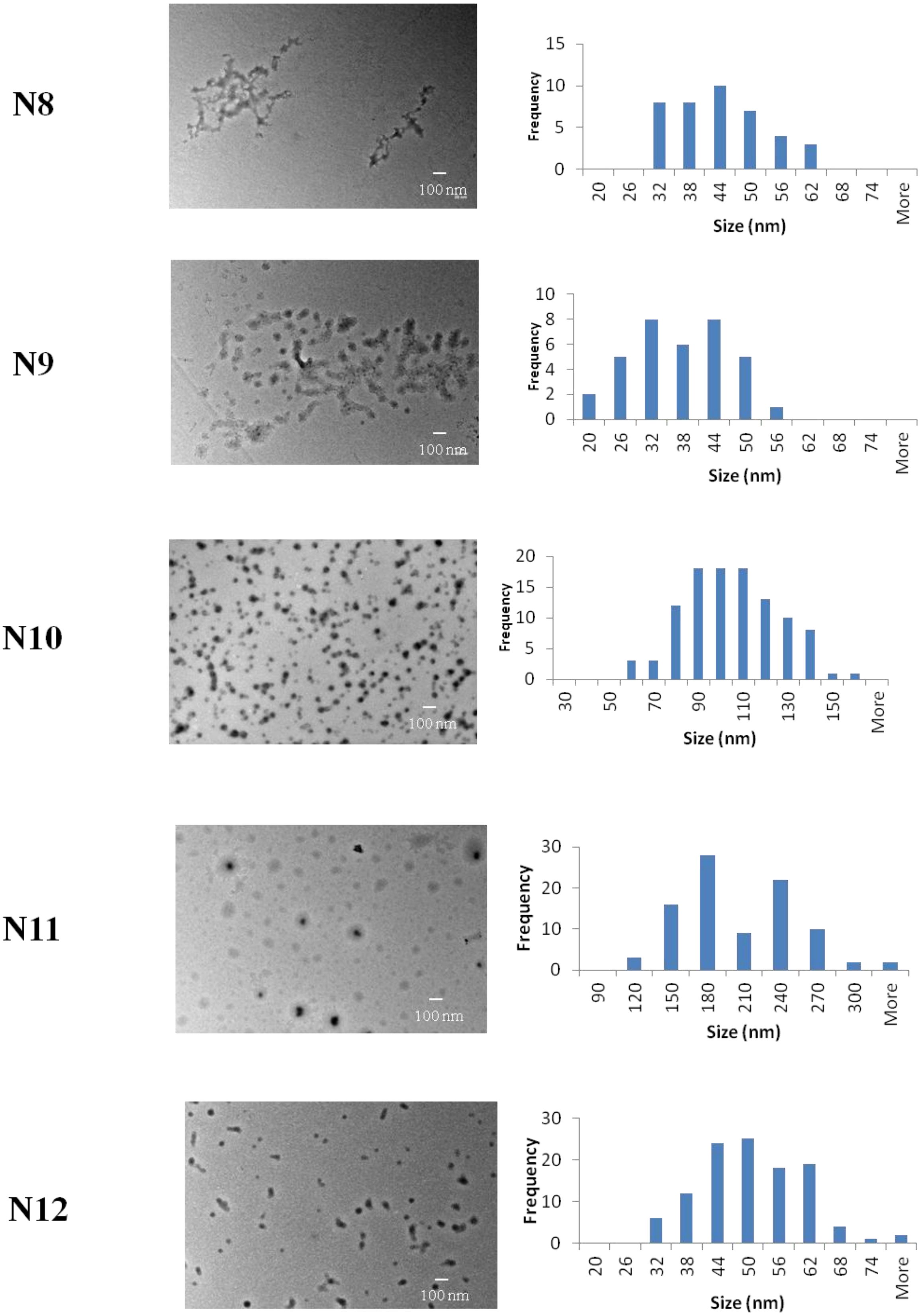


Figure S2. Dry state TEM images without staining and frequency count of the each of the nanogels, **N1**-**N12**.

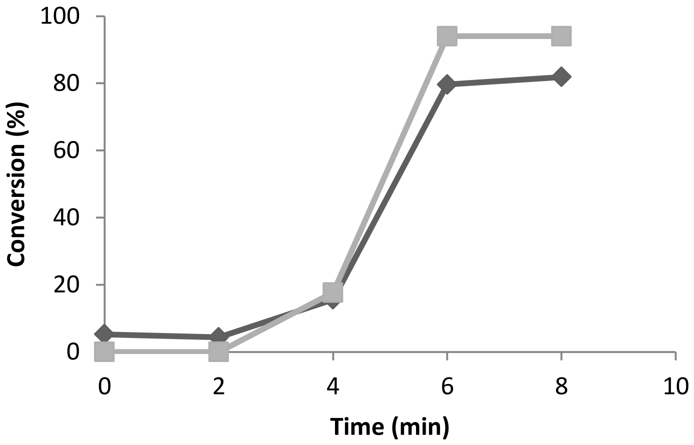


Figure S3. Conversions of the monomers in the nanogel with EMA (grey) (relative conversion) and **M1** (black).

The conversion in Figure S3 was calculated by synthesizing a nanogel with no cross-linker in order to analyse the resulting polymer by ^{1}H NMR spectroscopy. The samples were swollen by the addition of THF which causes the nanostructures to become unstable. After the removal of excess solvent the ^{1}H NMR spectra were recorded for at different time-interval with sampling and the integration of monomer: polymer for **M1** was used to determine the conversion. As EMA monomer will have been removed on removal of THF, the final ^{1}H NMR spectrum was taken to be 100% conversion for EMA and the relative integration of EMA polymer to **M1** polymer was used to determine the conversion of EMA.

Table S1. The conversions of the DA reaction after 24 h between cinnamaldehyde and cyclopentadiene conducted with the nanogels **N4** – **N6** at 5 mol% in the same volume of 1.365 mL.

Nanogel	DoF (%)	Amount of Nanogel (mL)	Amount of water (mL)	Conv. (%)
N4	15	1.365	0	26
N5	20	1.02	0.345	60
N6	25	0.815	0.550	62

The volume was kept the same (in the reactions shown in Table S1) by the addition of water to **N5** and **N6**. This corresponds to Figure 1C in the main text. These conditions have allowed for the effect of nano-environment concentration to be examined and whilst **N5** and **N6** conversion has dropped on dilution at these conditions they still outperform **N4** despite **N4** having a higher nanogel concentration.

Table S2. The conversions and turnover number (TON) of the Diels Alder reaction after 24 h between cinnamaldehyde and cyclopentadiene conducted with the nanogels **N5** and **N6** at various mol%.

Nanogel	Mol%	Conv. (%)	Nanogel Volume (mL)	TON	Conv. (%)	Nanogel Volume (mL)	TON
		Vary Substrate Volume			Vary Nanogel Volume		
N5	**1**	40	1.02	40	15	0.255	15
	2.5	53	1.02	21	40	0.51	16
	5	72	1.02	15	72	1.02	15
	10	80	1.02	8	95	2.04	10
N6	**1**	44	0.815	44	28	0.204	28
	2.5	57	0.815	23	48	0.407	20
	5	82	0.815	16	82	0.815	16
	10	60	0.815	6	94	1.63	10

The changing mol% has been achieved using two different methods either varying the amount of substrate added to a fixed volume of nanogel or by varying the amount of nanogel added to a fixed amount of substrate. At higher mol% the conversion has increased, however, the two methods have not achieved the same result for the same mol%, with the reactions conducted in the higher volume (highlighted in red) consistently outperforming the lower volumes. This is likely to be due to a physical affect such as how effective the stirring is in different volumes of reaction which could produce different levels of emulsion.

Table S3. The conversions and selectivities of the Diels Alder reaction after 24 h between cyclopentadiene and a range of dieneophiles conducted at 5 mol% with **N5**.

Dieneophile	Conversion	*exo*:*endo*	*exo* ee %	*endo* ee %
Acrolein	0			
***trans* 2-hexen-1-al**	40	1.0:1.3	76	85
***trans* 2-nonen-1-al**	49	1.0:1.5	80	85
Cinnemaldehyde	72	1.0:0.8	70	77

In order to analyze the reactions with lower boiling point dieneophiles it was necessary to synthesize a nanogel using deuterated water so that the solvent did not have to be removed before analysis. The nanogel was synthesized in the same manner but with D_2O instead of H_2O. The reactions were performed as detailed in the experimental section. The work up differed with the nanogels being dispersed by the addition of THF and taking a sample of the reaction mixture for ^{1}NMR spectroscopy analysis which was conducted on a long acquisition. The selectivities were measured using GC with slight alterations to the analsysis conditions.

Table S4. The core-shell nanogels synthesized from the seed **N5** with the shell monomer of NiPAM (**N10)** or TEGMA (**N11**).

Nanogel	Shell	Size (nm), (Đ)

N10	NiPAM	151 (0.062)
N11	TEGMA	175 (0.172)

The increase in size from **N5** of 35 nm to the 151 and 175 is indicative of a shell addition. size and dispersity (measured by DLS).

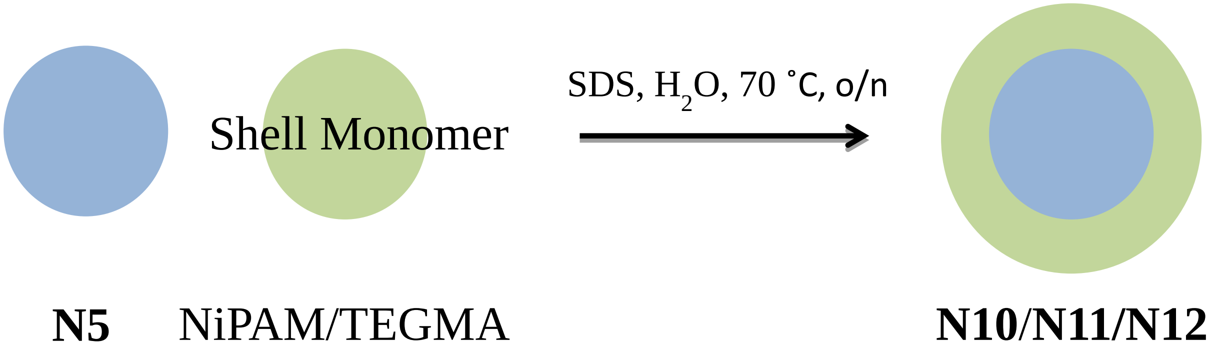


Figure S4. A schematic representation of the synthesis of core-shell nanogel particles starting from the seed **N5** with the addition of NiPAM or TEGMA under emulsion polymerization conditions yields larger particles which contain the shell.

Table S5. The Diels Alder reaction between cinnamaldehyde and cyclopentadiene results catalyzed by the core shell particles **N10** and **N11** at different catalyst loading.

Nanogel	Catalyst loading (mol %)	Conversion (%)
N10	5	10
N11	5	7
N10	2.5	8
N11	2.5	5
N10a	2.5	0
N10a	5	13
N10a	10	13
N10a	20	30
N11a	5	18

In order to try an increase conversion the nanogels were concentrated to twice their original concentration to mimic the catalysts concentration of **N5** to give the nanogels **N10a** and **N11a**. These reactions were conducted at room temperature and in some cases varying the mol% of the reaction. Unfortunately only very low conversions were obtained.

Table S6. The selectivities of the Diels Alder reaction after 24 h between cinnamaldehyde and cyclopentadiene at 5 mol% using the core-shell particles **N10**, **N11** and **N12**, the conversions can be seen in Table S4.

Catalyst	*exo*:*endo*	*exo* ee %	*endo* ee %
N10	0.7	52	56
N11	0.7	35	60
N12	1.3	51	38

The enantioselectivity of the catalyst has been compromised in this scenario with very low enantioselectivities reported.

Table S7. The conversions of the Diels Alder reaction after 24 h between cinnamaldehyde and cyclopentadiene conducted with **N10a** and **N11a** at various temperatures.

Nanogel	Mol %	Temp (˚C)	Conv. %
N10a	5	4	10
N10a	5	20	13
N10a	5	40	0
N11a	5	4	13
N11a	5	20	18
N11a	5	40	12

As these core-shell nanoparticles have thermoresponsive shells a change in temperature affects the structure with an increase causing the shell to become hydrophobic and collapse. Therefore the higher temperatures do not yield increased conversions as would be anticipated due to the change in nanogel structure making the catalyst inaccessible.