

In-situ formation of crosslinked core-corona polymeric nanoparticles from a novel hyperbranched core

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SUPPORTING INFORMATION

^1H NMR spectrum for hyperbranched polyDVB core (Fig. S1) and calculation of branching ratio (Eq. S1). The kinetic study and initiation efficiency of homopolymerization of styrene and methyl methacrylate with DE-ATRP approach (Table S1). Composition data of CCC nanogel by ^1H NMR spectroscopy (Table S2). AFM topology image for CCC nanogel deposited on silica substrate (Fig. S2).

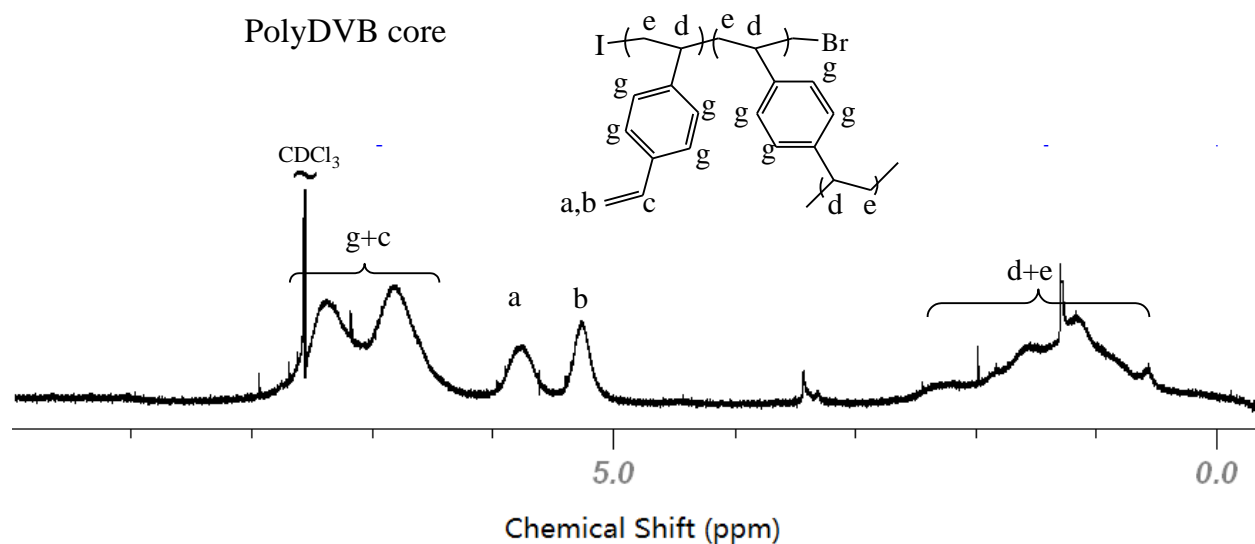


Figure S1. The ^1H NMR spectrum for a hyperbranched polyDVB core (Entry 1, Table 1). The calculation of branching ratio was given in Eq.S1.

$$\text{Branching ratio} = \frac{\text{Branched DVB units}}{\text{Linear DVB units}} = \frac{[\text{integral of } (d + e) - 3 \times (\text{integral of } b)] / 6}{\text{integral of } b} \quad (\text{Eq. S1})$$

Table S1. Homopolymerisation of styrene and methyl methacrylate with DE-ATRP approach. The initiation efficiency was calculated from the kinetic study.

	Reaction Time (hrs)	Conv ^c	M _n (g.mol ⁻¹) ^d	PDI ^d	M _{theo} (g.mol ⁻¹) ^e	Initiation Efficient ^f
1. Styrene^a	9	21%	4630	1.12	4541	98%
2. MMA^b	6	24.2%	5210	1.1	5011	95.8%

[a]. Polymerisation condition: [Styrene]/[EBriB]/CuBr/CuBr₂/bpy =200:1:0.4:0.133:1.06 [Sty]=3M in toluene, T=90 °C

[b]. Polymerisation condition: [MMA]/[EBriB]/CuBr/CuBr₂/bpy =200:1:0.4:0.133:1.06 [MMA]=3M in butanone, T=60 °C

[c]. Monomer conversion is determined by ¹H NMR

[d]. M_n and PDI is determined by GPC-RI detector with linear PMMA standard

[e]. theoretical molecular weight= 200 x FW_{monomer} x Conv+FW_{initiator}

[f]. Initiation Efficiency=M_{theor}/M_n

Table S2. Characterization composition of DVB and MMA units for hyperbranched core (entry 1) and crosslinked core-corona nanogel (entry 2-4) formed using DE-ATRP. The compositions were calculated by comparing the integrals of different resonance of protons from DVB and MMA in the ¹H NMR spectra (see Eq. 2 and Fig.5 in main text). It worth noting that the ratio of MMA to DVB could be an underestimate due to the presence of solvent (CDCl₃) peak at 7.26 ppm.

	Reaction time	DVB: MMA
Core	0	-
Core-Crosslinked Corona (CCC)	0.5	1: 2.3
	2	1:4.1
	10	1:5.2

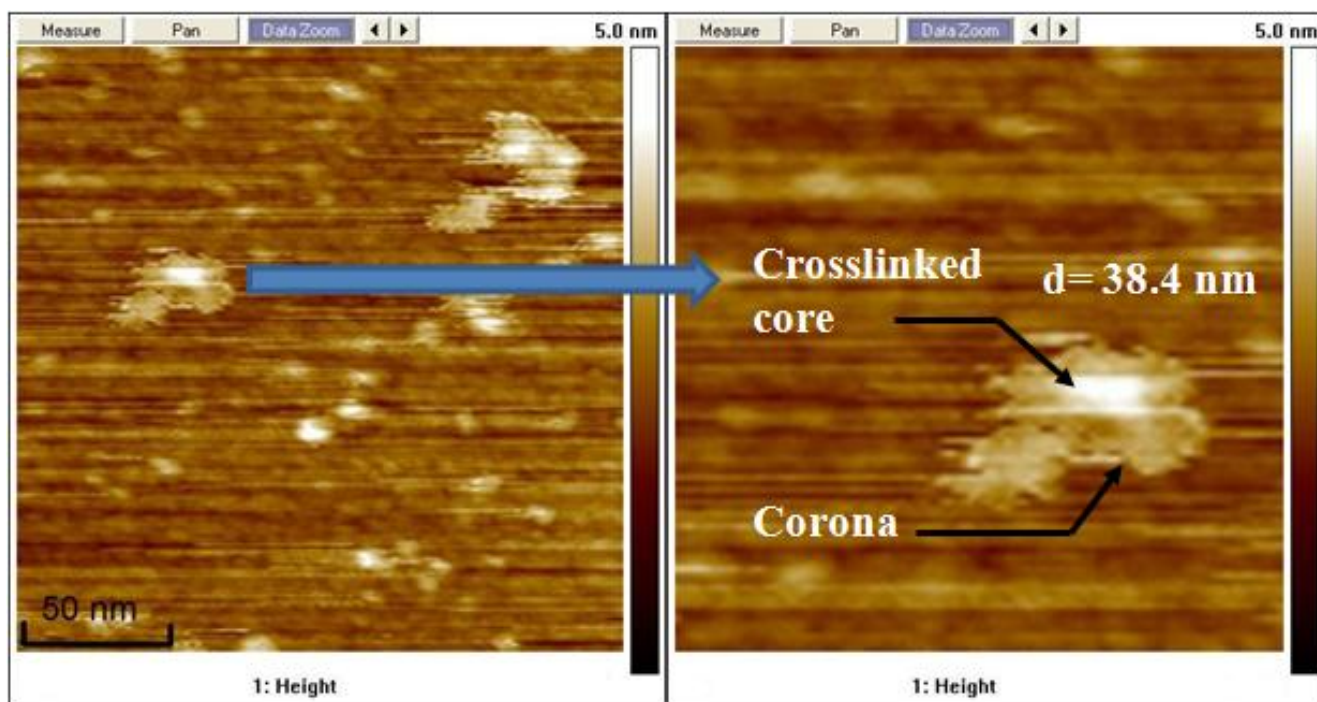


Figure S2 AFM topology image for CCC microgel deposited on silica substrate. The samples are prepared in a dilute solution ($10 \mu\text{g/L}$) in THF and dropped on silica substrate by spin coating (1000 rpm). The enlarged image (right) clearly shows the core-shell like molecule was formed during the reaction. The core-shell polymer is displayed as a ‘fried egg’ shape on the dry silica substrate.