Electronic Supplementary Material (ESI) for Polymer Chemistry
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Supplementary Information

Biodegradable Core Crosslinked Star Polymer Nanoparticles as ^{19}F MRI Contrast Agents for Selective Imaging

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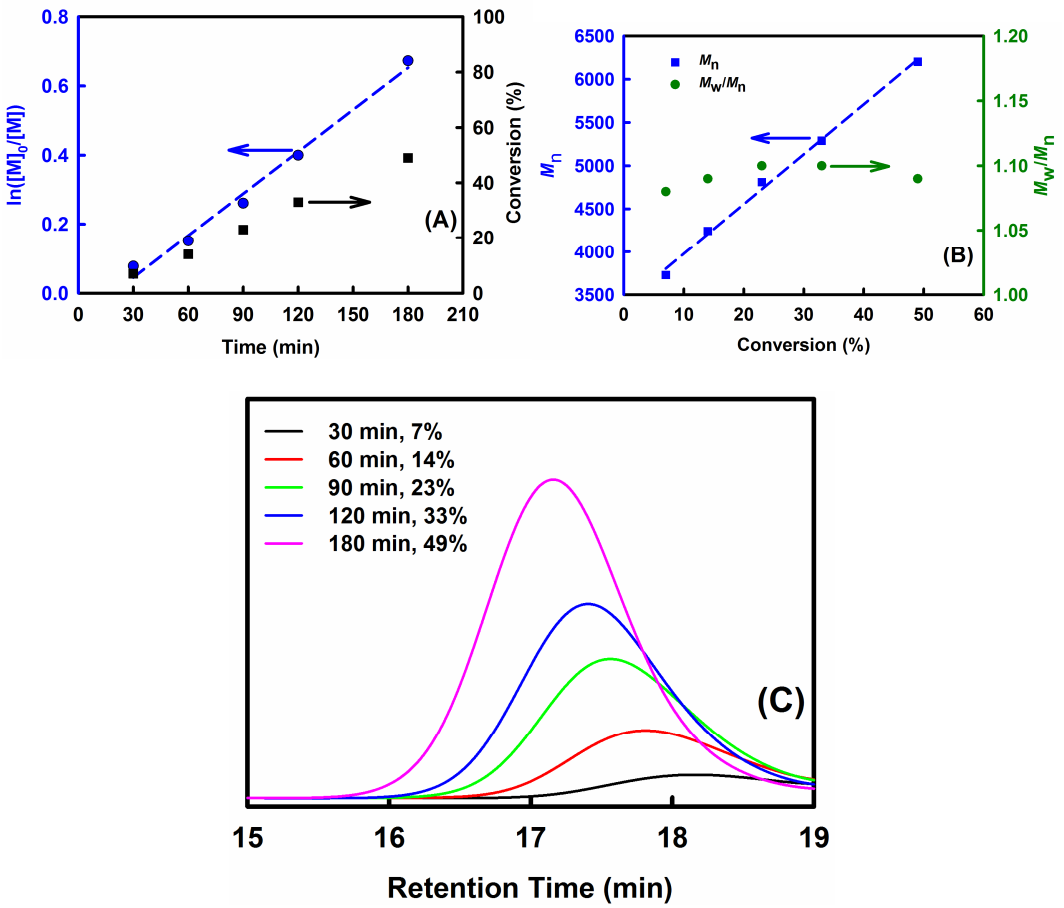

Fig. S1 RAFT polymerisation of PEGMA using alkyne-CTA. (A) Pseudo-first-order kinetic plot of the polymerisation. (B) Dependence of number-average molecular weight (M_n, determined by GPC) and molar-mass dispersity ($Đ_M$) on monomer conversion. (C) GPC traces during the polymerisation.

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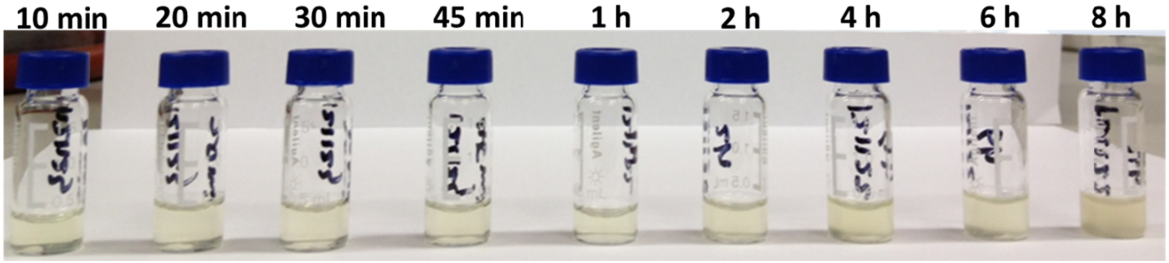

Fig. S2 Digital photo of the samples withdrawn at different time intervals during the synthesis of CCS polymer by RAFT dispersion polymerisation. The samples were at room temperature (~25 oC).

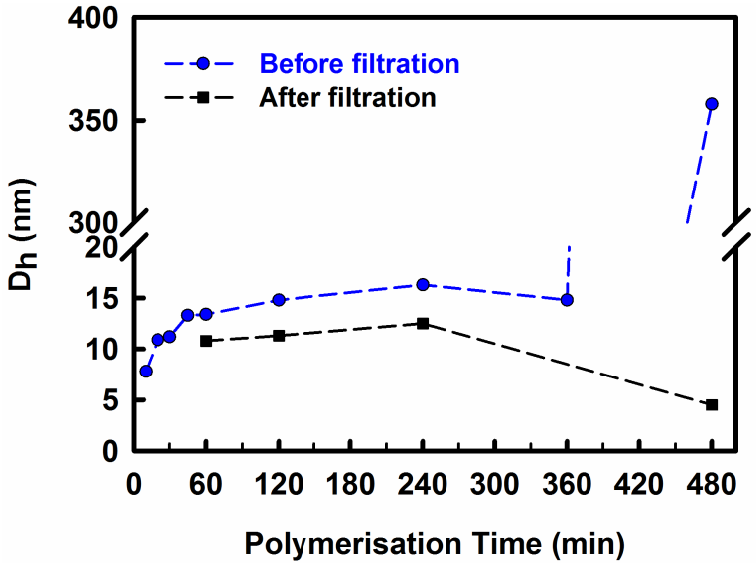

Fig. S3 DLS results of the samples at different polymerisation time before and after filtration using 450 μm syringe filters. Each size was the average of five measurements at 25 oC.

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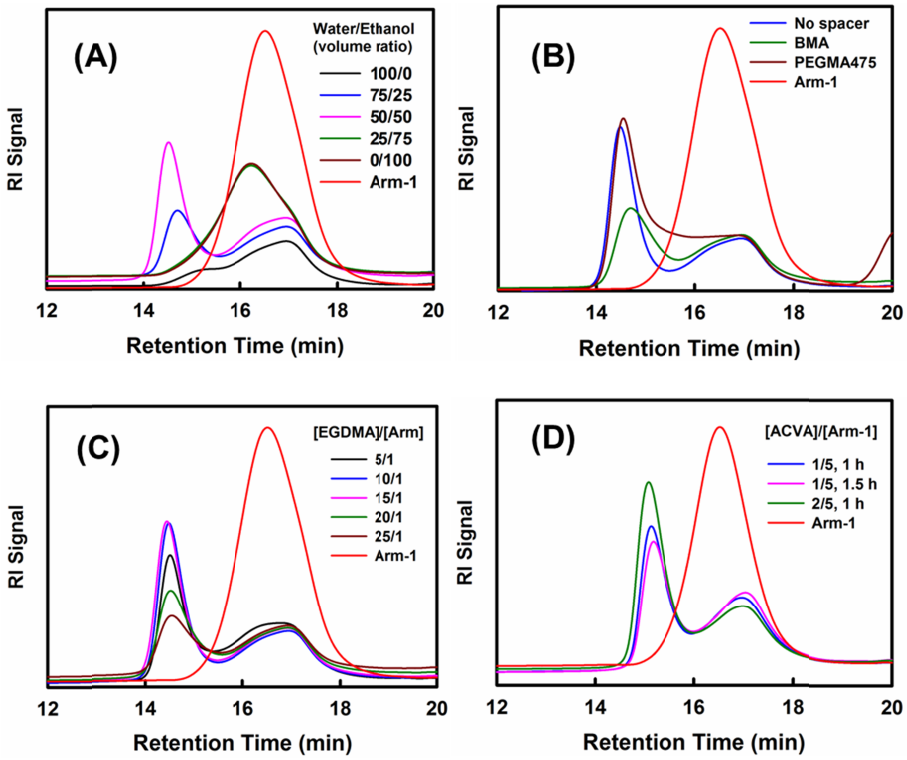

Fig. S4 GPC traces of CCS polymers synthesised at (A) different water/ethanol ratios, (B) with or without spacer and (C) different EGDMA/arm ratios. Conditions: (A) [Arm-1]/[EGDMA]/[BMA]/[ACVA] = 1/5/5/0.2, [arm-1] = 5 mM, 70 ^{o}C,1 h. (B) [Arm-1]/[EGDMA]/[Spacer]/[ACVA] = 1/10/10/0.2, [arm-1] = 5 mM, water/ethanol (50/50, v/v), 70 ^{o}C,1 h. (C) [Arm-1]/[ACVA] = 1/0.2, [arm-1] = 5 mM, water/ethanol (50/50, v/v), 70 ^{o}C, 1 h. (D) [Arm-1]/[EGDMA] = 1/10, [arm-1] = 5 mM, water/ethanol (50/50, v/v), 70 ^{o}C.

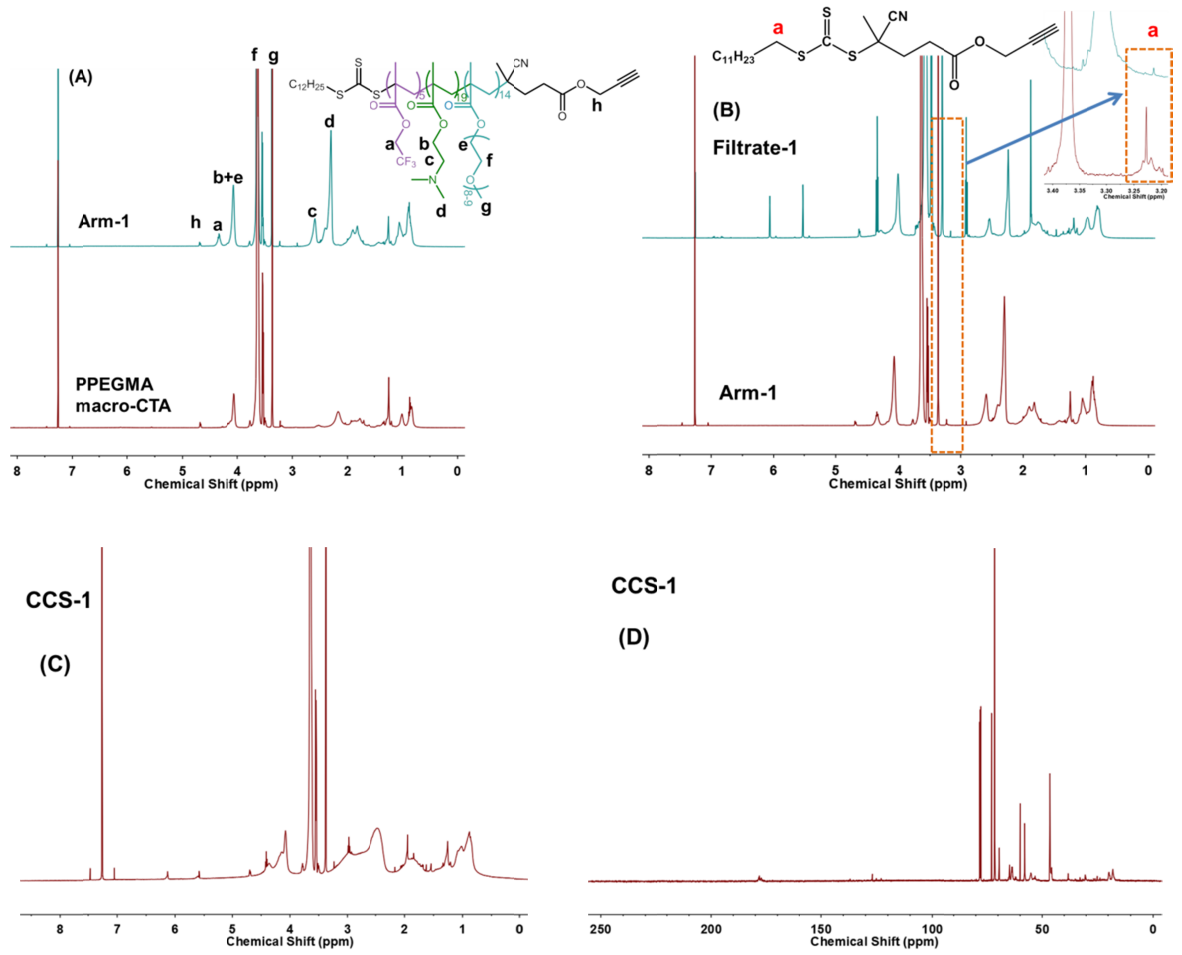

Fig. S5 (A), (B) and (C) 1H NMR spectra of macro-CTA, Arm-1, filtrate-1 and CCS-1. 'e' represents the two protons of the CH_2 adjacent to −COO− in PEGMA. (D) 13C NMR spectrum of CCS-1.

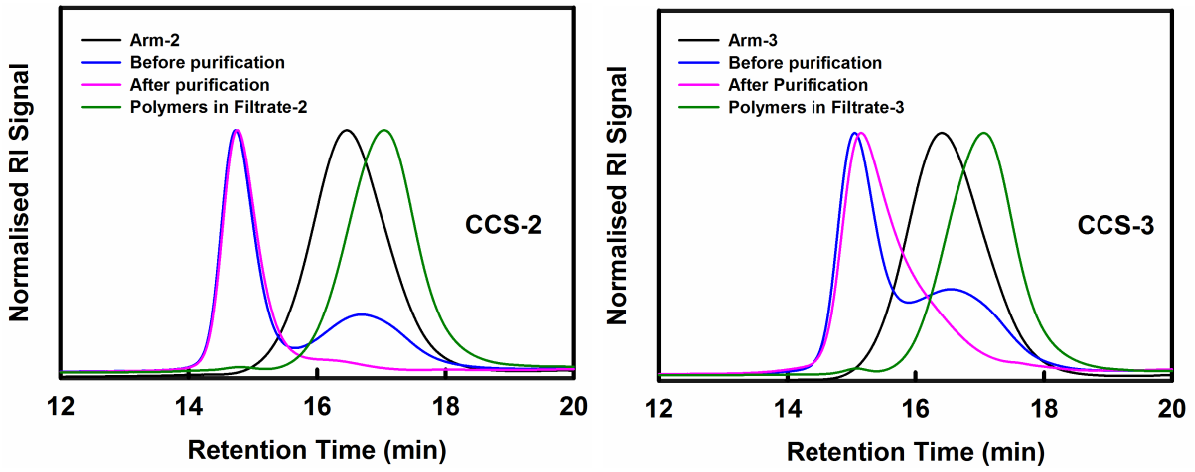

Fig. S6 GPC traces of the polymers related to the synthesis of CCS-2 and CCS-3

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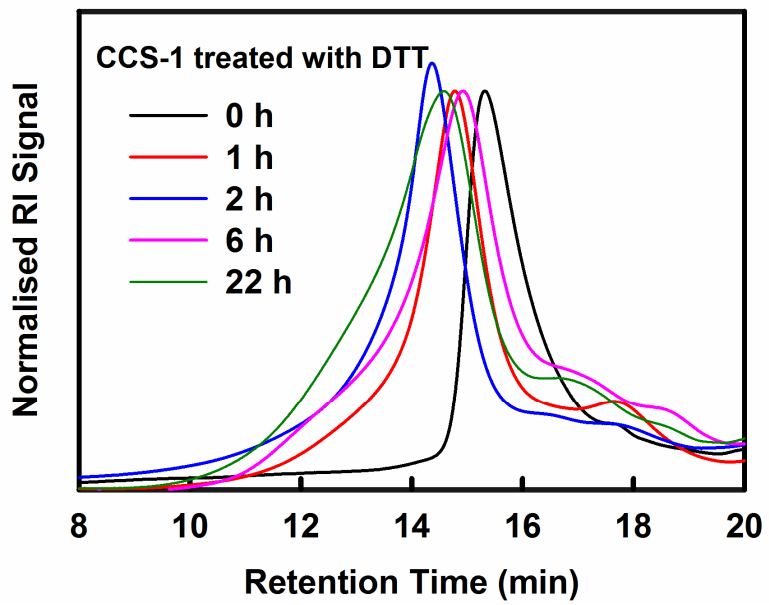

Fig. S7 GPC traces during the degradation of CCS-1 using DTT in THF. [DTT] = 50 mM, [CCS-1] = 1.15×10^{-3} mM.

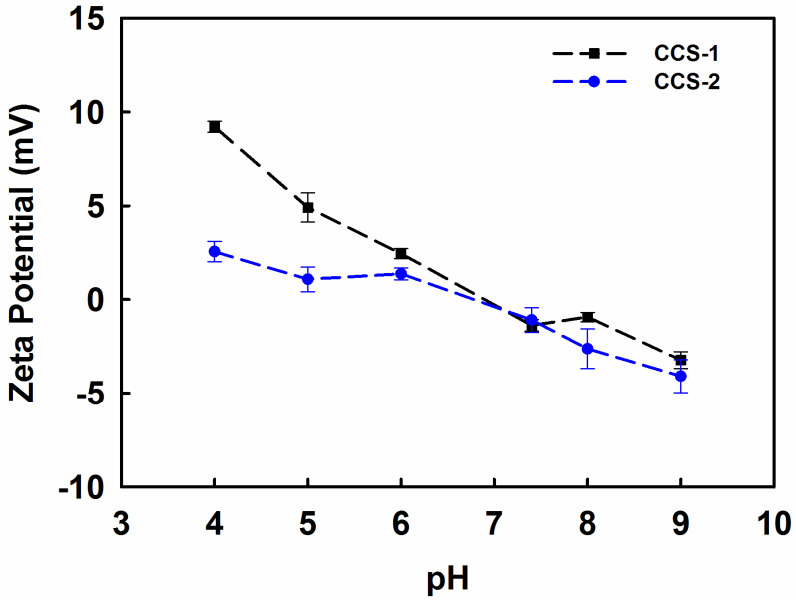

Fig. S8 Zeta potential of CCS-1 and CCS-2 at different pH in PBS.

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Calculation of arm number

The arm number can be calculated according to the previously published methods. [1, 2]

First, the weight fractional of arms in CCS polymer can be calculated based on the **Eq. (1)**

$$\mathrm{WF_{arm}} = \frac{\mathrm{m_{arm}} \times X_{\mathrm{arm}}}{\mathrm{m_{arm}} \times X_{\mathrm{arm}} + \mathrm{m_{CL}} \times X_{\mathrm{CL}}} \quad \textbf{(1)},$$

where $\mathrm{WF_{arm}}$ is the weight fractional of arms in CCS polymer, $\mathrm{m_{arm}}$ is the mass of arms, X_{arm} is the conversion of arms that are incorporated into CCS polymer, $\mathrm{m_{CL}}$ is the mass of crosslinker, and X_{CL} is the conversion of crosslinker. We assume that the conversion of crosslinker is 100% because of the high polymerisation rate in a RAFT dispersion polymerisation.

Then the arm number can be obtained using the **Eq. (2)**

$$f = \frac{M_{\mathrm{w(CCS)}} \times \mathrm{WF_{arm}}}{M_{\mathrm{w(arm)}}} \quad \textbf{(2)},$$

where f is arm number, $M_{\mathrm{w(CCS)}}$ is weight-average molecular weight of CCS polymer and $M_{\mathrm{w(arm)}}$ is weight-average molecular weight of arms.

The details are listed in the following table.

Table S1 Details for the calculation of arm numbers.

Sample	$\mathrm{m_{arm}}$ (g)	X_{arm}	$\mathrm{m_{CL}}$	X_{CL}	$M_{\mathrm{w(CCS)}}$	$M_{\mathrm{w(arm)}}$ [a]	$\mathrm{WF_{arm}}$	f
CCS-1	2.16	0.74	0.58	1	764400	10500	0.734	53
CCS-2	0.39	0.65	0.1	1	516300	11300	0.717	33
CCS-3	0.53	0.6	0.139	1	785500	11700	0.713	49

[a] M_{n} (^{1}H NMR) was used for $M_{\mathrm{w(arm)}}$

References

1. A. Blencowe, J. F. Tan, T. K. Goh and G. G. Qiao, *Polymer*, 2009, **50**, 5-32.
2. X. F. Shi, W. Zhou, Q. Qiu and Z. S. An, *Chem Commun*, 2012, **48**, 7389-7391.