Electronic Supplementary Material (ESI) for Chemical Communications

Amphiphilic heteroarm star polymer synthesized by RAFT dispersion polymerization in water/ethanol solution

Supporting Information

Xiaofang Shi, Wei Zhou, Qian Qiu and Zesheng An*

Institute of Nanochemistry and Nanobiology, College of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, P. R. China.

E-mail: an.zesheng@shu.edu.cn

Materials.

2,2′-Azobis(2-methylpropionamidine)dihydrochloride (V-50, 97%) and 2-methoxyethyl acrylate (MEA, 98%) were purchased from Sigma-Aldrich. *N*,*N*'-Dimethylacrylamide (98%) was purchased from J&k. 1,6-Hexanediol diacrylate (HDDA) (90%) was purchased from Aladdin Reagent (China). *n*-Butyl acrylate (BA) (CP) and 2,2'-azobis(2-methylpropionitrile) (AIBN, CP), were purchased from Sinopharm Chemical Reagent Co. Ltd. AIBN was recrystallized from methanol twice. All monomers were passed through a column of Al_2O_3 to remove the inhibitor before use.

Characterization.

NMR spectra were collected on a Bruker AV 500 MHz spectrometer and chemical shifts were reported using the solvent residue as the reference.

RI-GPC: GPC measurement was performed on a Waters Alliance e2695 GPC system, equipped with a styragel guard column, a Waters styragel HR3 (molecular weight range $5.0 \times 10^2 - 3.0 \times 10^4$), a Waters styragel HR4 (molecular weight range $5.0 \times 10^3 - 6.0 \times 10^5$), and a Waters styragel HR5 (molecular weight range $5.0 \times 10^4 - 4.0 \times 10^6$). Detection was performed on a 2414 refractometer using DMF (HPLC grade, containing 1 mg/mL LiBr) as the eluent at a flow rate of 0.8 mL/min. The temperature of the columns was set at 65 °C and the temperature of the refractometer was set at 45 °C. Analysis of molecular weight and polydispersity index of polymers was performed using Empower 2 software against PMMA standard (molecular weight range $2.4 \times 10^2 - 1.0 \times 10^6$).

Triple-detection GPC: Measurement was performed by Malvern Instruments (China) on a Viscotek/Malvern GPC system consisting of a GPCMax auto-injector fitted to a TDA 305 triple detector array (differential RI, right angle light scattering (RALS), low angle static light scattering (LALS) and four-capillary differential viscometer detectors). The column was

Viscotek I MBMMW, DMF containing 0.02 M LiBr was used as the eluent at a flow rate of 0.7 mL/min, and the temperature of the column was controlled at 50 °C. PMMA standard was used for calibration.

Star polymer sizing was analyzed using dynamic light scattering (DLS) on a Malvern Zetasizer 3000HSA at 25 °C.

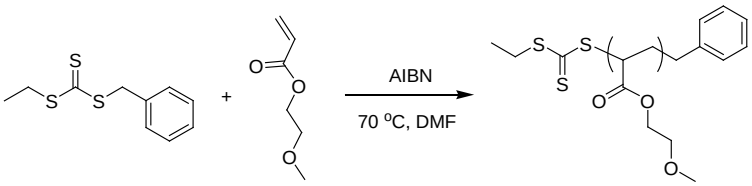
Transmission electron microscopy (TEM) imaging was performed on a Jeol 200CX microscope operating at 200 kV. The TEM samples were prepared by depositing the star polymer solution onto the copper grid with a glass capillary tube and were stained with iodine vapor in a sealed vial with a grain of iodine overnight.

Atomic force microscopy (AFM) was performed on a Shimadzu SPM-9600 operating in the tapping mode. The AFM samples were prepared by depositing the star polymer solution onto freshly cleaved mica and dried in air.

Preparation of arm polymers.

Poly(*N,N'*-dimethylacrylamide) (PDMA) was synthesized similarly as previously reported.[1] M_n = 8 kDa (RI-GPC), M_w/M_n = 1.10 (RI-GPC).

(1) Poly(2-methoxy ethyl acrylate) (PMEA):



PMEA was synthesized in DMF at an MEA concentration of 50% w/v at 70 °C. Chain transfer agent benzyl ethyl trithiocarbonate (0.35 g, 1.54 mmol) and MEA (20 g, 0.154 mol) were dissolved in 40 mL of DMF. The solution was degassed with nitrogen at 0 °C for 40 min before immersion into a preheated oil bath at 70 °C. After the temperature was stabilized, a degassed

solution of AIBN (5.1 mg, 0.03 mmol) in DMF was injected via a microsyringe. The polymerization was last for 3 h. The conversion of monomers was calculated to be 74%. The polymer was purified by pouring the polymerization mixture into HCl solution (pH=4) to precipitate the polymer, which was then redissolved into THF and precipitated into acid solution. The collected polymer was dried under vacuum to get 14.7 g (72% yield) of a viscous liquid. M_n = 14 kDa (RI-GPC), M_w/M_n = 1.12 (RI-GPC).

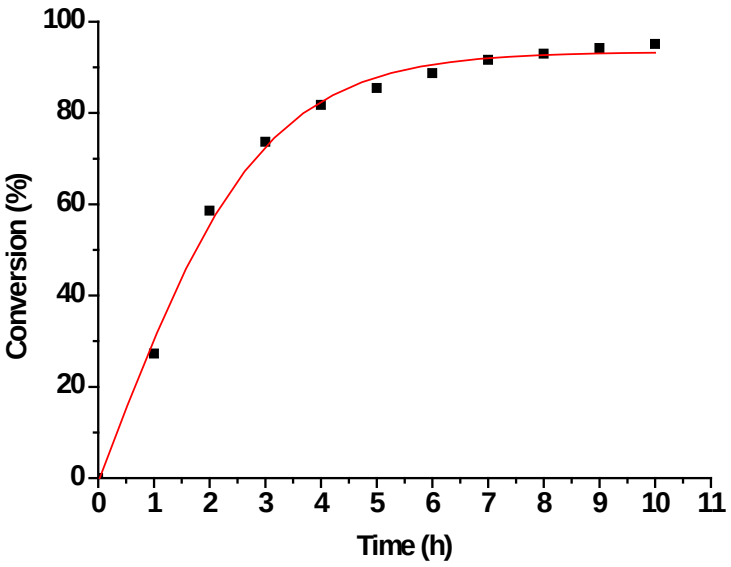


Fig. S1 MEA conversion *vs* time under the polymerization condition described above. [CTA]:[MEA]:[AIBN]=1:100:0.02, [MEA]=50% w/v in DMF, 70°C.

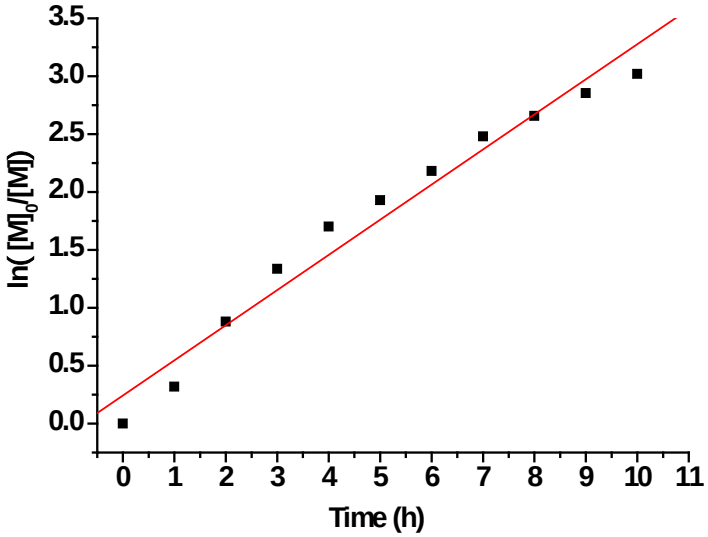


Fig. S2 Pseudo first-order kinetic plot of MEA polymerization under the polymerization condition described above. [CTA]:[MEA]:[AIBN]=1:100:0.02, [MEA]=50% w/v in DMF, 70°C.

Preparation of star polymers

The homoarm and heteroarm CCSs were synthesized at 70 °C using BA as the spacing monomer, HDDA as the cross-linker and V-50 as the initiator. The concentration of the arm polymer(s) was maintained at 10.7 mmol/L (10% w/v for PMEA). The molar ratio of arm polymer:BA:HDDA:V-50 was 1:10:5:0.1. The conversion of arm polymer to star polymer was monitored with GPC. To quantify the arm polymer conversion, 0.2 mL of the CCS synthesis solution was withdrawn at pre-determined time intervals, the solvent of which was removed, and the left material was dissolved in 1 mL of HPLC grade DMF for GPC measurement. The arm conversion was calculated as:

Arm conversion = (Intensity of Arm GPC peak before reaction - Intensity of Arm GPC peak at a specific reaction time) / Intensity of Arm GPC peak before reaction.

(1) Optimization of conditions for PMEA homoarm CCS

The solvent polarity of water/ethanol solution was optimized in order to obtain well-defined PEMA homoarm CCS. The water/ethanol solution composition was varied by increasing the

volumetric fraction of water from 20%, 30%, 40%, 50% to 60%. It was found that in 20% and 30% water/ethanol solution, no CCSs were formed. Defined CCSs were formed in 40%-60% water/ethanol solutions but some precipitate was observed in 60% water/ethanol solution due to the decreased solubility. The formation of PMEA CCS in 40% and 50% water/ethanol solution is shown in Fig. S3 and Fig. S4, respectively.

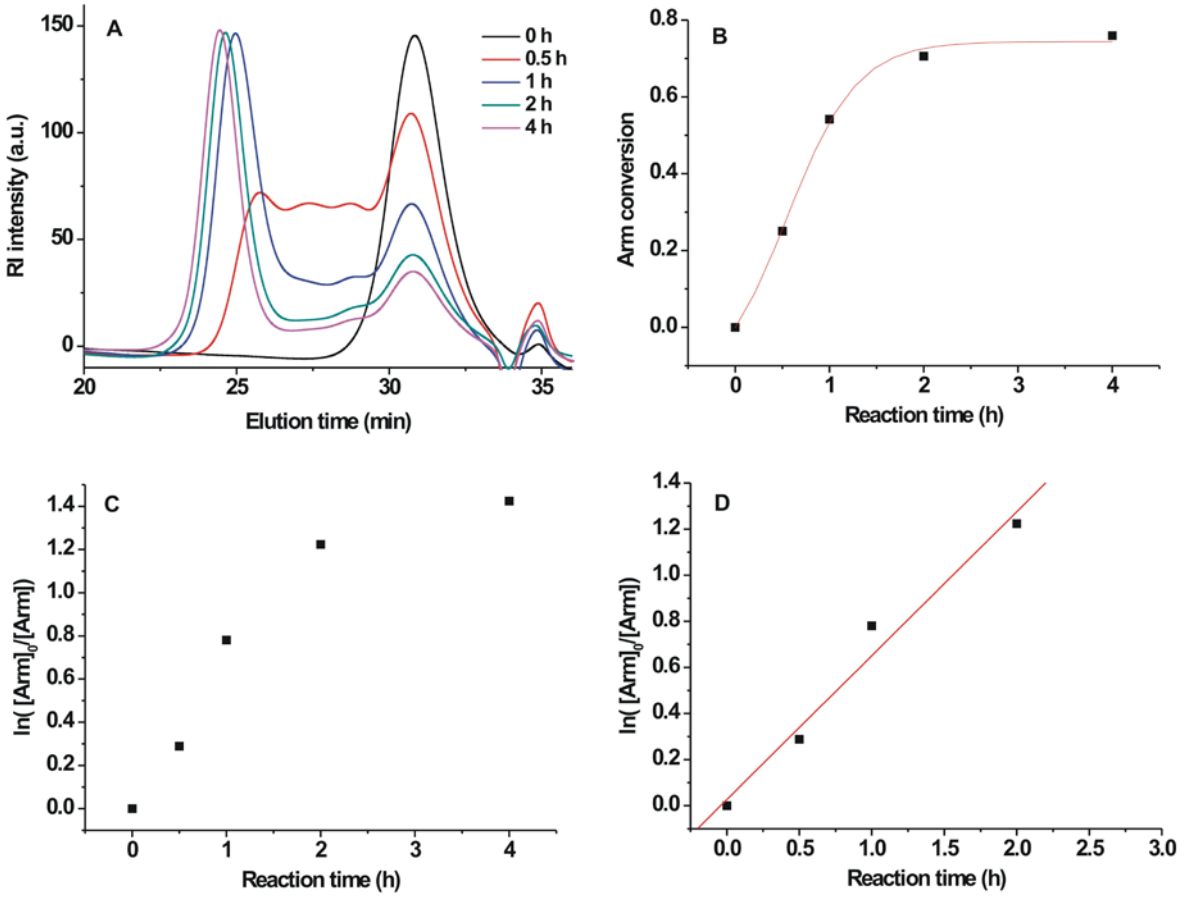


Fig. S3 PMEA homoarm CCS synthesis in 40% water/ethanol, [PMEA]=10.7 mmol/L, [PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C. (A) GPC curves of CCS synthesis at different reaction times; (B) PMEA arm conversion as a function of reaction time; (C) kinetic plot of $\ln([Arm]_0/[Arm])$ *vs* reaction time; and (D) linear fit of kinetic plot within the first 2 h of reaction.

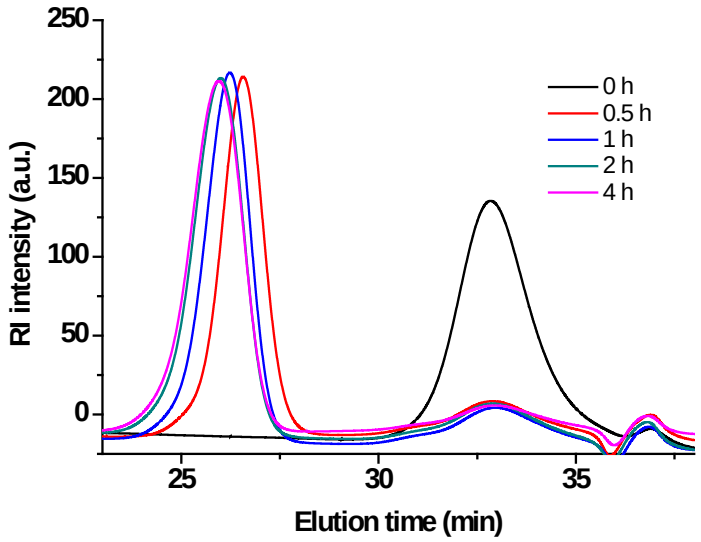


Fig. S4 GPC curves of PMEA homoarm CCS synthesis in 50% water/ethanol at different reaction times. [PMEA]=10.7 mmol/L, [PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.

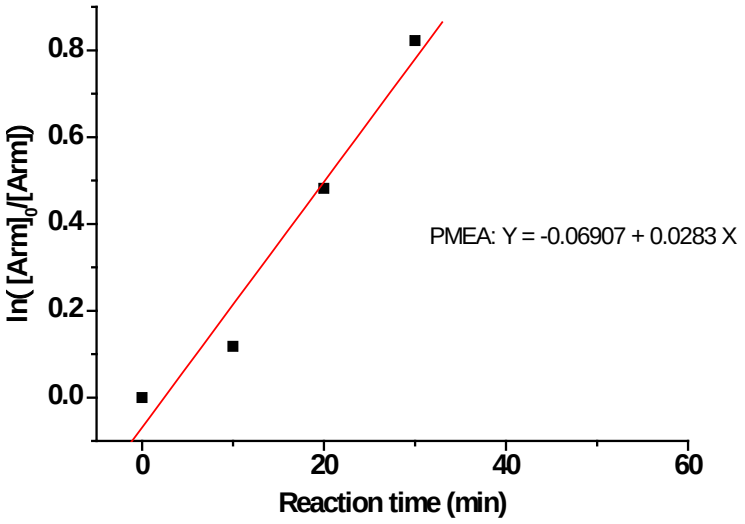


Fig. S5 Linear plot of ln($[Arm]_0$/[Arm]) *vs* time for PMEA homoarm CCS synthesis within the first 30 min of reaction in 50% water/ethanol. [PMEA]=10.7 mmol/L, [PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.

(2) Preparation of PDMA homoarm CCS

Because PDMA is well soluble in water, ethanol and their mixtures of any ratios, PDMA homoarm CCS was prepared directly in 50% water/ethanol solution. Similarly, the molar ratio of

PDMA arm:BA:HDDA:V-50 was controlled at 1:10:5:0.1. The formation of PDMA CCS as a function of time is shown in Fig. S6.

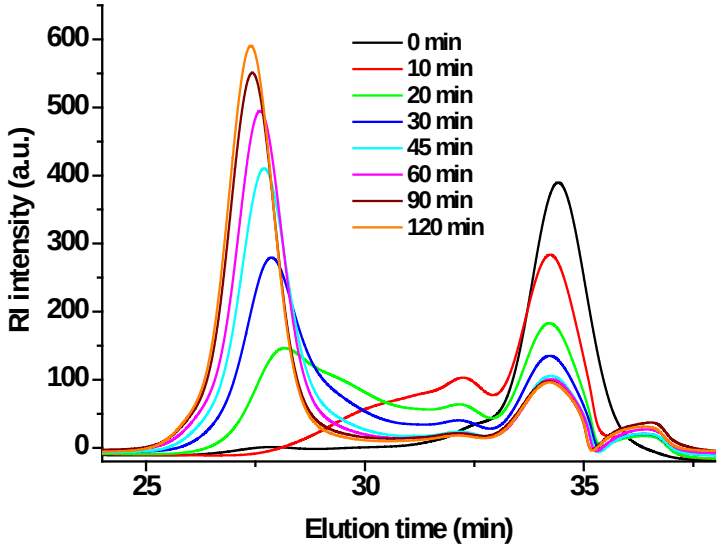


Fig. S6 GPC curves of PDMA homoarm CCS synthesis in 50% water/ethanol at different reaction times. [PDMA]=10.7 mmol/L, [PDMA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.

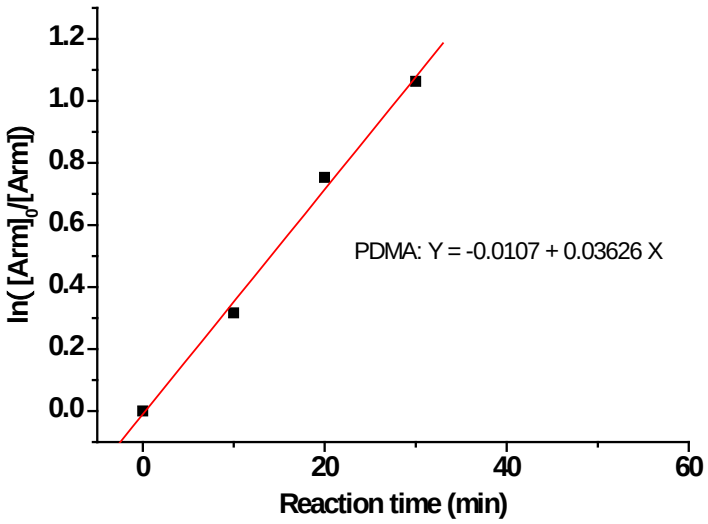


Fig. S7 Linear plot of ln([Arm]$_0$/[Arm]) *vs* time for PDMA homoarm CCS synthesis within the first 30 min of reaction in 50% water/ethanol. [PDMA]=10.7 mmol/L, [PDMA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.

(3) Preparation of PDMA-PMEA amphiphilic heteroarm CCS

PDMA-PMEA amphiphilic heteroarm CCSs were synthesized in either 40% or 50% water/ethanol under conditions similar to PMEA and PDMA homoarm CCS synthesis. The molar ratio (calculated from theoretical molecular weight) of PDMA and PMEA was maintained at 1:1, and the molar ratio of total arm polymer (PDMA+PMEA):BA:HDDA:V-50 was 1:10:5:0.1. For kinetic study, samples were withdrawn at predetermined time intervals. The heteroarm CCS synthesized in 50% water/ethanol was purified by first dialysis against acetone using dialysis tubing (MWCO 25 kDa), followed by precipitation into diethyl ether. The collected polymer was re-dissolved in THF and precipitated into ether.

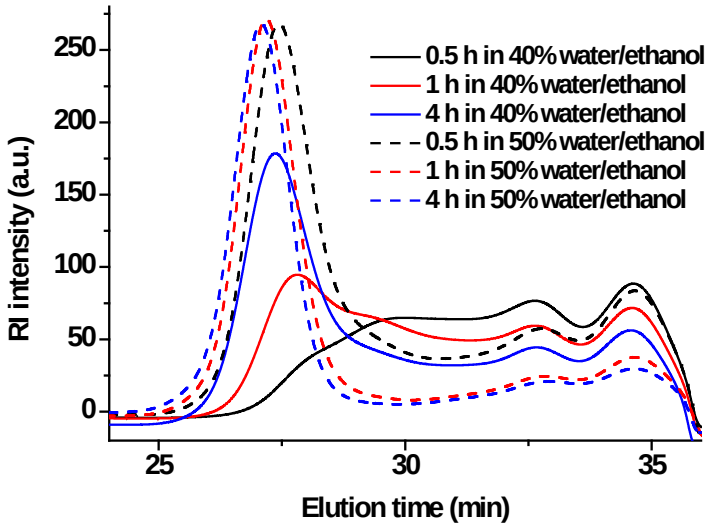


Fig. S8 GPC curves of PDMA-PMEA heteroarm CCS synthesis at different reaction times in 40% and 50% water/ethanol solutions. [PDMA+PMEA]=10.7 mmol/L, [PDMA+PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.

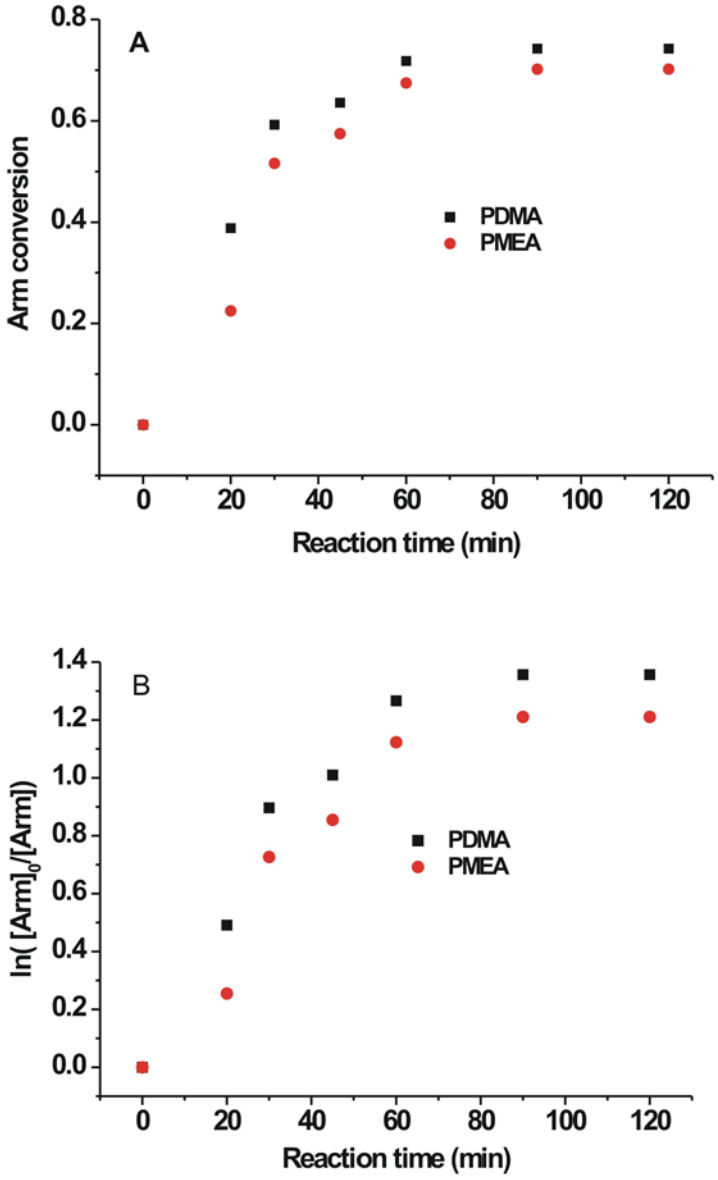


Fig. S9 PDMA-PMEA heteroarm CCS synthesis in 50% water/ethanol solution, [PDMA+PMEA]=10.7 mmol/L, [PDMA+PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C. (A) Conversion of arm polymer as a function of reaction time; (C) kinetic plot of $\ln([Arm]_0/[Arm])$ *vs* reaction time. *The data point at 10 min was not used due to significant overlap of the formed polymers with the arm polymers.*

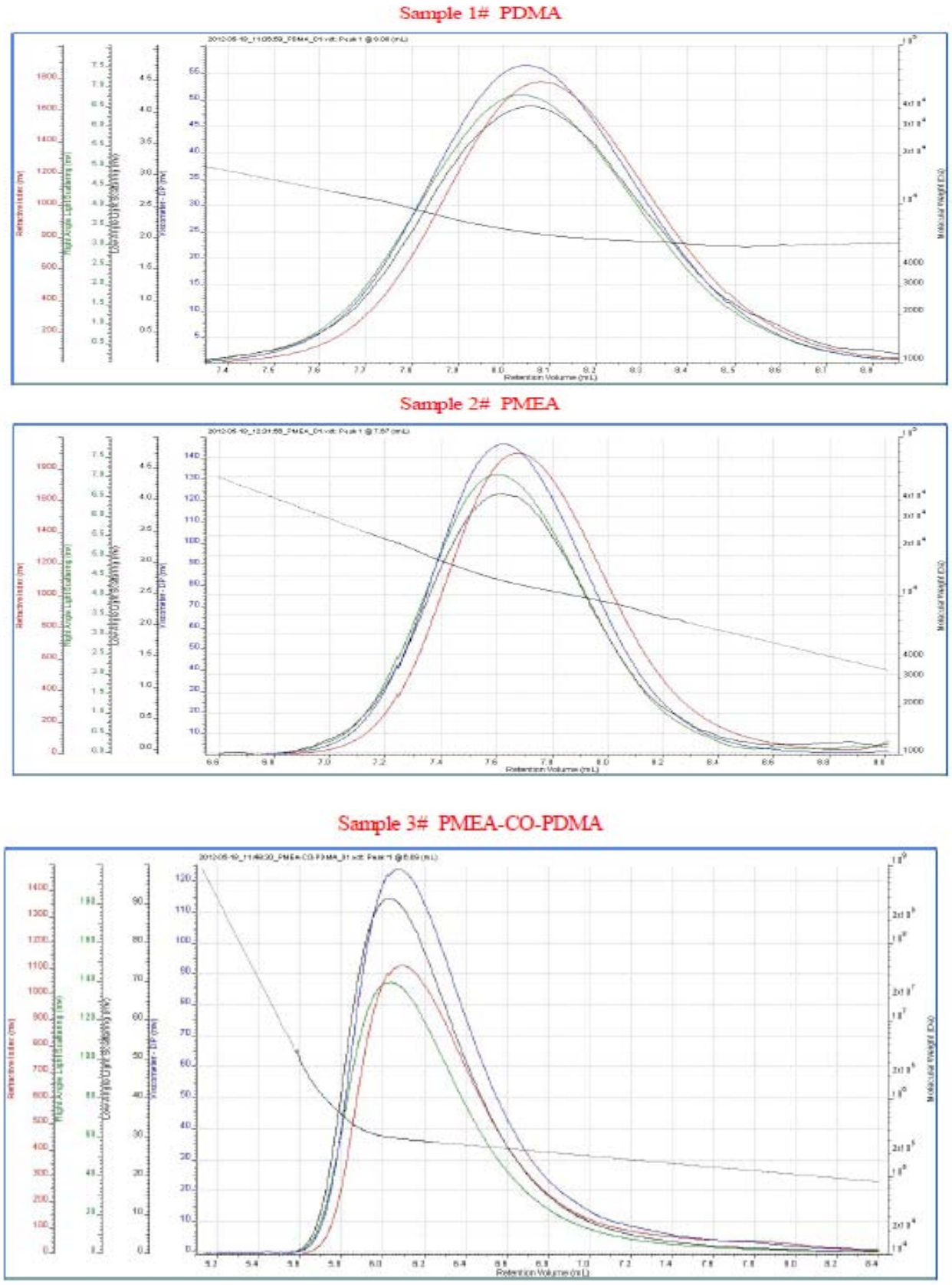


Fig. S10 GPC curves for PDMA and PMEA arm polymers and their heteroarm CCS measured by triple-detection GPC.

Table S1 Macromolecular parameters for PDMA arm measured by triple-detection GPC.

	PDMA arm		Average	RSD%
M_n (Da)	6 602	6 425	6 514	1.92
M_w (Da)	6 862	6 738	6 800	1.29
M_w/M_n	1.039	1.049	1.044	0.68
Mark-Houwink α	0.731	0.720	0.726	1.07
Hydrodynamic radius R_h (nm)	1.766	1.754	1.760	0.48
dn/dc	0.0728	0.0731	0.0730	0.29

Table S2 Macromolecular parameters for PMEA arm measured by triple-detection GPC.

	PMEA arm		Average	RSD%
M_n (Da)	11 652	10 981	11 317	4.19
M_w (Da)	12 494	12 050	12 272	2.56
M_w/M_n	1.072	1.097	1.085	1.63
Mark-Houwink α	0.790	0.749	0.770	3.77
Hydrodynamic radius R_h (nm)	2.267	2.240	2.254	0.85
dn/dc	0.0373	0.0375	0.0374	0.38

Table S3 Macromolecular parameters for PDMA-PMEA heteroarm CCS measured by triple-detection GPC.

	Heteroarm CCS		Average	RSD%
M_n (Da)	259 766	272 828	266 297	3.47
M_w (Da)	289 263	298 357	293 810	2.19
M_w/M_n	1.114	1.094	1.104	1.28
Mark-Houwink α	0.556	0.531	0.544	3.25
Hydrodynamic radius R_h (nm)	8.065	8.162	8.114	0.85
dn/dc	0.0504	0.0503	0.0504	0.14

Calculation of arm numbers in heteroarm CCS.

In the calculation, we assumed that conversion of BA and HDDA was 100%, which is reasonable considering the high polymerization rate and high conversion in heterogeneous polymerization systems.

The arm weight fraction in the heteroarm CCS is given by

$$\chi_{arm} = \frac{m_{PDMA}conv_{PDMA} + m_{PMEA}conv_{PMEA}}{(m_{PDMA}conv_{PDMA} + m_{PMEA}conv_{PMEA}) + (m_{BA}conv_{BA} + m_{HDDA}conv_{HDDA})}$$

in which, $m_{PDMA} = 0.5465$ g, $conv_{PDMA} = 0.74$, $m_{PMEA} = 1.0093$ g, $conv_{PMEA} = 0.70$, $m_{BA} = 0.2759$ g, $conv_{BA} = 1.0$, $m_{HDDA} = 0.2424$ g, $conv_{HDDA} = 1.0$.

Thus, $\chi_{arm} = 0.68$.

The molar ratio of PDMA and PMEA in the final heteroarm CCS was estimated from ^{1}H NMR, which was 1.14:1.

According to the following equation, we calculated the number of arm in the heteroarm CCS:

$$\chi_{arm} M_{w,star} = N_{PDMA} M_{w,PDMA} + N_{PMEA} M_{w,PMEA}$$

in which, χ_{arm} = 0.68, $M_{w,star}$ = 293 810, $N_{PDMA} = 1.14 N_{PMEA}$, $M_{w,PDMA}$ = 6 800, $M_{w,PMEA}$ = 12 272.

Thus, N_{PDMA} = 11, N_{PMEA} = 10.

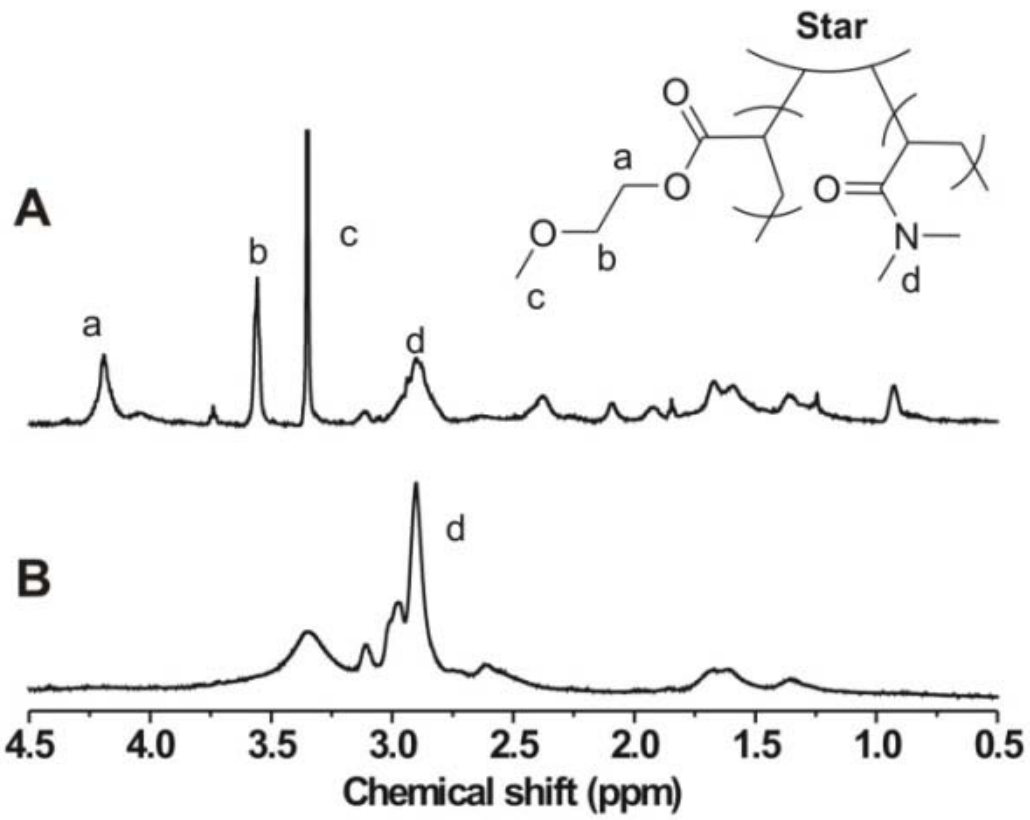


Fig.S11 ^{1}H NMR spectra of heteroarm CCS in (A) $CDCl_3$ and (B) D_2O.

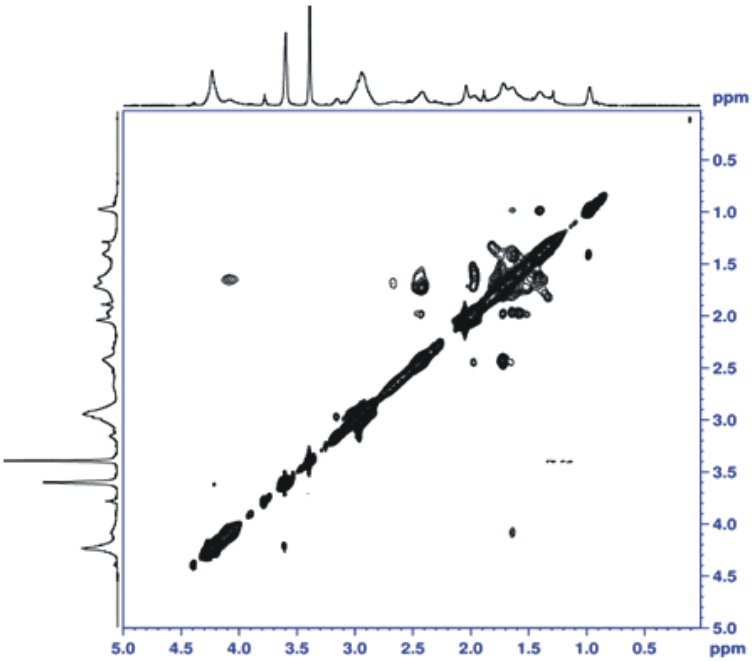


Fig. S12 2D NOESY ^{1}H NMR of PDMA-PMEA heteroarm CCS in $CDCl_3$.

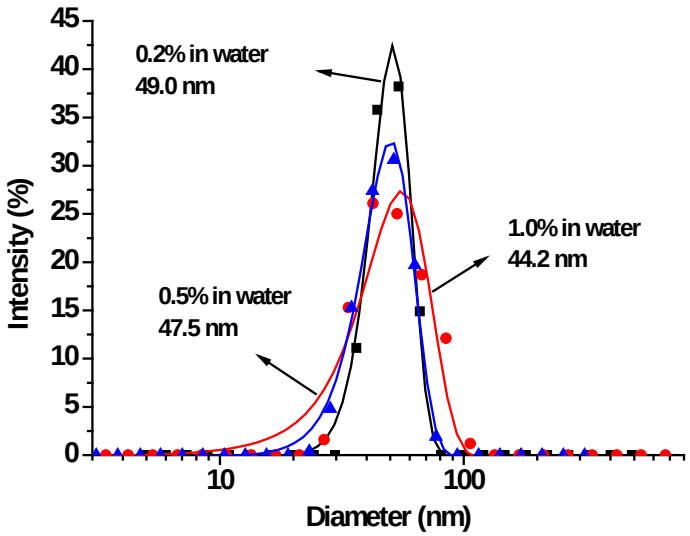


Fig. S13 DLS results of 0.2%, 0.5% and 1.0% amphiphilic PDMA-PMEA heteroarm CCS in water.

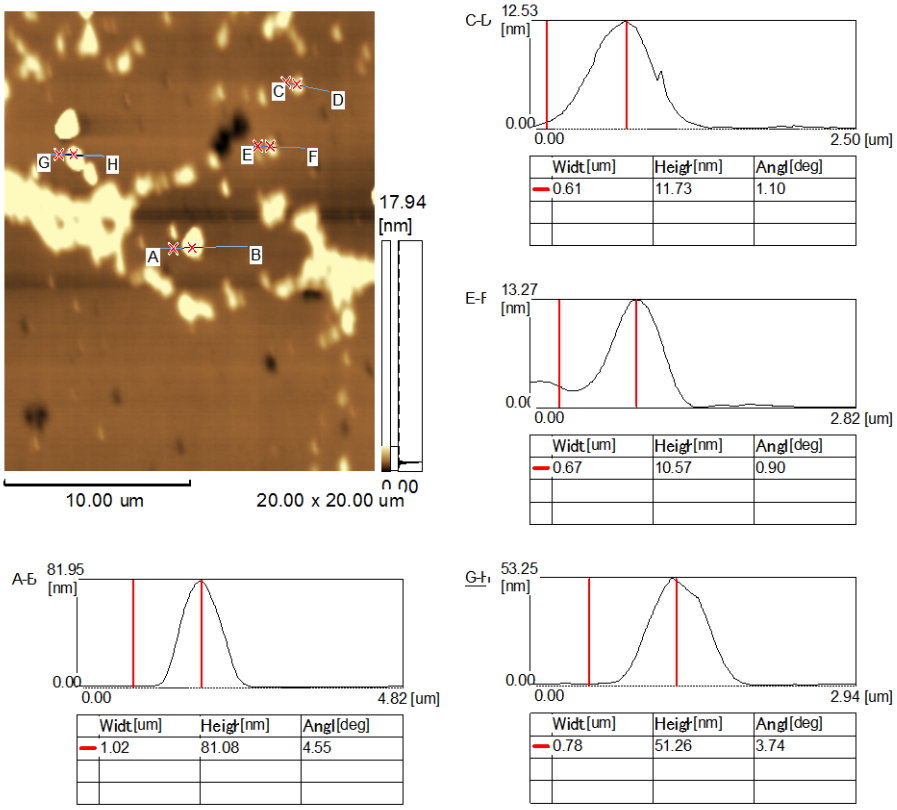


Fig. S14 AFM micrograph and data analysis of a sample prepared from 0.1% amphiphilic heteroarm CCS in water.

Reference

1. Q. Qiu, G. Liu and Z. An, *Chem. Commun.*, 2011, **47**, 12685-12687.