

## Supporting Information

# Synthesis of Star-Shaped Polyzwitterions with Adjustable UCST and Fast Responsiveness by a Facile RAFT Polymerization

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*KEYWORDS: Star-shaped polymers; polyzwitterions; upper critical solution temperature (UCST); end-group effects*

## Small-angle X-ray scattering (SAXS) measurements

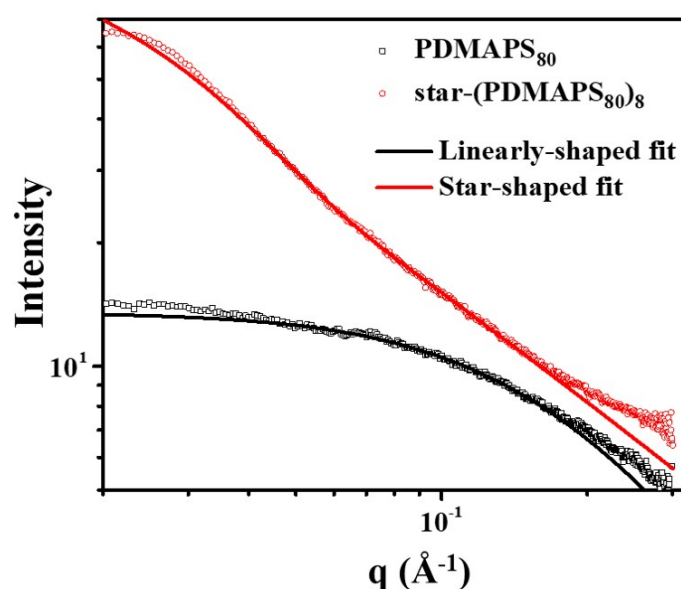
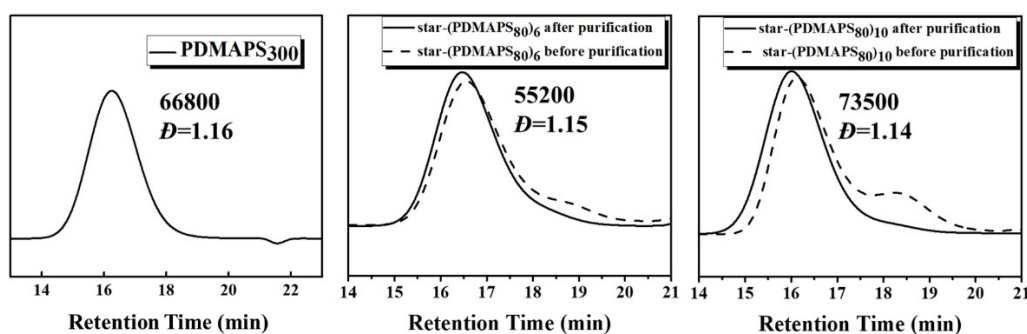
SAXS measurements of PDMAPS<sub>80</sub> and star-(PDMAPS<sub>80</sub>)<sub>8</sub> (1 mg mL<sup>-1</sup>) in an aqueous medium were carried out at Xeuss 2.0 SAXS/WAXS System (Xenocs, France) with an X-ray (wavelength,  $\lambda_{Cu} = 1.5148 \text{ \AA}$ ). All samples were loaded in quartz glass capillaries (d= 0.01 mm, l= 80 mm). Two dimensional (2D) SAXS patterns were collected by using a Pilatus detector (Switzerland), possessing a resolution of 487 x 619 pixels (pixel size= 172 x 172  $\mu\text{m}$ ). The sample-to-detector distance was 1196.26 mm, which was determined by a Silver behenate ( $\text{AgC}_{22}\text{H}_{43}\text{O}_2$ ) standard and measurements were carried out at 30 °C. Two-dimensional scattering patterns were radially averaged and corrected for the background and the empty sample scattering using standard methods. The 1D scattering intensities were fitted as a function of q using one or two different form factors, detailed below, where the scattering variable  $q = (4\pi/\lambda) \sin(\theta/2)$ , where  $\theta$  refer to half of the scattering angle and  $\lambda$  stands for the wavelength of the incident radiation. Sasfit (0.94.1.1) and OriginPro (2015) software were used to plot and analyze the data. Scattering intensities of samples were fitted by Gaussian model and DozierStar polymer model.

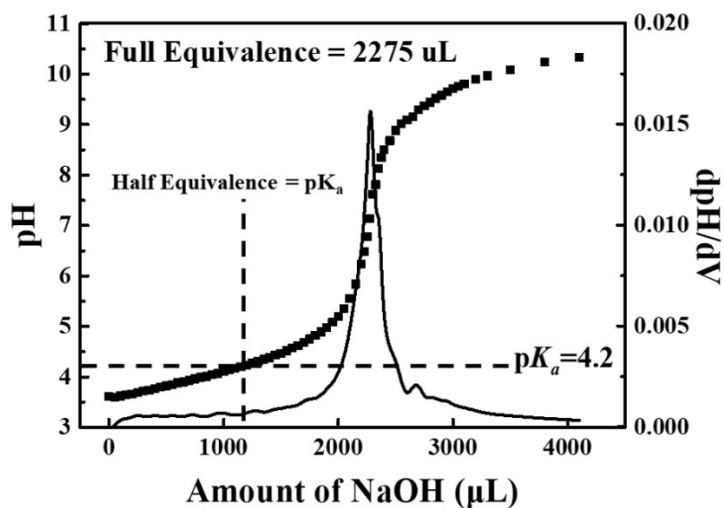
**Table S1. Characteristics of linearly and star-shaped PDMAPS.**

Entry	[MBA]/ [PDMAPS <sub>80</sub> ]	Arm Conv. <sup>a</sup> (%)	$M_n^b$ $\times 10^{-3}$	$M_w^b$ $\times 10^{-3}$	$\bar{D}^b$	$N_{\text{arm}}$
PDMAPS <sub>80</sub>			16.9	20.0	1.15	
PDMAPS <sub>300</sub>			66.8	77.6	1.16	
star-(PDMAPS <sub>80</sub> ) <sub>6</sub>	6.5	93.2	55.2	67.1	1.15	6.06
star-(PDMAPS <sub>80</sub> ) <sub>8</sub>	8.5	93.0	67.8	79.9	1.13	7.91
star-(PDMAPS <sub>80</sub> ) <sub>10</sub>	11	90.6	73.5	88.5	1.14	9.97

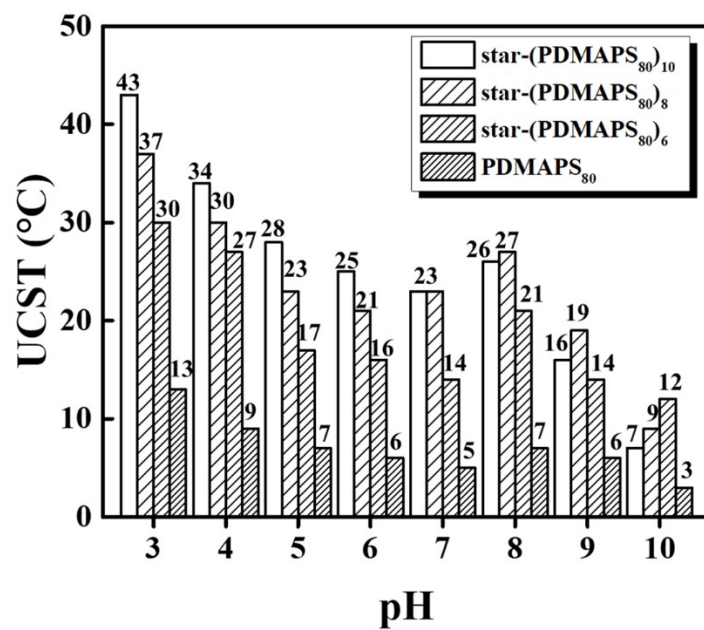
<sup>a</sup> Arm conversion was calculated from GPC traces =  $\text{Area}_{\text{star}} / (\text{Area}_{\text{star}} + \text{Area}_{\text{macroRAFT}})$ .

<sup>b</sup> Molecular weight and dispersity were determined by GPC (see Experimental section).

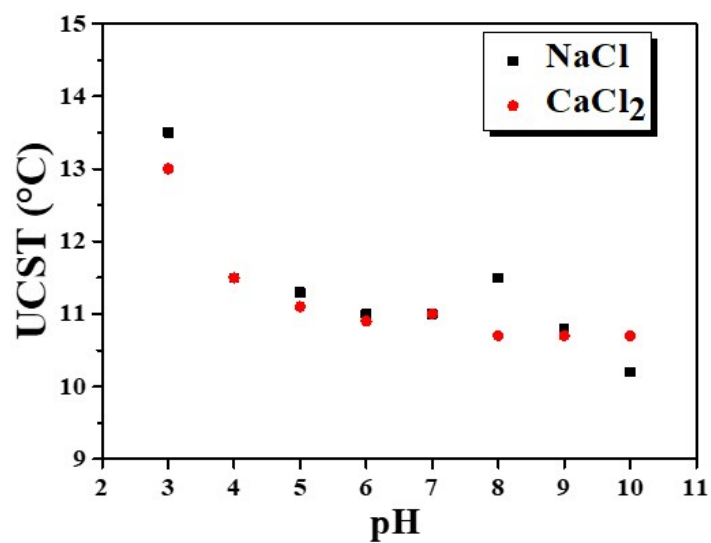
**Figure S1** SAXS data and fit results of PDMAPS<sub>80</sub> and star-(PDMAPS<sub>80</sub>)<sub>8</sub>.**Figure S2** (a) GPC trace of PDMAPS<sub>300</sub> after purification. (b) GPC trace of star-(PDMAPS<sub>80</sub>)<sub>6</sub> after purification. (c) GPC trace of star-(PDMAPS<sub>80</sub>)<sub>10</sub> after purification.



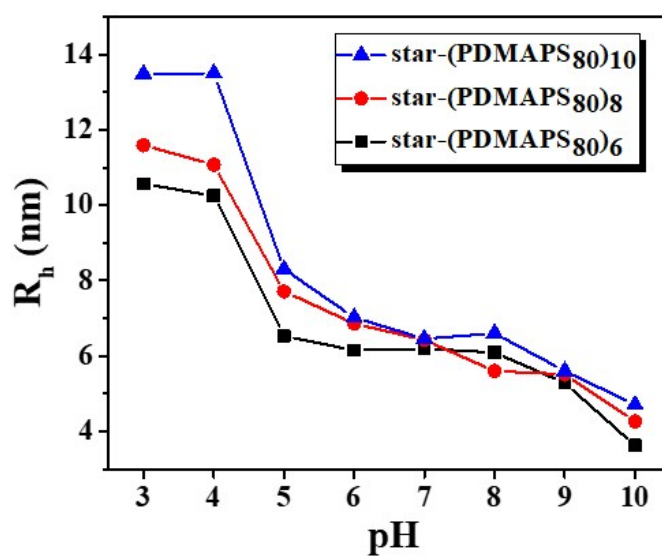
**Figure S3** Acid titration curve obtained for the ECT agent used in this work.



**Figure S4** UCST of star-(PDMAPS<sub>80</sub>)<sub>6</sub>, star-(PDMAPS<sub>80</sub>)<sub>8</sub> and star-(PDMAPS<sub>80</sub>)<sub>10</sub> aqueous solution ( $10 \text{ mg mL}^{-1}$ ) under different pH values.



**Figure S5** UCST of PDMAPS<sub>145</sub> (10 mg mL<sup>-1</sup>) at NaCl and CaCl<sub>2</sub> aqueous solution (20 mM).



**Figure S6** DLS results of the star-(PDMAPS<sub>80</sub>)<sub>6</sub>, star-(PDMAPS<sub>80</sub>)<sub>8</sub> and star-(PDMAPS<sub>80</sub>)<sub>10</sub> aqueous solution (10 mg mL<sup>-1</sup>) with different pH values.