

## Supporting information for

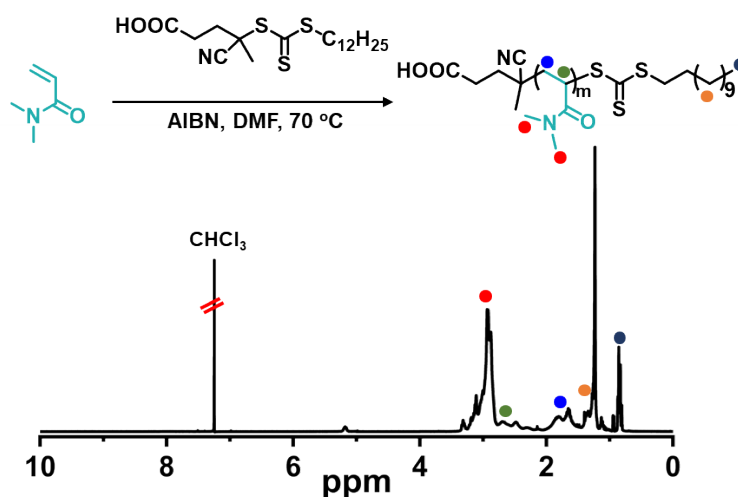
### Pyroglutamate pendant block copolymers: evolution of inverse and conventional morphologies from RAFT-mediated PISA

Pampa Chowdhury,<sup>a</sup> Kamal Bauri,<sup>\*,b</sup> Priyadarsi De<sup>\*,a</sup>

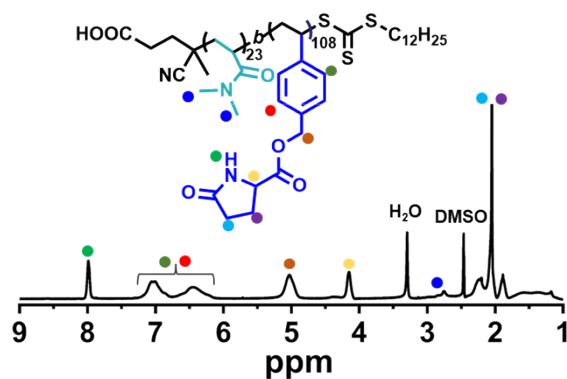
<sup>a</sup>Polymer Research Centre and Centre for Advanced Functional Materials, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur - 741246, Nadia, West Bengal, India.

<sup>b</sup>Department of Chemistry, Raghunathpur College, Raghunathpur - 723133, Purulia, West Bengal, India.

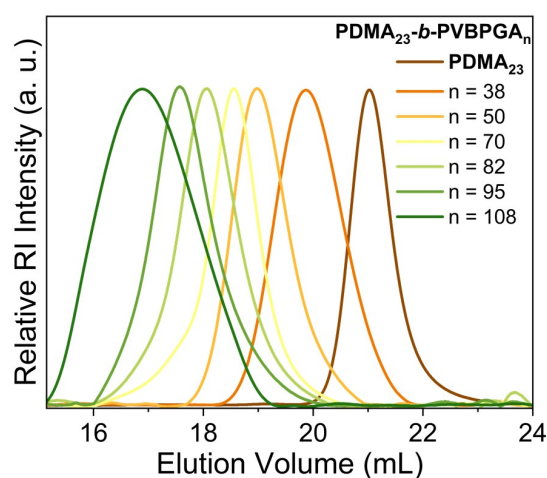
\*Corresponding Authors: E-mails: kamalsom98@gmail.com (KB); p\_de@iiserkol.ac.in (PD)



**Fig. S1** Schematic representation of the synthesis of PDMA<sub>23</sub> macro-CTA and corresponding <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>.



**Fig. S2**  $^1\text{H}$  NMR spectrum of  $\text{PDMA}_{23}\text{-}b\text{-PVBPGA}_{108}$  in  $\text{DMSO-}d_6$ .

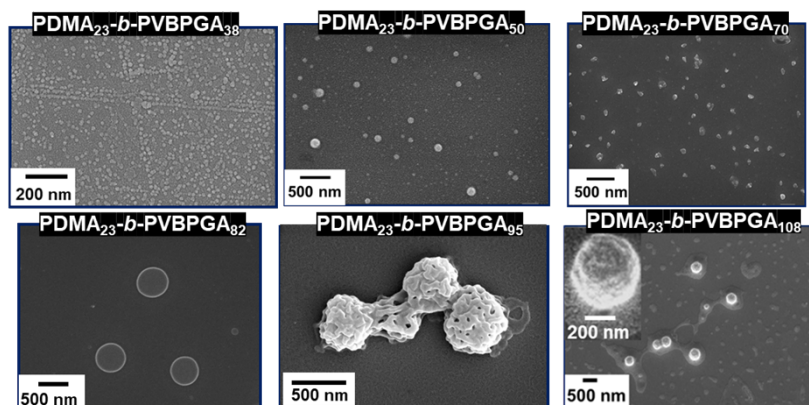


**Fig. S3** SEC RI traces of the  $\text{PDMA}_{23}\text{-}b\text{-PVBPGA}_n$  block copolymers from the RAFT dispersion polymerization of VBPGA in the presence of  $\text{PDMA}_{23}$  macro-CTA at 20 wt% solid content.

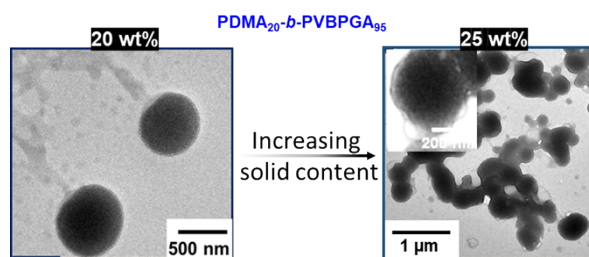
**Table S1** Characterization of  $\text{PDMA}$  homopolymers.

Composition	$[\text{DMA}]/[\text{CDP}]$	Conv. <sup>a</sup> (%)	$M_{n,\text{NMR}}^b$ ( $\text{g mol}^{-1}$ )	$M_{n,\text{SEC}}^c$ ( $\text{g mol}^{-1}$ )	$(\bar{D})^c$
$\text{PDMA}_{12}$	10	92	1600	1400	1.1
$\text{PDMA}_{23}$	20	90	2680	2300	1.1
$\text{PDMA}_{38}$	40	95	4170	4200	1.1

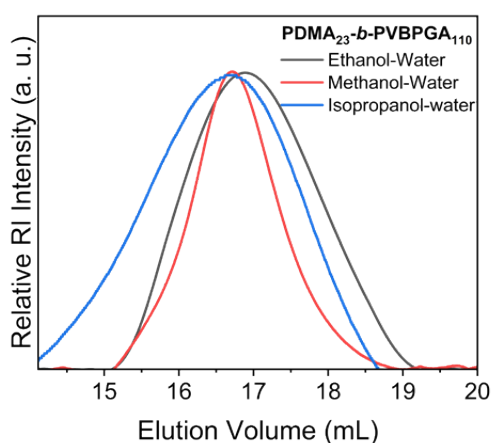
<sup>a</sup>Determined gravimetrically. <sup>b</sup>Determined from NMR analysis. <sup>c</sup>Determined from SEC analysis.



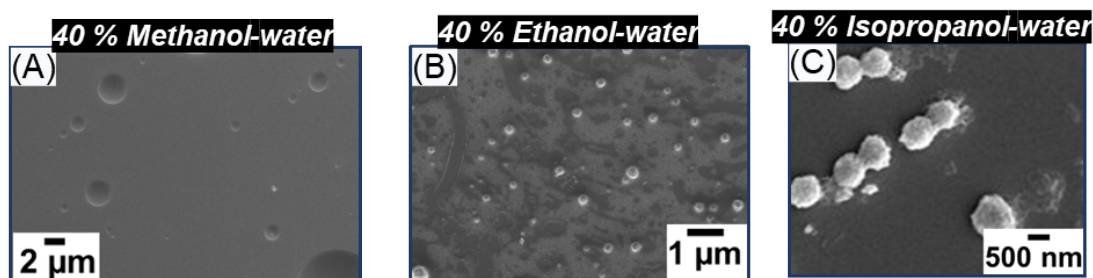
**Fig. S4** FESEM images of the morphological behaviour of corresponding  $\text{PDMA}_{23}\text{-}b\text{-PVBPGA}_n$  block copolymers, prepared at 65 °C using an ethanol-water mixture (40/60, v/v) *via* RAFT dispersion polymerization at 20 wt% solid content.



**Fig. S5** TEM images of  $\text{PDMA}_{23}\text{-}b\text{-PVBPGA}_{95}$  in an ethanol-water binary mixture (40/60, v/v) at two different solid contents (20 wt% and 25 wt%).



**Fig. S6** SEC traces of  $\text{PDMA}_{23}\text{-}b\text{-PVBPGA}_{110}$  block copolymers, prepared using different alcohol-water mixtures (40/60, v/v) at 65 °C *via* RAFT dispersion polymerization at 20 wt% solid content.

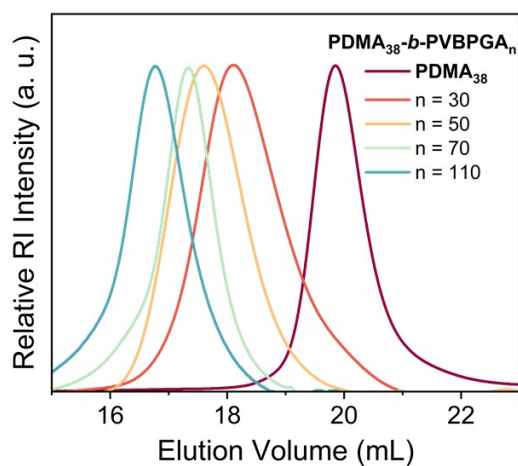


**Fig. S7** FESEM images of  $\text{PDMA}_{23}\text{-}b\text{-PVBPGA}_n$  ( $n = 105\text{-}110$ ) in different binary mixtures of alcohol-water (40/60, v/v) at 20 wt% solid content.

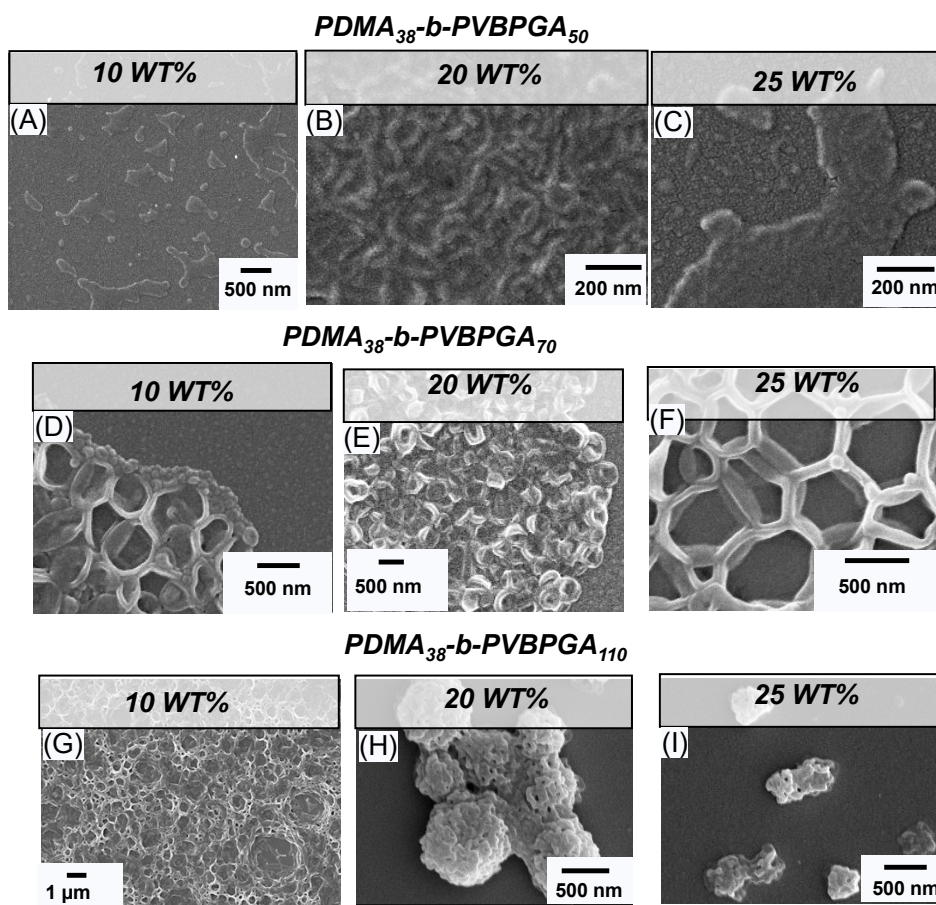
**Table S2** Summarization of the synthesis and characterization of  $\text{PDMA-}b\text{-PVBPGA}$  block copolymers at 20 wt% solid content.

Composition	[VBPGA]/ [PDMA <sub>23</sub> ]	Conv. <sup>a</sup> (%)	$M_{n,\text{NMR}}^b$ (g mol <sup>-1</sup> )	$M_{n,\text{SEC}}^c$ (g mol <sup>-1</sup> )	( $\bar{D}$ ) <sup>c</sup>	Morphology <sup>d</sup>
$\text{PDMA}_{23}\text{-}b\text{-PVBPGA}_{110}$ (I)	120	90	29600	26200	1.3	R
$\text{PDMA}_{23}\text{-}b\text{-PVBPGA}_{105}$ (M)	120	85	28400	27800	1.19	S
$\text{PDMA}_{38}\text{-}b\text{-PVBPGA}_{50}$ Stirring rate = 250	50	85	-	17600	1.21	L
$\text{PDMA}_{38}\text{-}b\text{-PVBPGA}_{50}$ Stirring rate = 0	50	80	-	15500	1.2	W
$\text{PDMA}_{38}\text{-}b\text{-PVBPGA}_{50}$ Stirring rate = 50	50	82	-	16300	1.2	W
$\text{PDMA}_{38}\text{-}b\text{-PVBPGA}_{50}$ Stirring rate = 150	50	80	-	17000	1.16	W

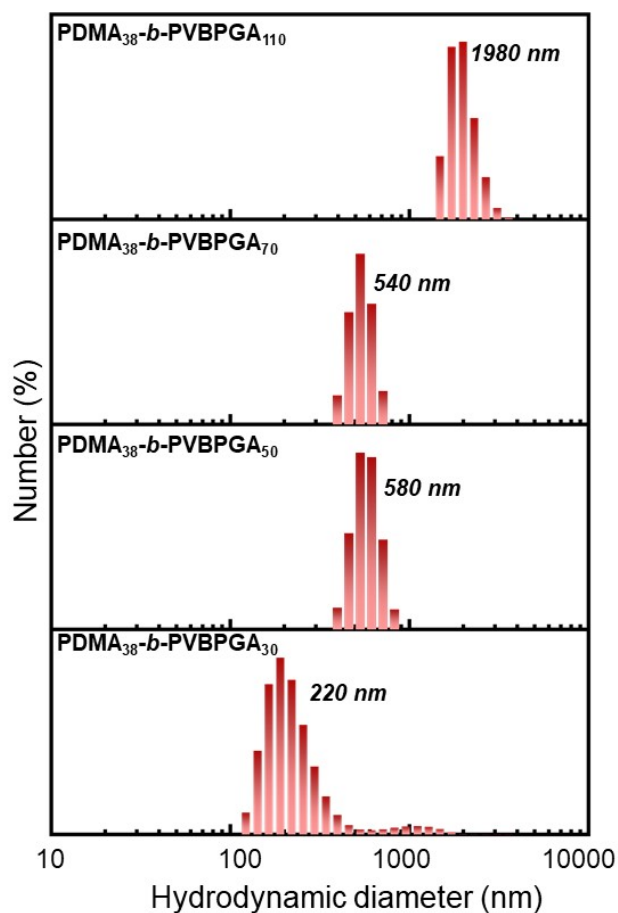
<sup>a</sup>Determined gravimetrically. <sup>b</sup>Measured by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Determined from SEC analysis. <sup>d</sup>Morphologies were obtained from FESEM and TEM analyses (S: spherical nanoparticles; W: worm; L: semi-circular lamellar; R: Raspberry-like inverted micelles. I = isopropanol-water mixture (40/60, v/v) and M = methanol-water mixture (40/60, v/v).



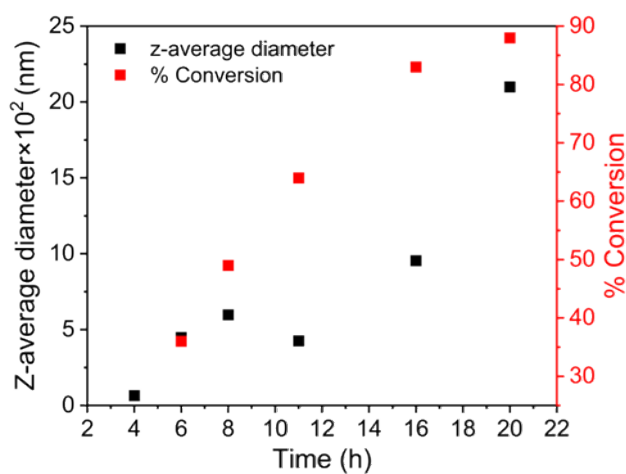
**Fig. S8** SEC RI traces of  $\text{PDMA}_{38}\text{-}b\text{-PVBPGA}_n$  block copolymers prepared at  $65\text{ }^\circ\text{C}$  using an ethanol/water mixture (40/60, v/v) via RAFT dispersion polymerization at 20 wt% solid content.



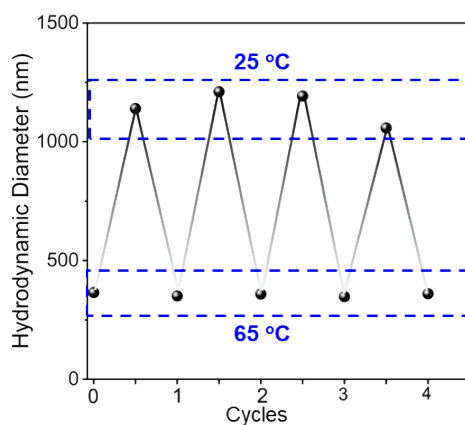
**Fig. S9** FESEM images of  $\text{PDMA}_{38}\text{-}b\text{-PVBPGA}_n$  ( $n = 50, 70,$  and  $110$ ) in ethanol-water binary mixture (40/60, v/v) at three different solid contents (10, 20, and 25 wt%).



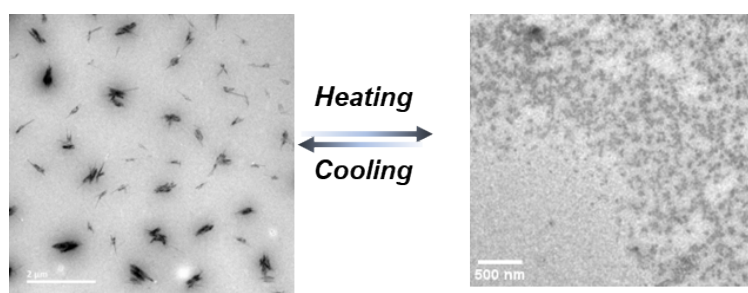
**Fig. S10** DLS analysis of PDMA<sub>38</sub>-*b*-PVBPGA<sub>n</sub> (n = 30, 50, 70, and 110) in ethanol-water binary mixture (40/60, v/v) at 20 wt% solid content.



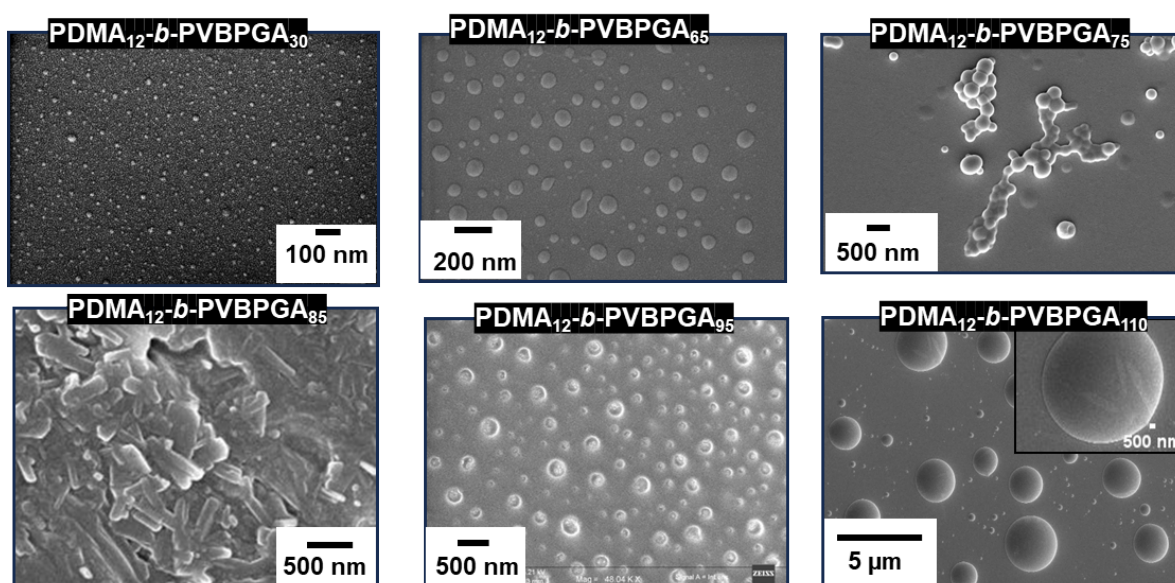
**Fig. S11** Z-average diameter in ethanol-water binary mixture (40/60, v/v) and % conversion versus time plot for PDMA<sub>38</sub>-*b*-PVBPGA<sub>n</sub>.



**Fig. S12** Thermal reversibility of the hydrodynamic diameter of  $\text{PDMA}_{38}\text{-}b\text{-PVBPGA}_{65}$  in an ethanol–water binary mixture (50/50, v/v) at 20 wt% solids, measured under heating (65 °C) and cooling (25 °C) conditions.



**Fig. S13** TEM analysis of  $\text{PDMA}_{38}\text{-}b\text{-PVBPGA}_{65}$  in ethanol-water binary mixture (50/50, v/v) at 20 wt% solid content.



**Fig. S14** FESEM images of  $\text{PDMA}_{12}\text{-}b\text{-PVBPGA}_n$  block copolymers.