

Surface active to non-surface active transition and micellization behaviour of zwitterionic amphiphilic diblock copolymers: hydrophobicity and salt dependency

Sivanantham Murugaboopathy and Hideki Matsuoka

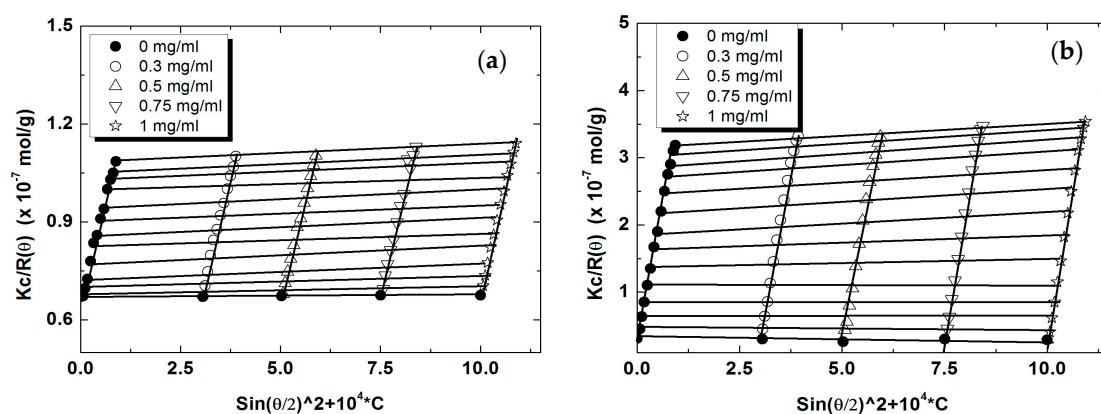


Figure S1. Typical Zimm plots for ZABC having P(*n*-BMA) and PEHA. (a) *n*-BMA₁₀₁-*b*-GLBT₁₅₆ in 1M NaCl and (b) EHA₂₀-*b*-GLBT₁₅₆ in water.

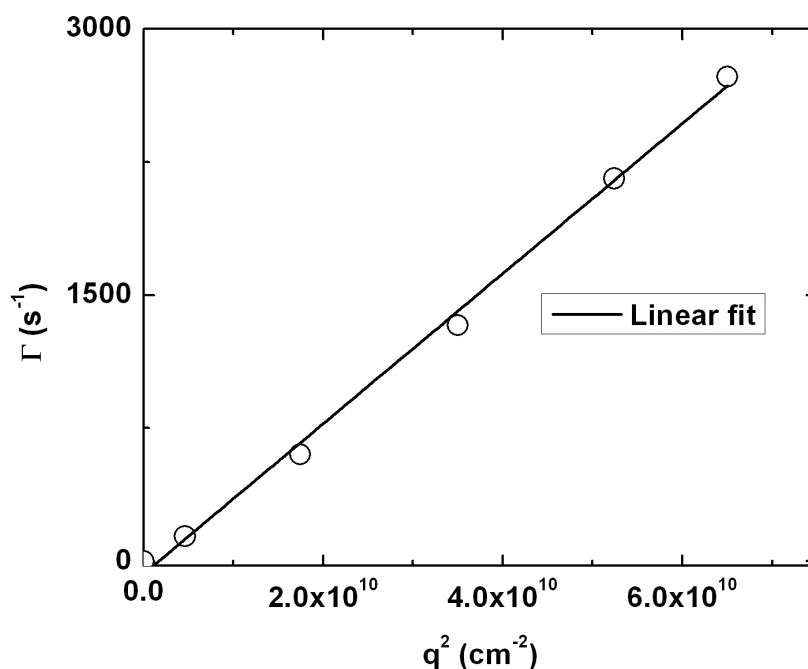


Figure S2. Plots between Γ vs. q^2 for *n*-BMA₃₅-*b*-GLBT₅₅ in water.

Table S1. Polymerization conditions for the synthesis of homopolymers(PGLBT) and block copolymers (P(*n*-BMA)-*b*-PGLBT) and (PEHA-*b*-PGLBT) (70 °C).

Polymer	Monomer (mmol)	RAFT Agent (mmol) ^a	Initiator (mmol) ^b	Water (mL)	DMF (mL)	Methanol (mL)	Polymerization Time (h)
PGLBT – 1	18.6	0.2	0.1	6	1.5		2
PGLBT – 2	37.2	0.2	0.1	6	1.5		1.5
PGLBT – 3	37.2	0.19	0.097	6	1.5		2
PGLBT – 4	37.2	0.099	0.1	6	1.5		2
<i>n</i> -BMA _m - <i>b</i> -GLBT _{n'} -1	6.4	0.064	0.52			5	24
<i>n</i> -BMA _m - <i>b</i> -GLBT _{n'} -2	6.4	0.074	0.35			5	24
<i>n</i> -BMA _m - <i>b</i> -GLBT _{n'} -3	3.2	0.032	0.26			5	24
<i>n</i> -BMA _m - <i>b</i> -GLBT _{n'} -4	4.8	0.032	0.26			5	24
EHA _m - <i>b</i> -GLBT _{n'} -1	2.4	0.097	0.39			5	24
EHA _m - <i>b</i> -GLBT _{n'} -2	0.6	0.024	0.2			5	24
EHA _m - <i>b</i> -GLBT _{n'} -3	0.6	0.024	0.2			5	24
EHA _m - <i>b</i> -GLBT _{n'} -4	2.4	0.014	0.43			5	24

^a For synthesis of diblock copolymers, amount of macro RAFT agent in mmol. ^b for synthesis of homopolymers and diblock copolymers, 4,4'-Azocyanovaleic acid (ACVA) and 2,2'-azobisisobutyronitrile (AIBN) were respectively used as initiator. DMF: dimethylformamide. GLBT: carboxybetaine. *n*-BMA: *n*-butylmethacrylate. EHA: 2-ethylhexylacrylate.

Table S2. Molecular characteristics of homopolymers(PGLBT) and diblock copolymers (P(*n*-BMA)-*b*-PGLBT) and (PEHA-*b*-PGLBT).

Polymer	M_n ^a (g/mol)	PDI ^b	Degree of polymerization	
			<i>m</i>	<i>n'</i>
PGLBT – 1	11900	1.13		55
PGLBT – 2	25200	1.2		117
PGLBT – 3	33600	1.15		156
PGLBT – 4	64500	1.16		300
<i>n</i> -BMA _m - <i>b</i> -GLBT _{n'} -1			35	55
<i>n</i> -BMA _m - <i>b</i> -GLBT _{n'} -2			62	117
<i>n</i> -BMA _m - <i>b</i> -GLBT _{n'} -3			101	156
<i>n</i> -BMA _m - <i>b</i> -GLBT _{n'} -4			42	300
EHA _m - <i>b</i> -GLBT _{n'} -1			22	55
EHA _m - <i>b</i> -GLBT _{n'} -2			15	117
EHA _m - <i>b</i> -GLBT _{n'} -3			20	156
EHA _m - <i>b</i> -GLBT _{n'} -4			19	300

^a M_n : Number averaged molecular weight (determined by GPC). ^b PDI: Polydispersity index (M_w/M_n) (determined by GPC). *m*, *n'*: The degree of polymerization of hydrophobic and hydrophilic blocks respectively(*m* was determined by NMR). GLBT: carboxybetaine; *n*-BMA: *n*-butylmethacrylate. EHA: 2-ethylhexylacrylate.