# **Electronic Supplementary Information**

# Study of structure-performance relationships of polymeric dispersants

# on particle dispersion and stabilisation

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# 1. Synthesis and characterisation of AB diblock copolymers



Scheme S1

General synthetic strategy of AB diblock copolymers.

## Synthetic procedure:

The synthetic procedure of AB diblock copolymers was described in the Experimental section of the manuscript.

## <sup>1</sup>H NMR characterisation:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, (CH<sub>3</sub>)<sub>4</sub>Si, Fig. S1),  $\delta$ /ppm: 0.78–1.12 (3 H, m, C(CH<sub>3</sub>)), 1.20–1.33 (3 H, m, OCH<sub>2</sub>CH<sub>3</sub>), 1.74–2.04 (2 H, m, C(CH<sub>3</sub>)CH<sub>2</sub>), 2.26–2.35 (6 H, m, N(CH<sub>3</sub>)<sub>2</sub>), 2.52–2.66 (2 H, m, OCH<sub>2</sub>CH<sub>2</sub>N) and 3.95–4.17 (2 H, m, COOCH<sub>2</sub> of PDMA and PEMA blocks).



Fig. S1 <sup>1</sup>H NMR spectrum of PD30-*b*-PE40 in CDCl<sub>3</sub>.

# 2. Synthesis and characterisation of ABA triblock copolymers



**Scheme S2** General synthetic strategy of ABA triblock copolymers.

#### Synthetic procedure:

ABA triblock copolymers were synthesised by a three-step RAFT polymerisation (Scheme S2). The typical reaction is as follows (PDMA30-*b*-PEMA60-*b*-PDMA30 (PD30-*b*-PE60-*b*-PD30)): the first step used RAFT CTA DDMAT (72.8 mg, 0.2 mmol), DMA (0.942 g, 6 mmol), AIBN

(3.28 mg, 0.02 mmol) and 1,4-dioxane (1.5 mL), which were added into a Schlenk tube. The mixture was carefully degassed by purging with N<sub>2</sub> gas for 30 min, and then reacted at 70 °C with stirring for 8 h. After the reaction, the Schlenk tube was quenched in liquid  $N_2$  and diluted with 1,4-dioxane (2 mL), before being precipitated in cold n-hexane twice. The purified product was vacuum dried overnight at room temperature, obtaining a yellow solid as the RAFT macromolecular CTA (PDMA-CTA). The second step used PDMA-CTA (1.016 g, 0.2 mmol), EMA (1.370 g, 12 mmol), AIBN (3.28 mg, 0.02 mmol) and 1,4-dioxane (3.5 mL), which were added into a Schlenk tube. The mixture was carefully degassed by purging with  $N_2$  gas for 30 min, and then reacted at 70 °C with stirring for 8 h. After the reaction, the Schlenk tube was quenched in liquid  $N_2$  and diluted with 1,4-dioxane (4 mL), before being precipitated in cold *n*-hexane twice. The purified product was vacuum dried overnight at room temperature, obtaining a yellow solid as the second step intermediate product PD30b-PE60. The third step used PD30-b-PE60 (2.386 g, 0.2 mmol), DMA (0.942 g, 6 mmol), AIBN (3.28 mg, 0.02 mmol) and 1,4-dioxane (5 mL), which were added into a Schlenk tube. The mixture was carefully degassed by purging with N<sub>2</sub> gas for 30 min, and then reacted at 70 °C with stirring for 8 h. After the reaction, the Schlenk tube was quenched in liquid  $N_2$  and diluted with 1,4-dioxane (5 mL), before being precipitated in cold n-hexane twice. The purified product was vacuum dried overnight at room temperature, obtaining a yellow solid as the final product PD30-*b*-PE60-*b*-PD30.

#### <sup>1</sup>H NMR characterisation:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, (CH<sub>3</sub>)<sub>4</sub>Si, Fig. S2),  $\delta$ /ppm: 0.70–1.05 (3 H, m, C(CH<sub>3</sub>)), 1.15–1.29 (3 H, m, OCH<sub>2</sub>CH<sub>3</sub>), 1.66–1.94 (2 H, m, C(CH<sub>3</sub>)CH<sub>2</sub>), 2.15–2.29 (6 H, m, N(CH<sub>3</sub>)<sub>2</sub>), 2.44–2.58 (2 H, m, OCH<sub>2</sub>CH<sub>2</sub>N) and 3.87–4.10 (2 H, m, COOCH<sub>2</sub> of PDMA and PEMA blocks).



#### 3. Synthesis and characterisation of comb copolymers



**Scheme S3** General synthetic strategy of comb copolymers.

#### Synthetic procedure:

Comb copolymers were synthesised by a one-step RAFT polymerisation (Scheme S3). The typical reaction is as follows (P(DMA30-*co*-PPGA15) (P(D30-*co*-PPGA15))): RAFT CTA DDMAT (72.8 mg, 0.2 mmol), DMA (0.942 g, 6 mmol), PPGA (1.425 g, 3 mmol), AIBN (3.28 mg, 0.02 mmol) and 1,4-dioxane (3.5 mL) were added into a Schlenk tube. The mixture was carefully degassed by purging with N<sub>2</sub> gas for 30 min, and then reacted at 70 °C with stirring for 10 h. After the reaction, the Schlenk tube was quenched in liquid N<sub>2</sub> and diluted with 1,4-dioxane (4 mL), before being precipitated in cold *n*-hexane twice. The purified product was vacuum dried overnight at room temperature, obtaining a yellow solid as the final product P(D30-*co*-PPGA15).

#### <sup>1</sup>H NMR characterisation:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, (CH<sub>3</sub>)<sub>4</sub>Si, Fig. S3),  $\delta$ /ppm: 0.77–1.10 (3 H, m, C(CH<sub>3</sub>)), 1.10–1.24 (3 H, m, CH(CH<sub>3</sub>)), 1.73–2.04 (2 H, m, C(CH<sub>3</sub>)CH<sub>2</sub> and CHCH<sub>2</sub>), 2.22–2.40 (6 H, m, N(CH<sub>3</sub>)<sub>2</sub>), 2.50–2.69 (2 H, m, OCH<sub>2</sub>CH<sub>2</sub>N), 3.25–3.85 (3 H, m, OCH<sub>2</sub>CH(CH<sub>3</sub>)) and 3.98–4.23 (2 H, m, COOCH<sub>2</sub>).



Fig. S3 <sup>1</sup>H NMR spectrum of P(D30-co-PPGA15) in CDCl<sub>3</sub>.

## 4. Summary of <sup>1</sup>H NMR and GPC characterisation of all copolymers

The number averaged molecular weight ( $M_n$ ) and polydispersity index (PDI) of all the synthesised copolymer dispersants were determined by <sup>1</sup>H NMR and GPC measurements, which are summarised in Table S1.

Sample	Designed	Synthesised	<i>M</i> <sub>n,NMR</sub> <sup>c</sup>	<i>M</i> <sub>n,GPC</sub> <sup>d</sup>	PDI <sup>d</sup>
	Structure <sup>a</sup>	Structure <sup>b</sup>			
<b>S1</b>	PD20-PE40 <sup>e</sup>	PD18-PE37	7400	7700	1.14
S2	PD30-PE40	PD28-PE37	9000	9600	1.15
<b>S</b> 3	PD40-PE40	PD40-PE38	11000	10400	1.18
<b>S4</b>	PD30-PE20	PD30-PE19	7300	7500	1.16
S5	PD30-PE60	PD29-PE49	10500	9700	1.19
<b>S6</b>	PD10-PE40-PD10	PD10-PE38-PD10	7800	8900	1.20
S7	PD20-PE40-PD20	PD19-PE40-PD16	10400	9700	1.22
<b>S8</b>	PD30-PE40-PD30	PD29-PE38-PD28	13700	10300	1.21
<b>S</b> 9	PD30-PE60-PD30	PD25-PE57-PD25	14700	12000	1.22
S10	PD30-PE80-PD30	PD28-PE74-PD27	17500	15300	1.24
S11	P(D30-PPGA10)	P(D27-PPGA7)	7900	8700	1.22
S12	P(D30-PPGA15)	P(D28-PPGA12)	10500	14700	1.24
S13	P(D30-PPGA20)	P(D29-PPGA15)	12000	15200	1.25

<sup>*a*</sup> Designed dispersant structure. <sup>*b*</sup> Synthesised dispersant structure estimated from <sup>1</sup>H NMR. <sup>*c*</sup> Estimated from <sup>1</sup>H NMR. <sup>*d*</sup> Determined by GPC. <sup>*e*</sup> PD: PDMA; PE: PEMA.

# 5. Dispersion of mesoporous silica nanoparticles

Mesoporous silica nanoparticles (MSNs) were synthesised according to literature.<sup>1,2</sup> Morphology images of dispersed MSNs were recorded by using a high-resolution JEOL JEM-2010 transmission electron microscope (TEM) with an accelerating voltage of 120 kV after the samples were initially drop-coated onto carbon-coated copper grids.



**Fig. S4** TEM images of dispersed MSNs in xylene: (a) control sample without dispersant; (b) AB diblock: PD30-*b*-PE40; (c) ABA triblock: PD30-*b*-PE60-*b*-PD30; (d) comb: P(D30-*co*-PPGA15).

## References

- 1. T. Wang, M. Wang, C. Ding and J. Fu, *Chem. Commun.*, 2014, **50**, 12469-12472.
- 2. C. Y. Hong, X. Li and C. Y. Pan, *J. Mater. Chem.*, 2009, **19**, 5155-5160.