

Supporting Information for

**EMULSION POLYMERIZATION USING IONIC LIQUID C1EG™ AND  
DTAB AS SURFACTANTS**

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**Table S1.** Conversion and average diameter after 120 min of reaction.

<b>Reaction number</b>	<b>Repetition</b>	<b>Conversion*, %</b>	<b>Average* ± Std. Dev.</b>	<b>D<sub>p</sub>*, nm</b>	<b>Average* ± Std. Dev.</b>
15	a	96.46	96.91 ± 0.63	65.46	66.21 ± 1.05
	b	97.35		66.95	
19	a	95.94	96.42 ± 0.67	58.88	59.24 ± 0.51
	b	96.89		59.60	
21	a	84.59	85.86 ± 1.76	63.72	64.26 ± 1.16
	b	87.87		63.47	
	c	85.11		65.60	
25	a	86.98	89.44 ± 3.47	54.33	53.71 ± 0.88
	b	91.89		53.09	
27	a	97.82	97.60 ± 0.33	71.11	71.49 ± 0.85
	b	97.77		72.47	
	c	97.22		70.90	
28	a	90.52	90.25 ± 0.39	61.23	61.18 ± 0.07
	b	89.97		61.13	
30	a	95.18	95.19 ± 0.01	61.20	60.90 ± 0.42
	b	95.20		60.60	
32	a	92.07	92.11 ± 0.05	54.61	54.27 ± 0.48
	b	92.14		53.93	

34	a	87.71	$88.21 \pm 0.71$	69.70	$69.58 \pm 0.18$
	b	88.71		69.45	
36	a	97.04	$94.90 \pm 3.03$	72.26	$72.48 \pm 0.31$
	b	92.75		72.70	

\* Two significant decimal figures are used here. They are rounded to one significant figure in the main manuscript.

**Table S2.** Effect of surfactant type on conversion and particle diameter for styrene polymerizations.

Monomers	Surfactant	Conversion [%]	PD [nm]
Styrene	<b>C1EG</b>	$89.7 \pm 5.2$ <b>a</b>	$66.3 \pm 2.5$ <b>a</b>
	<b>DTAB</b>	$92.0 \pm 3.8$ <b>a</b>	$58.0 \pm 3.5$ <b>b</b>

\* Different letters indicate significant differences ( $p \leq 0.05$ ). ANOVA and *post hoc* Tukey's test.

**Table S3.** Effect of surfactant type on conversion and particle diameter for MMA polymerizations.

Monomers	Surfactant	Conversion [%]	PD [nm]
MMA	<b>C1EG</b>	$96.1 \pm 1.9$ <b>a</b>	$68.8 \pm 5.4$ <b>a</b>
	<b>DTAB</b>	$92.1 \pm 0.1$ <b>b</b>	$54.3 \pm 0.5$ <b>b</b>

\* Different letters indicate significant differences ( $p \leq 0.05$ ). ANOVA and *post hoc* Tukey's test.

**Table S4.** Effects of surfactant and initiator concentrations on conversion and particle diameter for styrene polymerizations with C1EG surfactant.

<b>[S] ×CMC</b>	<b>Conversion [%]</b>	<b>PD [nm]</b>	<b>Initiator [mol×10<sup>4</sup>]</b>	<b>Conversion [%]</b>	<b>PD [nm]</b>
<b>10.9</b>	96.9 ± 0.6 <b>a</b>	66.2 ± 1.1 <b>ab</b>	<b>3.85</b>	96.9 ± 0.6 <b>a</b>	66.2 ± 1.1 <b>ab</b>
<b>7.7</b>	85.9 ± 1.8 <b>b</b>	64.3 ± 1.2 <b>b</b>	<b>5.53</b>	85.9 ± 1.8 <b>b</b>	64.3 ± 1.2 <b>b</b>
<b>7.7</b>	88.2 ± 0.7 <b>b</b>	69.6 ± 0.2 <b>a</b>	<b>3.68</b>	88.2 ± 0.7 <b>b</b>	69.6 ± 0.2 <b>a</b>

\* Different letters indicate significant differences (p≤0.05). ANOVA and *post hoc* Tukey's test.

**Table S5.** Effects of surfactant and initiator concentrations on conversion and particle diameter for styrene polymerizations with DTAB surfactant.

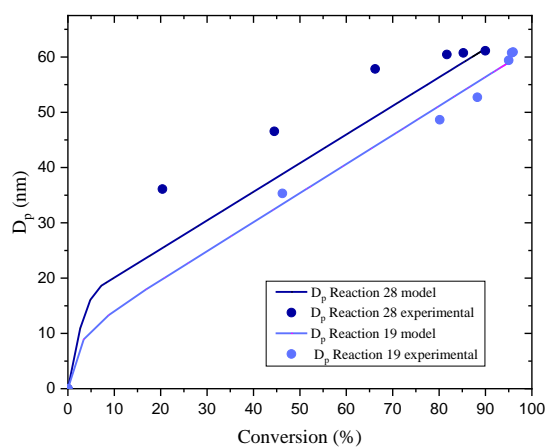
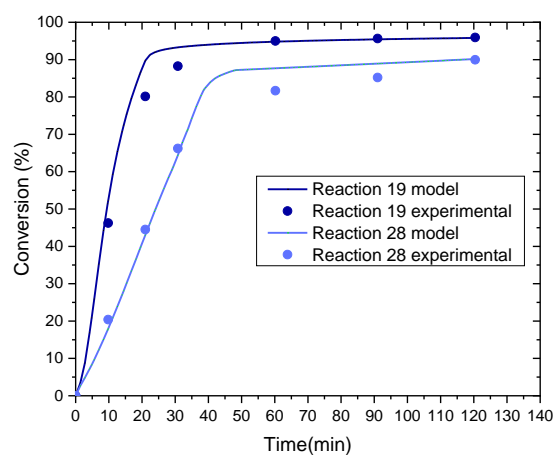
<b>[S] ×CMC</b>	<b>Conversion [%]</b>	<b>PD [nm]</b>	<b>Initiator [mol×10<sup>4</sup>]</b>	<b>Conversion [%]</b>	<b>PD [nm]</b>
<b>3.5</b>	96.4 ± 0.7 <b>a</b>	59.2 ± 0.5 <b>a</b>	<b>3.93</b>	96.4 ± 0.7 <b>a</b>	59.2 ± 0.5 <b>a</b>
<b>3</b>	89.4 ± 3.5 <b>a</b>	53.7 ± 0.9 <b>b</b>	<b>3.14</b>	89.4 ± 3.5 <b>a</b>	53.7 ± 0.9 <b>b</b>
<b>2</b>	90.3 ± 0.4 <b>a</b>	61.2 ± 0.1 <b>a</b>			

\* Different letters indicate significant differences (p≤0.05). ANOVA and *post hoc* Tukey's test.

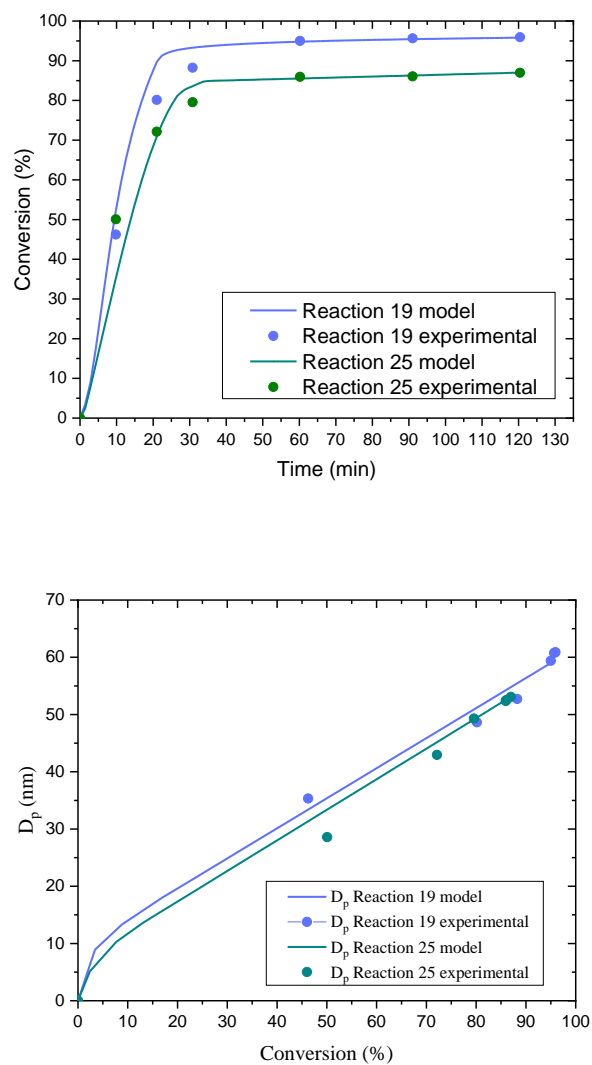
**Table S6.** Effects of surfactant and initiator concentrations on conversion and particle diameter for MMA polymerizations with C1EG surfactant.

<b>[S] ×CMC</b>	<b>Conversion [%]</b>	<b>PD [nm]</b>	<b>Initiator [mol×10<sup>4</sup>]</b>	<b>Conversion [%]</b>	<b>PD [nm]</b>
<b>7.7</b>	94.9 ± 2.4 <b>a</b>	72.5 ± 7.9 <b>a</b>	<b>3.68</b>	94.9 ± 2.4 <b>a</b>	72.5 ± 7.9 <b>a</b>
<b>10.1</b>	97.6 ± 0.3 <b>a</b>	71.5 ± 0.9 <b>a</b>	<b>3.80</b>	97.6 ± 0.3 <b>a</b>	71.5 ± 0.9 <b>a</b>
<b>7.7</b>	95.2 ± 0.0 <b>a</b>	60.9 ± 0.4 <b>b</b>	<b>5.57</b>	95.2 ± 0.0 <b>a</b>	60.9 ± 0.4 <b>b</b>

\* Different letters indicate significant differences (p≤0.05). ANOVA and *post hoc* Tukey's test.



**Figure S1.** Comparison of simulation (POLYRED) and experimental data for conversion vs. time of reaction (left) and  $D_p$  vs. conversion (right) for experiments E19 and E28.



**Figure S2.** Comparison of simulation (POLYRED) and experimental data for conversion vs. time of reaction (upper) and  $D_p$  vs. conversion (lower) for experiments E19 and E25.

**Table S7.** Main physical and kinetic parameters used in the POLYRED simulations (70 °C)

Parameter [reference]	Description	Value
C1EG $r_h$ (nm) [63]	Micellar radius	1.90
DTAB $r_h$ (nm) [64]	Idem	1.30
$K_d$ ( $s^{-1}$ ) V-50	Initiator kinetic constant	$2.038 \times 10^{+11}$
$k_{p, St}$ ( $L mol^{-1} s^{-1}$ ) [65]	St propagation kinetic constant	126
$k_{p, MMA}$ ( $L mol^{-1} s^{-1}$ ) [65]	St propagation kinetic constant	646
$K_t, MMA$ ( $L mol^{-1} s^{-1}$ ) [66]	MMA termination kinetic constant	$1.05 \times 10^{-9}$
$K_t, St$ ( $L mol^{-1} s^{-1}$ ) [67]	St termination kinetic constant	$1.75 \times 10^{-9}$
$D_{p, St}$ ( $g L^{-1}$ ) [67]	PSt density	1054
$D_{p, MMA}$ ( $g L^{-1}$ ) [67]	PMMA density	1170
T, K	Temperature of reaction	343.15
$X_{St}$ [67]		4.8
$X_{MMA}$ [67]		2.4

## References

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- [67] Thickett, C.; Gilbert, R.G. Emulsion polymerization: State of the art in kinetics and mechanisms. *Polymer* **2007**, *48*, 6965-6991.