Supporting Information

Confined polymerisation of bis-thyminyl monomers within nanoreactors: Towards molecular weight control

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DLS measurements of w/o microemulsions

The water-in-oil microemulsions components are CTAB (a surfactant), distilled water, DMF containing 0.01 M of the monomer, pentanol (a co-surfactant) and hexane. Water-in-oil microemulsions were combined in sealed glass vials and shaken vigorously for 5 min and then sonicated for 5 min. Tables S1-S4 show the sizes of microemulsions utilizing different ratios of microemulsions components. In all tables, (NA) means the microemulsions did not form.

Table S1. DLS measurements for w/o microemulsions. (CTAB = 0.2 g) [a]

Pentanol = 2 mL				Pentanol = 3 mL				Pentanol = 4 mL			
Entry	H_2O (mL)	Size (nm)	PDI	Entry	H_2O (mL)	Size (nm)	PDI	Entry	H_2O (mL)	Size (nm)	PDI
1	**0.1**	NA	NA	11	**0.1**	NA	NA	21	**0.1**	NA	NA
2	**0.2**	5	0.21	12	**0.2**	NA	NA	22	**0.2**	NA	NA
3	**0.3**	NA	NA	13	**0.3**	NA	NA	23	**0.3**	NA	NA
4	**0.4**	NA	NA	14	**0.4**	8	0.10	24	**0.4**	NA	NA
5	**0.5**	NA	NA	15	**0.5**	NA	NA	25	**0.5**	10	0.12
6	**0.6**	NA	NA	16	**0.6**	NA	NA	26	**0.6**	NA	NA
7	**0.7**	NA	NA	17	**0.7**	NA	NA	27	**0.7**	NA	NA
8	**0.8**	NA	NA	18	**0.8**	NA	NA	28	**0.8**	NA	NA
9	**0.9**	NA	NA	19	**0.9**	NA	NA	29	**0.9**	NA	NA
10	**1**	NA	NA	20	**1**	NA	NA	30	**1**	NA	NA

[a] The amounts of hexane and DMF were constant (27.3 mL and 0.3 mL, respectively).

Table S2. DLS measurements for w/o microemulsions. (CTAB = 0.3 g) [a]

Pentanol = 2 mL				Pentanol = 3 mL				Pentanol = 4 mL			
Entry	H_2O (mL)	Size (nm)	PDI	Entry	H_2O (mL)	Size (nm)	PDI	Entry	H_2O (mL)	Size (nm)	PDI
1	**0.1**	NA	NA	11	**0.1**	NA	NA	21	**0.1**	NA	NA
2	**0.2**	NA	NA	12	**0.2**	NA	NA	22	**0.2**	NA	NA
3	**0.3**	NA	NA	13	**0.3**	NA	NA	23	**0.3**	NA	NA
4	**0.4**	5	0.06	14	**0.4**	NA	NA	24	**0.4**	NA	NA
5	**0.5**	NA	NA	15	**0.5**	NA	NA	25	**0.5**	NA	NA
6	**0.6**	NA	NA	16	**0.6**	8	0.21	26	**0.6**	NA	NA
7	**0.7**	NA	NA	17	**0.7**	6	0.10	27	**0.7**	5	0.18
8	**0.8**	NA	NA	18	**0.8**	8	0.10	28	**0.8**	6	0.20
9	**0.9**	NA	NA	19	**0.9**	18	0.31	29	**0.9**	NA	NA
10	**1**	NA	NA	20	**1**	NA	NA	30	**1**	NA	NA

[a] The amounts of hexane and DMF were constant (27.3 mL and 0.3 mL, respectively).

Table S3. DLS measurements for w/o microemulsions. (CTAB = 0.4 g) [a]

Pentanol = 2 mL				Pentanol = 3 mL				Pentanol = 4 mL			
Entry	H_2O (mL)	Size (nm)	PDI	Entry	H_2O (mL)	Size (nm)	PDI	Entry	H_2O (mL)	Size (nm)	PDI
1	**0.1**	NA	NA	11	**0.1**	NA	NA	21	**0.1**	NA	NA
2	**0.2**	NA	NA	12	**0.2**	NA	NA	22	**0.2**	NA	NA
3	**0.3**	NA	NA	13	**0.3**	NA	NA	23	**0.3**	NA	NA
4	**0.4**	NA	NA	14	**0.4**	NA	NA	24	**0.4**	NA	NA
5	**0.5**	NA	NA	15	**0.5**	NA	NA	25	**0.5**	NA	NA
6	**0.6**	6	0.07	16	**0.6**	NA	NA	26	**0.6**	NA	NA
7	**0.7**	10	0.20	17	**0.7**	NA	NA	27	**0.7**	NA	NA
8	**0.8**	12	0.24	18	**0.8**	NA	NA	28	**0.8**	5	0.33
9	**0.9**	22	0.42	19	**0.9**	NA	NA	29	**0.9**	NA	NA
10	**1**	NA	NA	20	**1**	5	0.10	30	**1**	NA	NA

[a] The amounts of hexane and DMF were constant (27.3 mL and 0.3 mL, respectively).

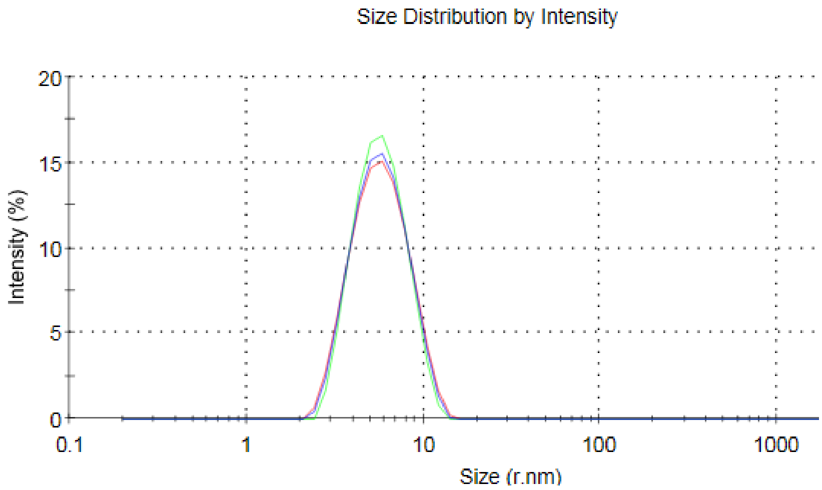
Table S4. DLS measurements for w/o microemulsions. (CTAB = 0.5 g) [a]

Pentanol = 2 mL				Pentanol = 3 mL				Pentanol = 4 mL			
Entry	H_2O (mL)	Size (nm)	PDI	Entry	H_2O (mL)	Size (nm)	PDI	Entry	H_2O (mL)	Size (nm)	PDI
1	**0.1**	NA	NA	11	**0.1**	NA	NA	21	**0.1**	NA	NA
2	**0.2**	NA	NA	12	**0.2**	NA	NA	22	**0.2**	NA	NA
3	**0.3**	NA	NA	13	**0.3**	NA	NA	23	**0.3**	NA	NA
4	**0.4**	NA	NA	14	**0.4**	NA	NA	24	**0.4**	NA	NA
5	**0.5**	NA	NA	15	**0.5**	NA	NA	25	**0.5**	NA	NA
6	**0.6**	NA	NA	16	**0.6**	NA	NA	26	**0.6**	NA	NA
7	**0.7**	NA	NA	17	**0.7**	NA	NA	27	**0.7**	NA	NA
8	**0.8**	5	0.06	18	**0.8**	NA	NA	28	**0.8**	NA	NA
9	**0.9**	8	0.08	19	**0.9**	NA	NA	29	**0.9**	NA	NA
10	**1**	13	0.1	20	**1**	NA	NA	30	**1**	NA	NA

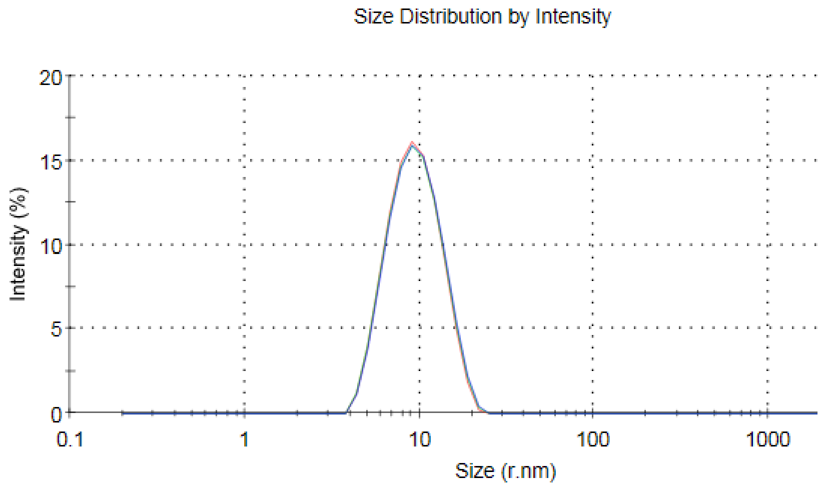
[a] The amounts of hexane and DMF were constant (27.3 ml and 0.3 ml, respectively).

Size distribution of the droplets

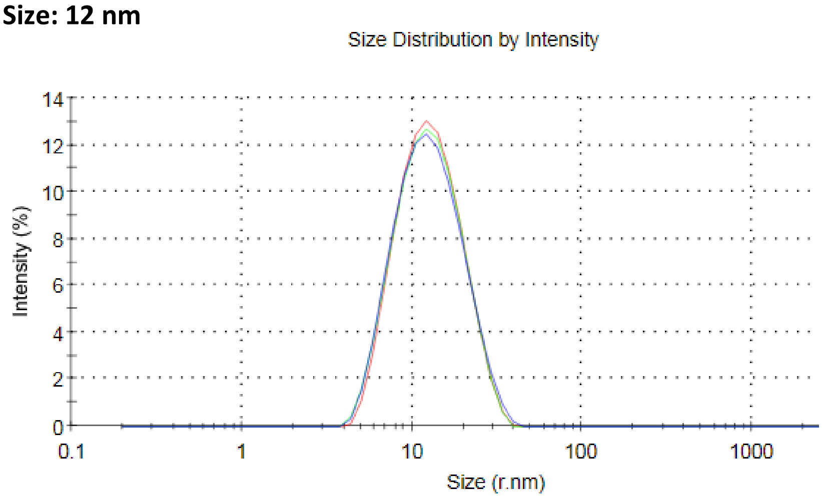
Size: 6 nm



Size: 10 nm

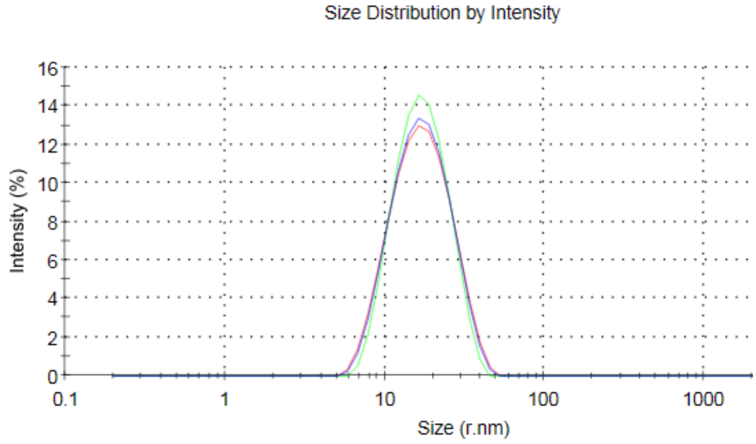


Size: 12 nm

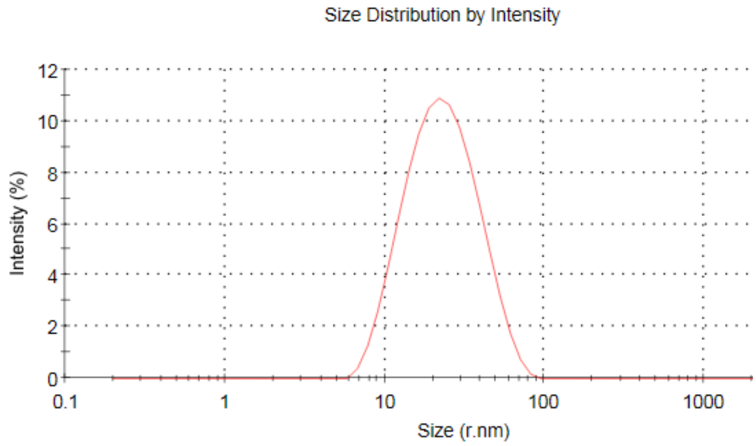


Size distribution of the droplets

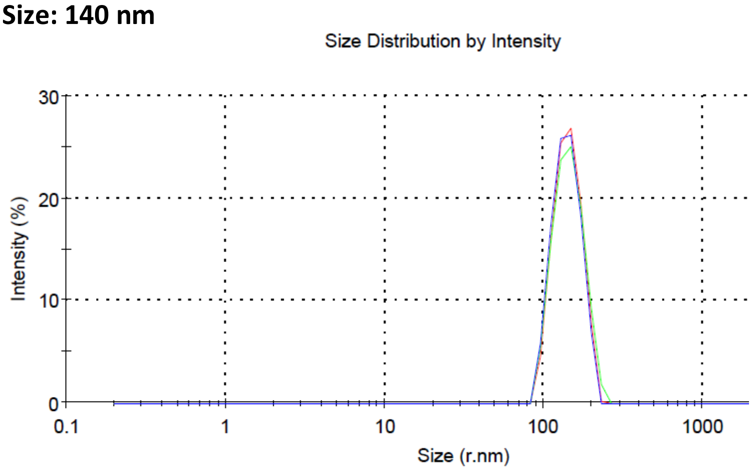
Size: 18 nm



Size: 22 nm



Size: 140 nm



GPC chromatograms

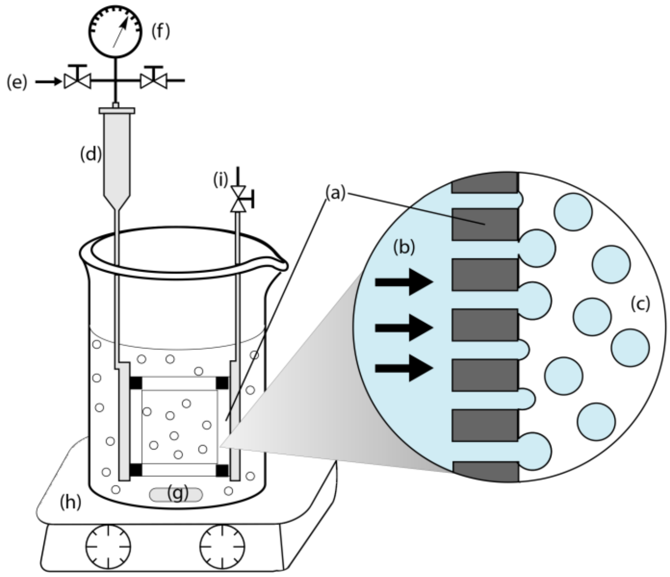


Figure. S1 Schematic illustration of SPG membrane emulsification process in the production of monodisperse droplets. (a) SPG membrane; (b) dispersed phase; (c) continuous phase; (d) dispersed phase tank; (e) N_2 inlet; (f) pressure gauge; (g) stir bar; (h) magnetic stirrer; (i) vent valve.

Table S5. Calculating monomer units depending on the overall monomer concentration of monomer in the dispersed phase and the droplet volume.

Droplet diameter (nm)	Droplet volume (cm^3)	Dispersed phase volume (cm^3)	Monomer Concentration in the dispersed phase (M)	Expected number of monomer units in each droplet
6	$1.13x10^{-19}$	0.1	0.1	$6.8 \approx 7$
10	$5.23x10^{-19}$	0.8	$3.75x10^{-3}$	$1.2 \approx 1$
12	$9.03x10^{-19}$	0.9	$2.73x10^{-3}$	$1.5 \approx 2$
18	$3.05x10^{-18}$	1.2	$2.5x10^{-3}$	$4.6 \approx 5$
22	$5.56x10^{-18}$	1.2	$2.5x10^{-3}$	$8.4 \approx 9$
140	$1.43x10^{-15}$	2.95	0.09	77,503.1

The monomer units in each droplet were calculated considering the overall monomer concentration in the entire volume of dispersed phase and the droplet volume.

Briefly, moles of monomer in the dispersed phase were calculated by multiply the concentration of the monomer in the dispersed phase by the volume (litre) of dispersed phase. Then, the moles of monomer was multiplied by Avogadro's number (6.022×10^{23}) to find the number of monomer molecules in the entire volume of dispersed phase.

The number of monomer units in each droplet can be calculated by multiplying the number of monomer molecules in the entire volume of dispersed phase by volume of the droplet then divided by the dispersed phase volume.

The following example clarifies the calculation of the monomer units inside a droplet with 6 nm diameter:

- Moles of monomer = concentration x dispersed phase volume (litre)

  = 0.1 x (0.1/1000)

  = 1×10^{-5} mole

- The number of monomer molecules = Moles of monomer x Avogadro's number

  = $(1 \times 10^{-5}) \times (6.022 \times 10^{23})$

  = 6.022×10^{18} molecules in the entire volume of dispersed phase (0.1 cm^3)

- The number of monomer units in each droplet can be calculated as follows:

$$\frac{(6.022\ x\ 10^{23}).(1.13\ x\ 10^{-19})}{0.1} = 6.8 \approx 7$$

In general, following equation can be used to calculate the monomer units inside the droplet.

$$\frac{\left(C.\frac{V}{1000}\right).N_A.D}{V}$$

Where:

C: Monomer concentration in the dispersed phase

V: dispersed phase volume

N_A: Avogadro's number (6.022×10^{23})

D: Droplet volume