

## Effect of shearing stress on the radial heterogeneity and chromatographic performance of styrene-based polymerised high internal phase emulsions prepared in capillary format

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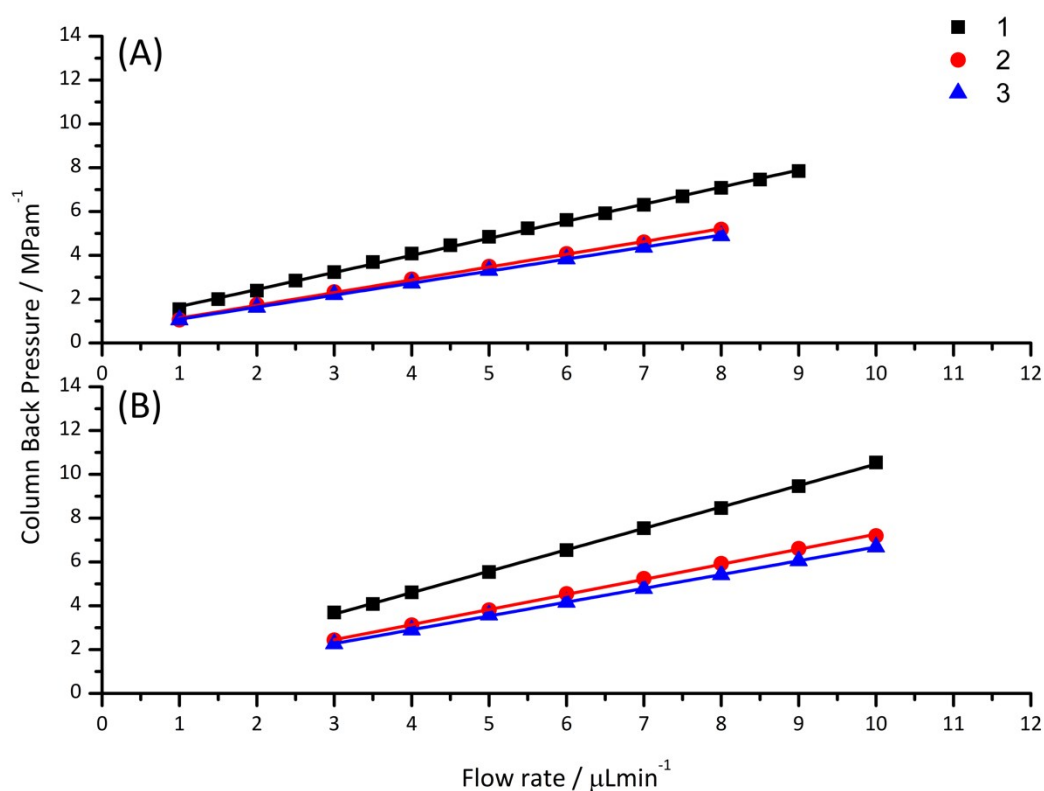
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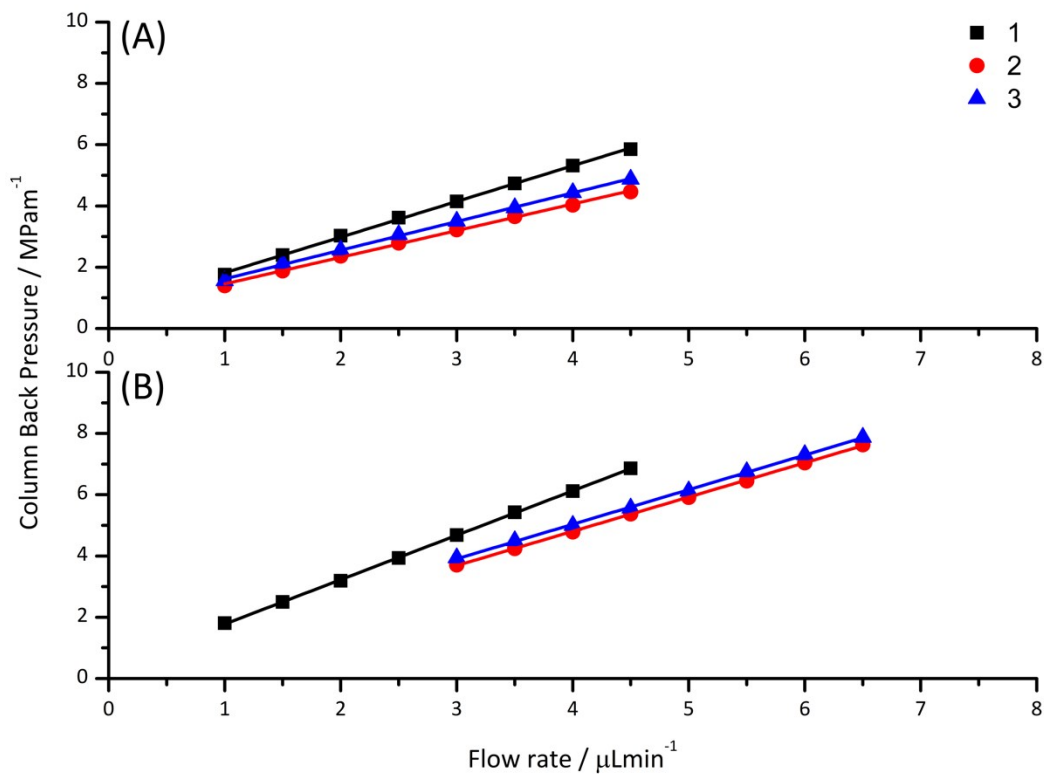
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### Supporting Information

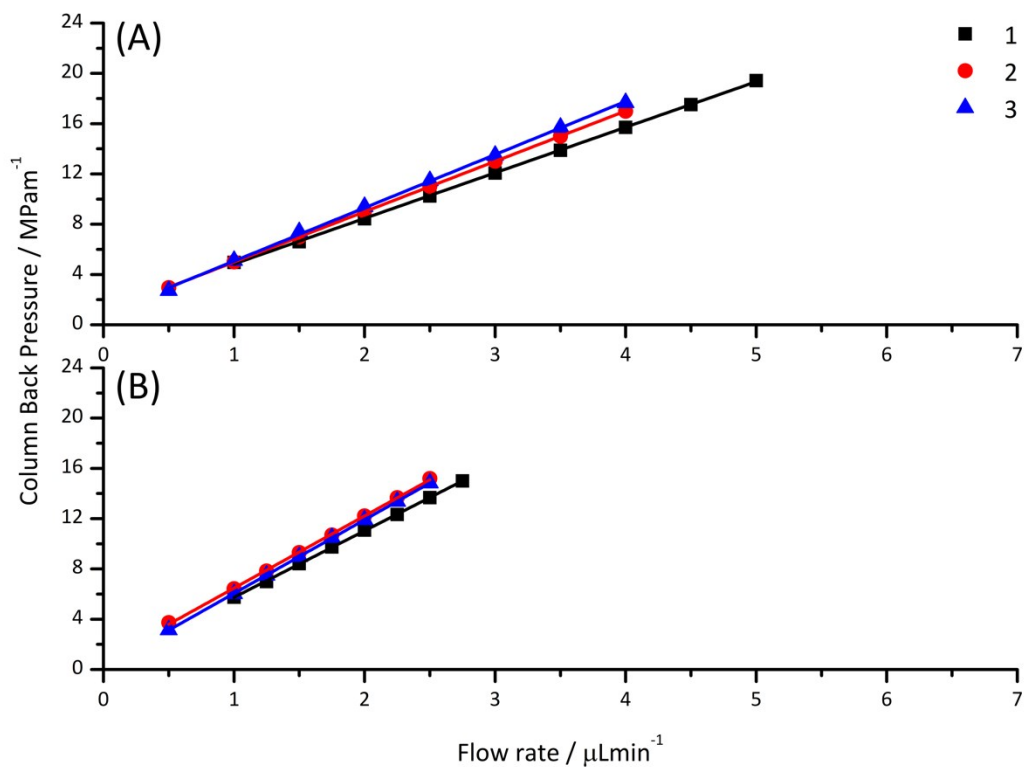
#### 1. Column Permeabilities



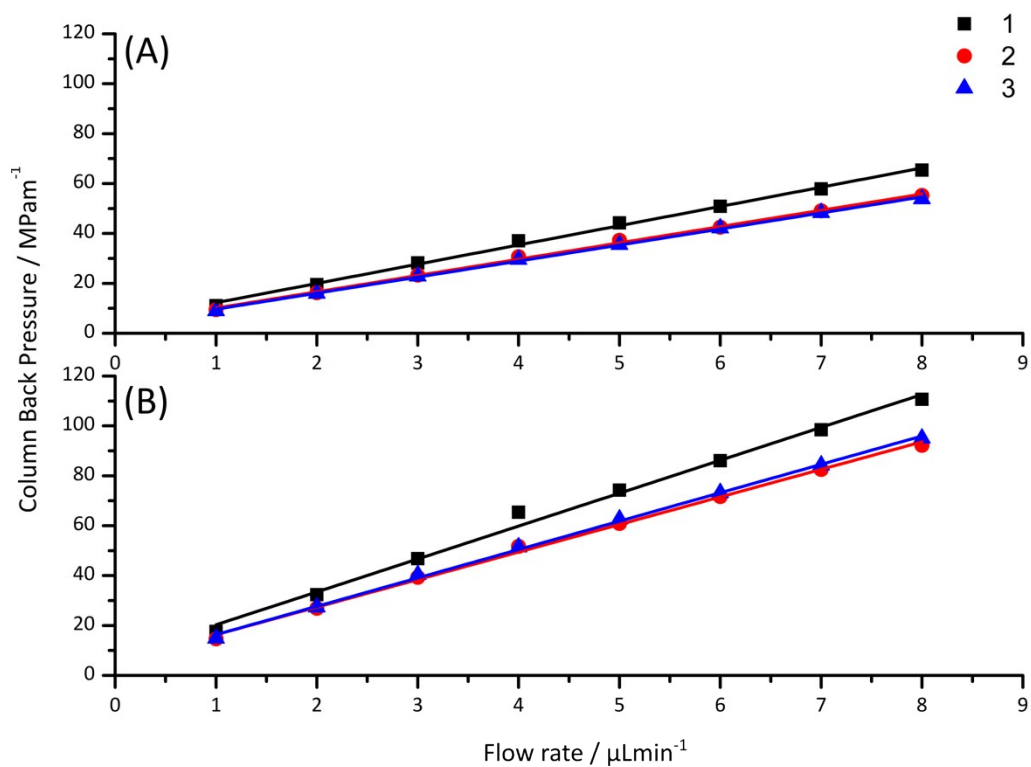
**Fig. S1** Plot of column back pressure (MPa/m) against flow rate (μL/min) for three poly(Sty-co-DVB) poly(HIPE)s prepared from the same batch, using a shear rate of 300 rpm, in 540 μm i.d. silica capillaries using: **A**) MeOH; **B**) H<sub>2</sub>O.



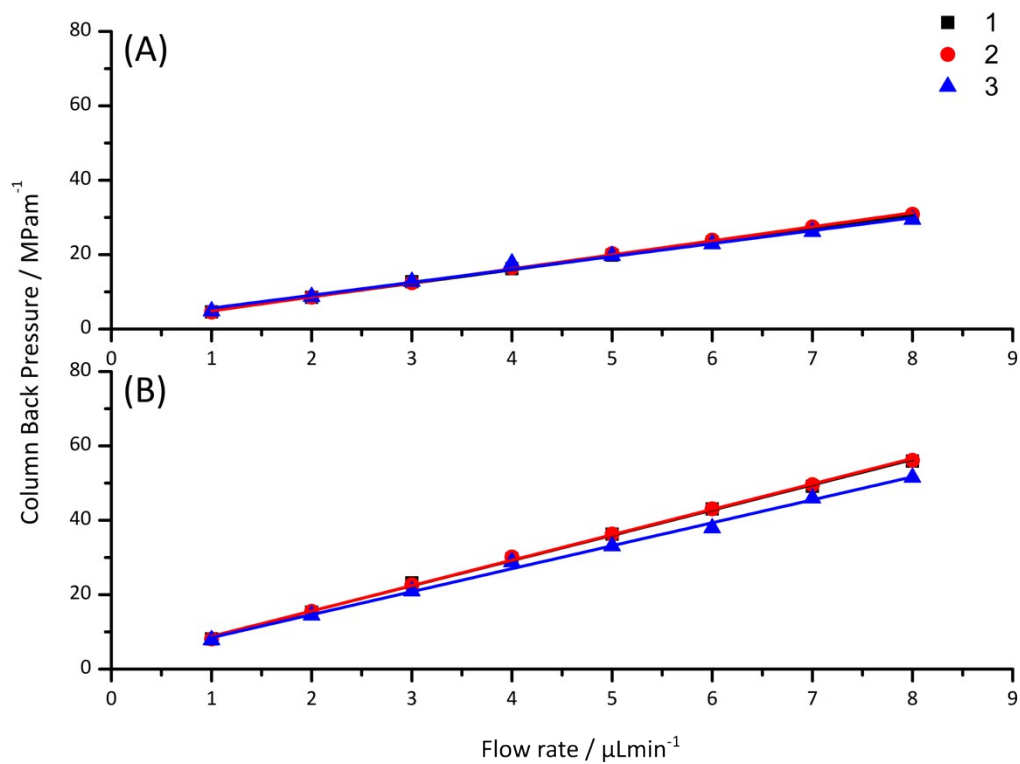
**Fig. S2** Plot of column back pressure (MPa/m) against flow rate ( $\mu\text{L}/\text{min}$ ) for three poly(Sty-co-DVB) poly(HIPE)s prepared from the same batch, using a shear rate of 300 rpm, in 250  $\mu\text{m}$  i.d. silica capillaries using: **A)** MeOH; **B)**  $\text{H}_2\text{O}$ .



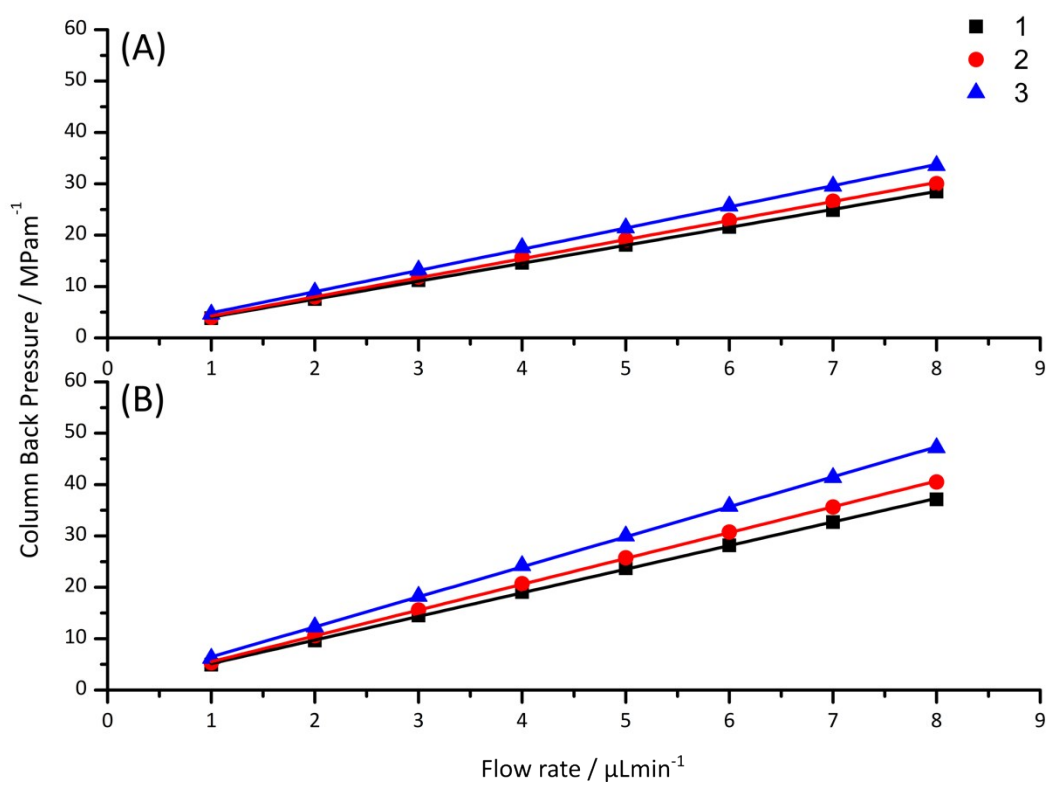
**Fig. S3** Plot of column back pressure (MPa/m) against flow rate ( $\mu\text{L}/\text{min}$ ) for three poly(Sty-co-DVB) poly(HIPE)s prepared from the same batch, using a shear rate of 300 rpm, in 150  $\mu\text{m}$  i.d. silica capillaries using: **A)** MeOH; **B)**  $\text{H}_2\text{O}$ .



**Fig. S4** Plot of column back pressure (MPa/m) against flow rate ( $\mu\text{L}/\text{min}$ ) for three poly(Sty-co-DVB) poly(HIPE)s prepared from the same batch, using a shear rate of 14 000 rpm, in 540  $\mu\text{m}$  i.d. silica capillaries using: **A)** MeOH; **B)**  $\text{H}_2\text{O}$ .

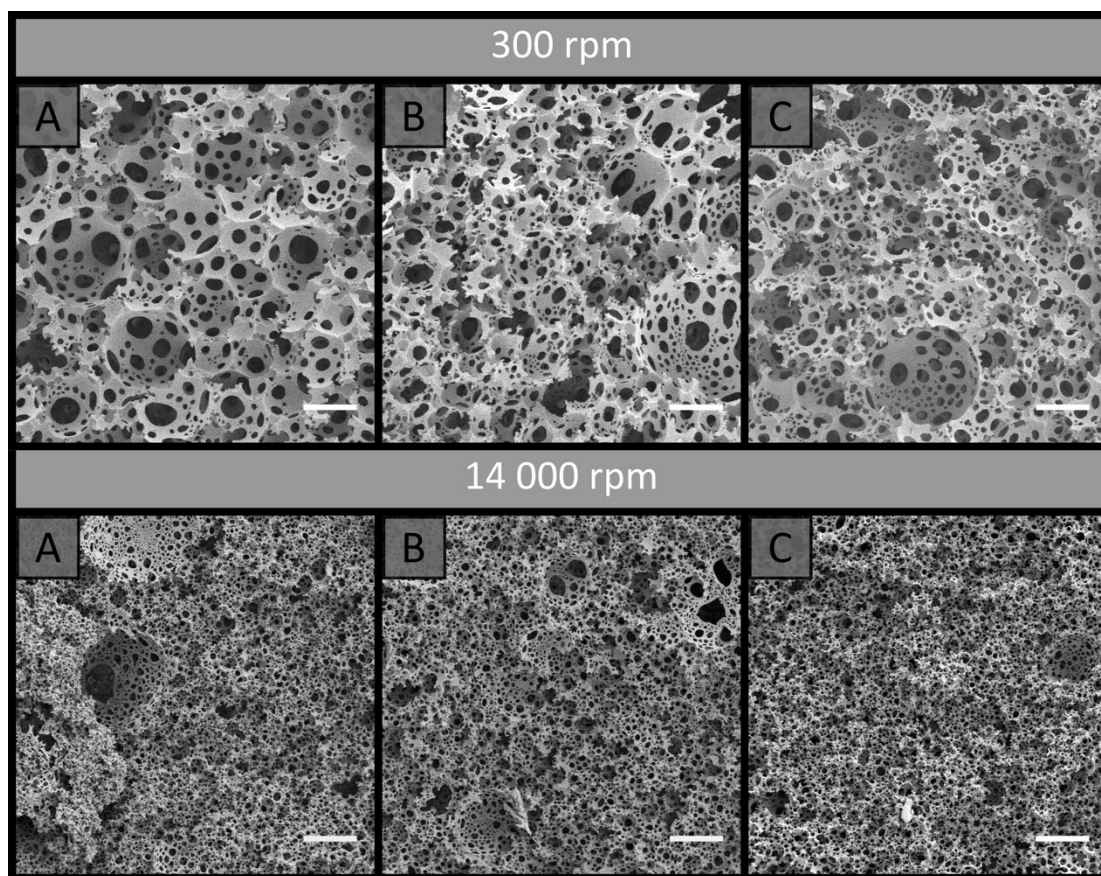


**Fig. S5** Plot of column back pressure (MPa/m) against flow rate ( $\mu\text{L}/\text{min}$ ) for three poly(Sty-co-DVB) poly(HIPE)s prepared from the same batch, using a shear rate of 14 000 rpm, in 250  $\mu\text{m}$  i.d. silica capillaries using: **A)** MeOH; **B)**  $\text{H}_2\text{O}$ .



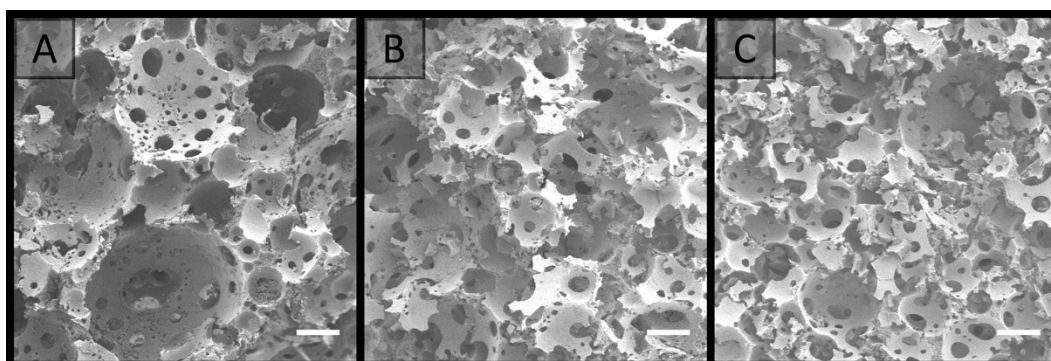
**Fig. S6** Plot of column back pressure (MPa/m) against flow rate ( $\mu\text{L}/\text{min}$ ) for three poly(Sty-*co*-DVB) poly(HIPE)s prepared from the same batch, using a shear rate of 14 000 rpm, in 150  $\mu\text{m}$  i.d. silica capillaries using: **A)** MeOH; **B)**  $\text{H}_2\text{O}$ .

## 2. Preparation in capillary format



**Fig. S7** SEM images of poly(HIPE)s prepared from emulsions emulsified at 300 rpm or 14 000 rpm in fused silica capillaries of different i.d.: **A)** 540  $\mu\text{m}$ ; **B)** 250  $\mu\text{m}$ ; **C)** 150  $\mu\text{m}$ . Scale bar is 15  $\mu\text{m}$ . Images obtained at 500 $\times$  magnification.

## 3. Longitudinal Heterogeneity Study



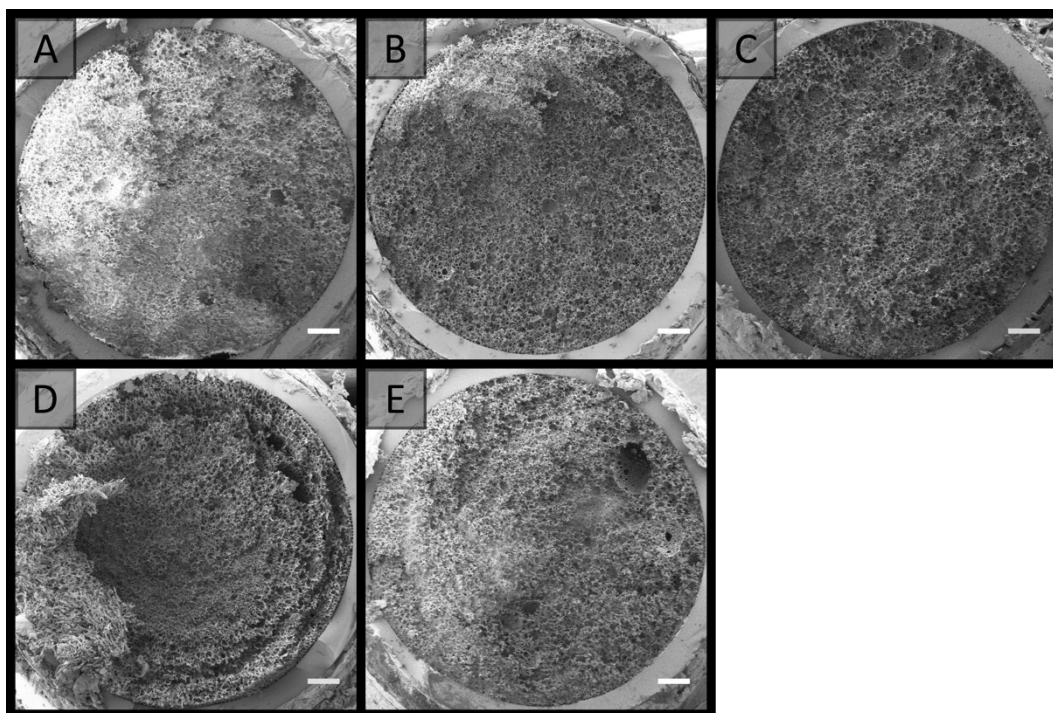
**Fig. S8** SEM images of poly(HIPE)s obtained by curing emulsions which had been emulsified at 300 rpm and passed through the syringe and/or needle. **A)** Bulk; **B)** Syringe; **C)** Syringe and needle. Scale bar is 20  $\mu\text{m}$ . Images were obtained at 500 $\times$  magnification.

**Table S1** Porous properties of cured emulsions which had been passed through the syringe and the syringe and needle.

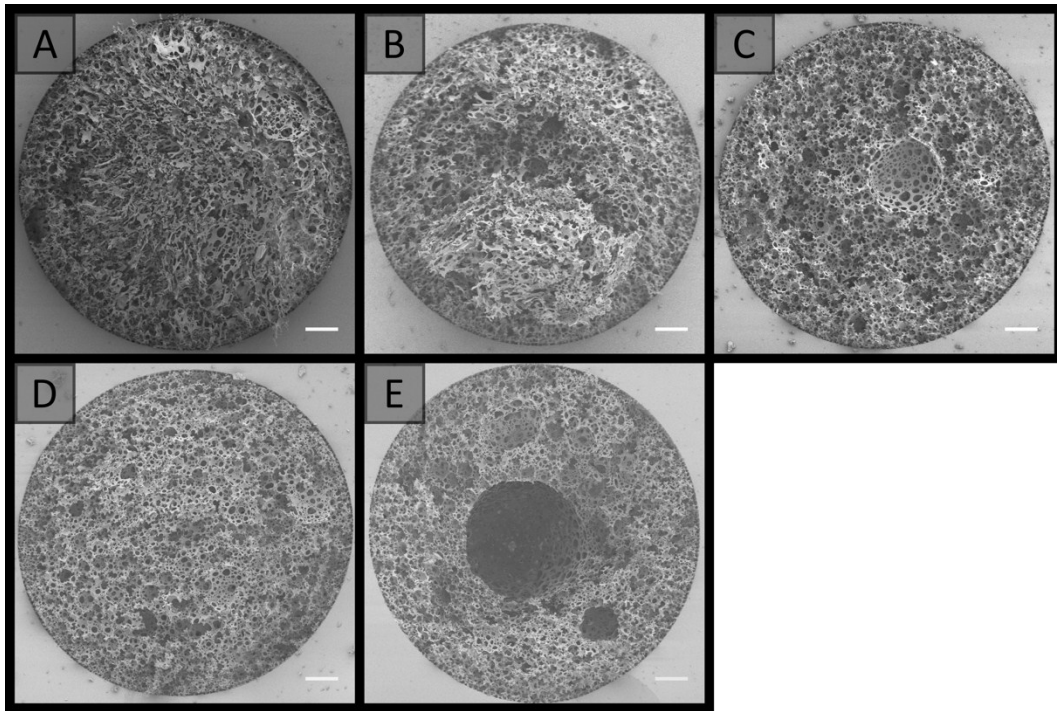
Sample	V <sup>a</sup> / $\mu\text{m}$	W <sup>b</sup> / $\mu\text{m}$	D <sup>c</sup> / $\mu\text{m}$
Bulk	$30 \pm 10$	$4 \pm 2$	$20 \pm 10$
Syringe	$30 \pm 10$	$4 \pm 2$	$13 \pm 8$
Syringe + Needle	$20 \pm 10$	$4 \pm 2$	$12 \pm 6$

<sup>a</sup> Average void diameter as determined from SEM. <sup>b</sup> Average window diameter as determined from SEM.

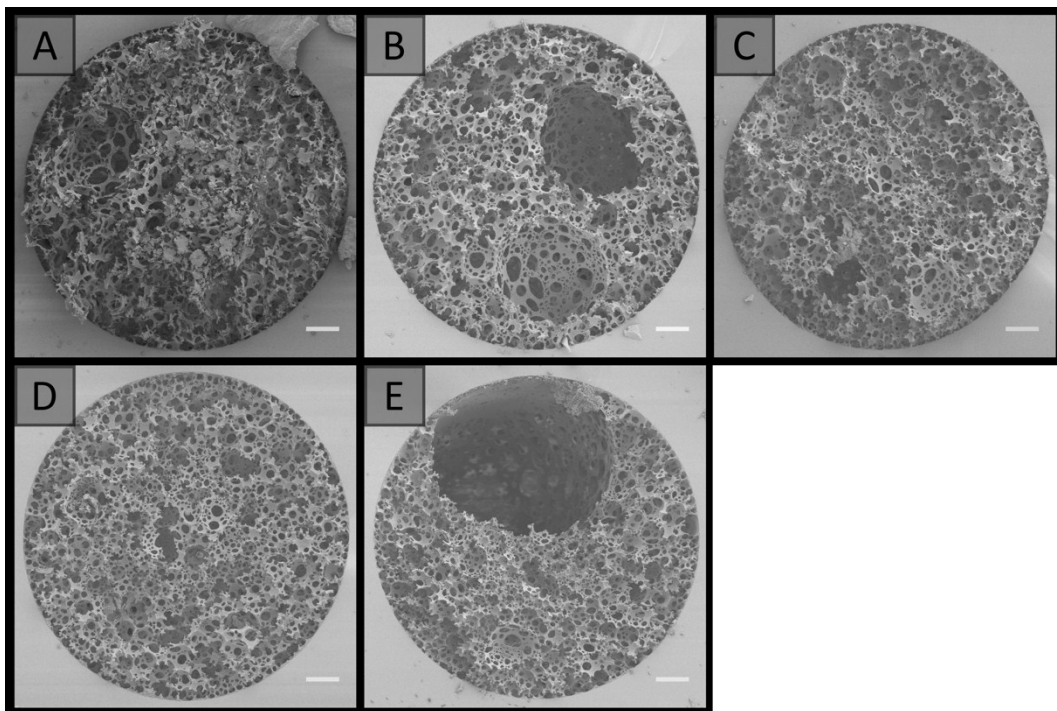
<sup>c</sup> Average droplet diameter immediately after preparation as determined from optical microscopy.



**Fig. S9** SEM images of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm and cured in 20 cm of a 540  $\mu\text{m}$  i.d. capillary then cut at different lengths from the capillary inlet. **A)** 2 cm; **B)** 5 cm; **C)** 10 cm; **D)** 15 cm; **E)** 18 cm. Scale bar is 50  $\mu\text{m}$ . Images obtained at 150 $\times$  magnification.



**Fig. S10** SEM images of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm and cured in 20 cm of a 250 μm i.d. capillary then cut at different lengths from the capillary inlet. **A)** 2 cm; **B)** 5 cm; **C)** 10 cm; **D)** 15 cm; **E)** 18 cm. Scale bar is 25 μm. Images obtained at 300X magnification.



**Fig. S11** SEM images of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm and cured in 20 cm of a 150 μm i.d. capillary then cut at different lengths from the capillary inlet. **A)** 2 cm; **B)** 5 cm; **C)** 10 cm; **D)** 15 cm; **E)** 18 cm. Scale bar is 15 μm. Images obtained at 500X magnification.

**Table S2** Porous properties of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm and cured in 20 cm of different i.d. capillaries then cut at different lengths from the capillary inlet.

540 $\mu\text{m}$ i.d.	$V^a / \mu\text{m}$	$W^b / \mu\text{m}$
2 cm	$12 \pm 5$	$3 \pm 1$
5 cm	$12 \pm 5$	$3 \pm 1$
10 cm	$14 \pm 6$	$3 \pm 2$
15 cm	$12 \pm 4$	$4 \pm 2$
18 cm	$12 \pm 7$	$2 \pm 1$
250 $\mu\text{m}$ i.d.	$V^a / \mu\text{m}$	$W^b / \mu\text{m}$
2 cm	$12 \pm 4$	$3 \pm 2$
5 cm	$9 \pm 3$	$3 \pm 2$
10 cm	$9 \pm 4$	$2 \pm 1$
15 cm	$8 \pm 4$	$2 \pm 1$
18 cm	$9 \pm 7$	$3 \pm 1$
150 $\mu\text{m}$ i.d.	$V^a / \mu\text{m}$	$W^b / \mu\text{m}$
2 cm	$9 \pm 4$	$3 \pm 1$
5 cm	$8 \pm 6$	$3 \pm 1$
10 cm	$9 \pm 4$	$2 \pm 1$
15 cm	$9 \pm 3$	$2.3 \pm 0.9$
18 cm	$8 \pm 6$	$2 \pm 1$

<sup>a</sup> Average void diameter as determined from SEM. <sup>b</sup> Average window diameter as determined from SEM.

#### 4. Influence of Filling Rate

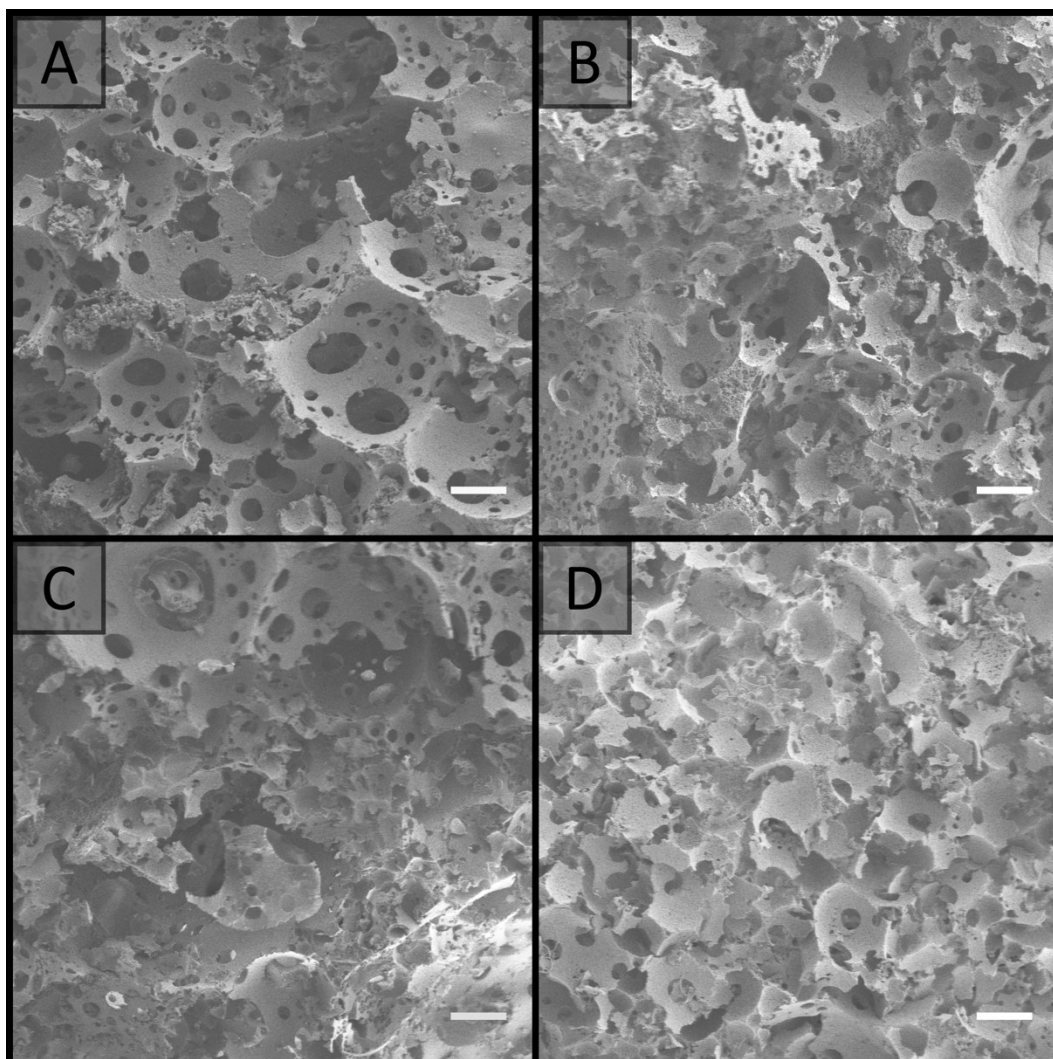
**Table S3** Porous properties of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm and passed through 20 cm of 250 or 150  $\mu\text{m}$  i.d. capillaries at different rates.

Filling Rate / $\mu\text{Lmin}^{-1}$	250 $\mu\text{m}$			150 $\mu\text{m}$		
	$V^a / \mu\text{m}$	$W^b / \mu\text{m}$	$D^c / \mu\text{m}$	$V^a / \mu\text{m}$	$W^b / \mu\text{m}$	$D^c / \mu\text{m}$
10	$30 \pm 10$	$5 \pm 3$	$10 \pm 5$	$21 \pm 7$	$4 \pm 2$	$9 \pm 5$
25	$30 \pm 10$	$4 \pm 2$	$11 \pm 6$	$30 \pm 10$	$5 \pm 4$	$8 \pm 4$
50	$30 \pm 10$	$4 \pm 2$	$8 \pm 5$	$30 \pm 10$	$4 \pm 2$	$9 \pm 5$
100	$21 \pm 9$	$3 \pm 2$	$9 \pm 5$	$19 \pm 8$	$3 \pm 1$	$9 \pm 5$

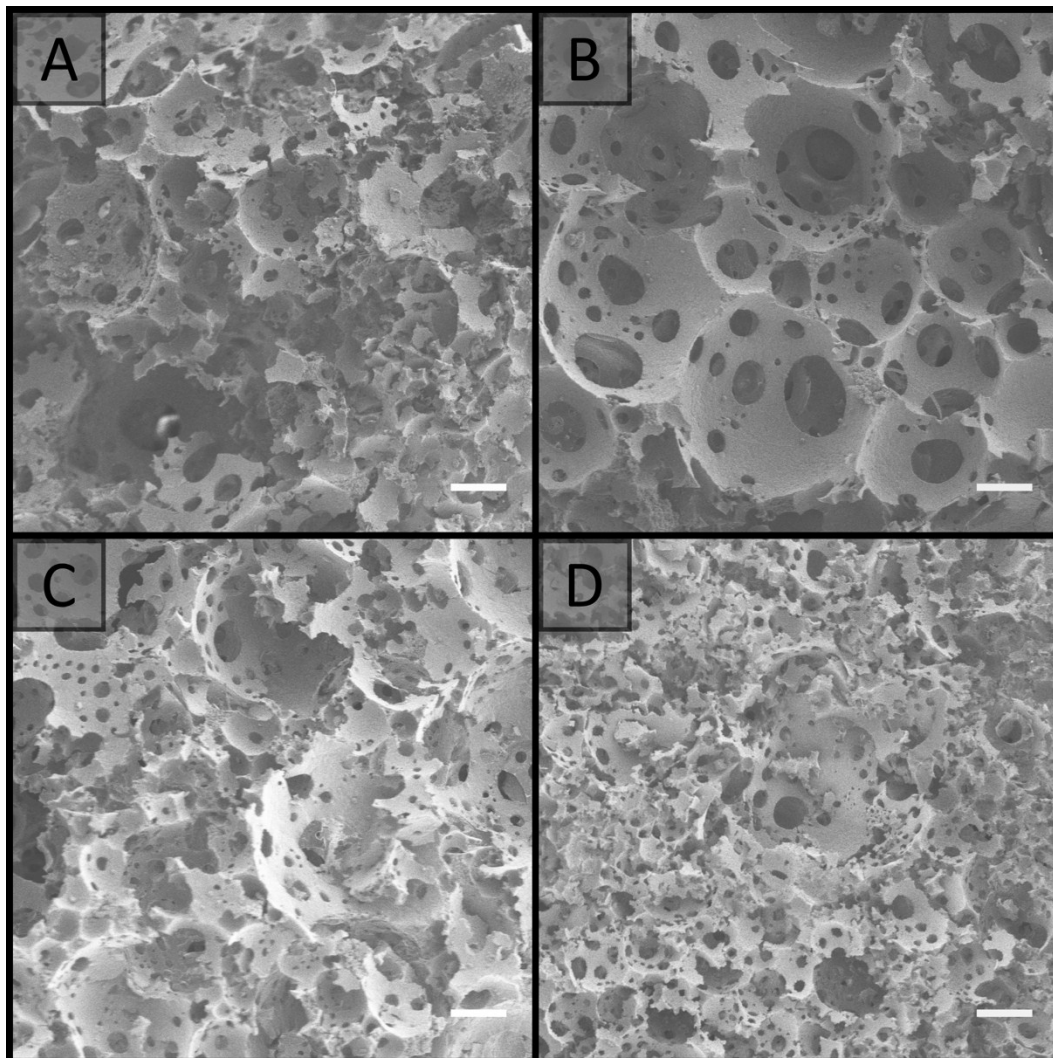
<sup>a</sup> Average void diameter as determined from SEM. <sup>b</sup> Average window diameter as determined from SEM.

<sup>c</sup> Average droplet diameter immediately after preparation as determined from optical microscopy.



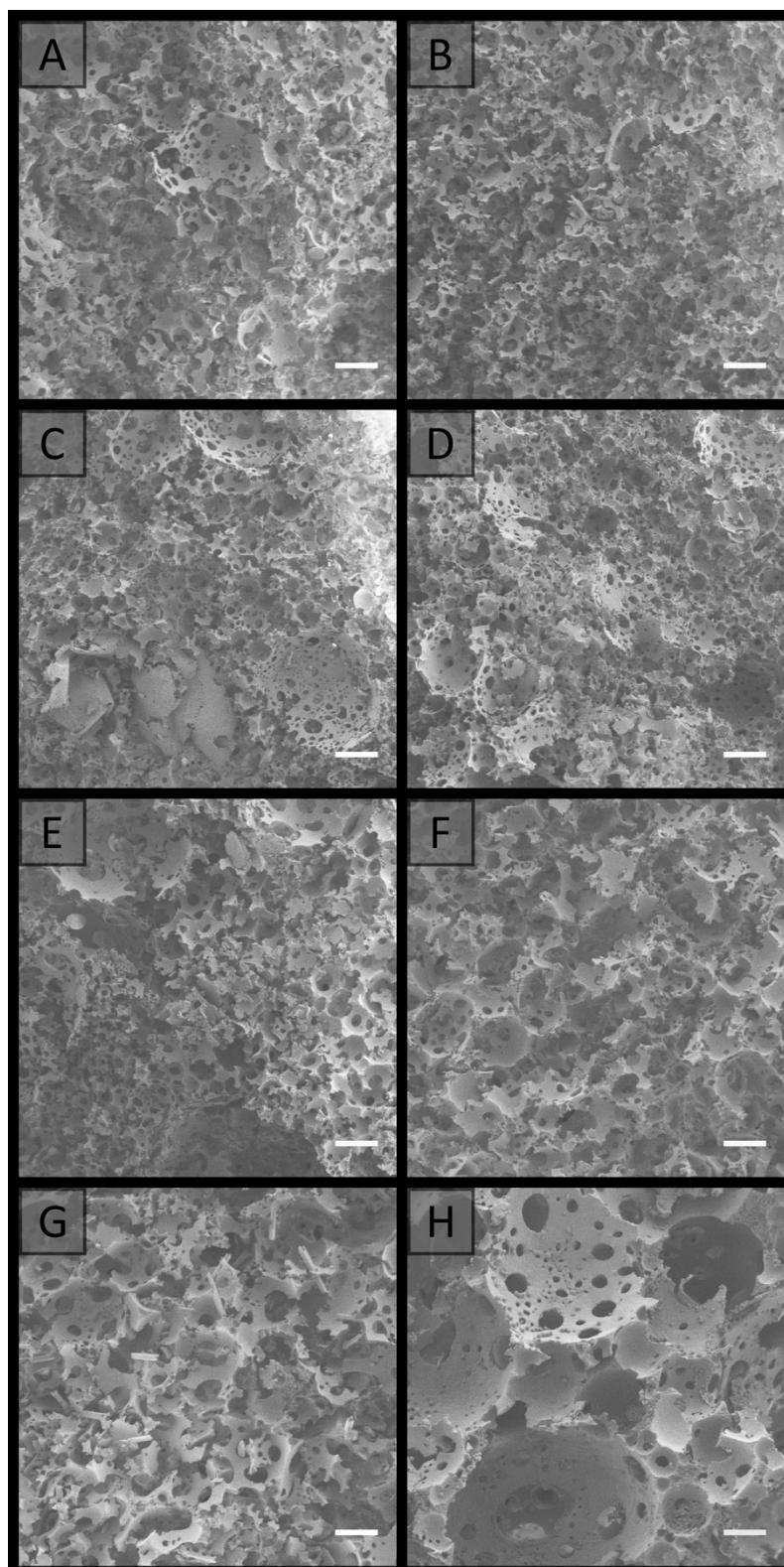


**Fig. S12** SEM images of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm, passed through 20 cm of 250  $\mu\text{m}$  i.d. capillary at different rates and cured. **A)** 10  $\mu\text{L}/\text{min}$ ; **B)** 25  $\mu\text{L}/\text{min}$ ; **C)** 50  $\mu\text{L}/\text{min}$ ; **D)** 100  $\mu\text{L}/\text{min}$ . Scale bar is 15  $\mu\text{m}$ . Images obtained at 500 $\times$  magnification.



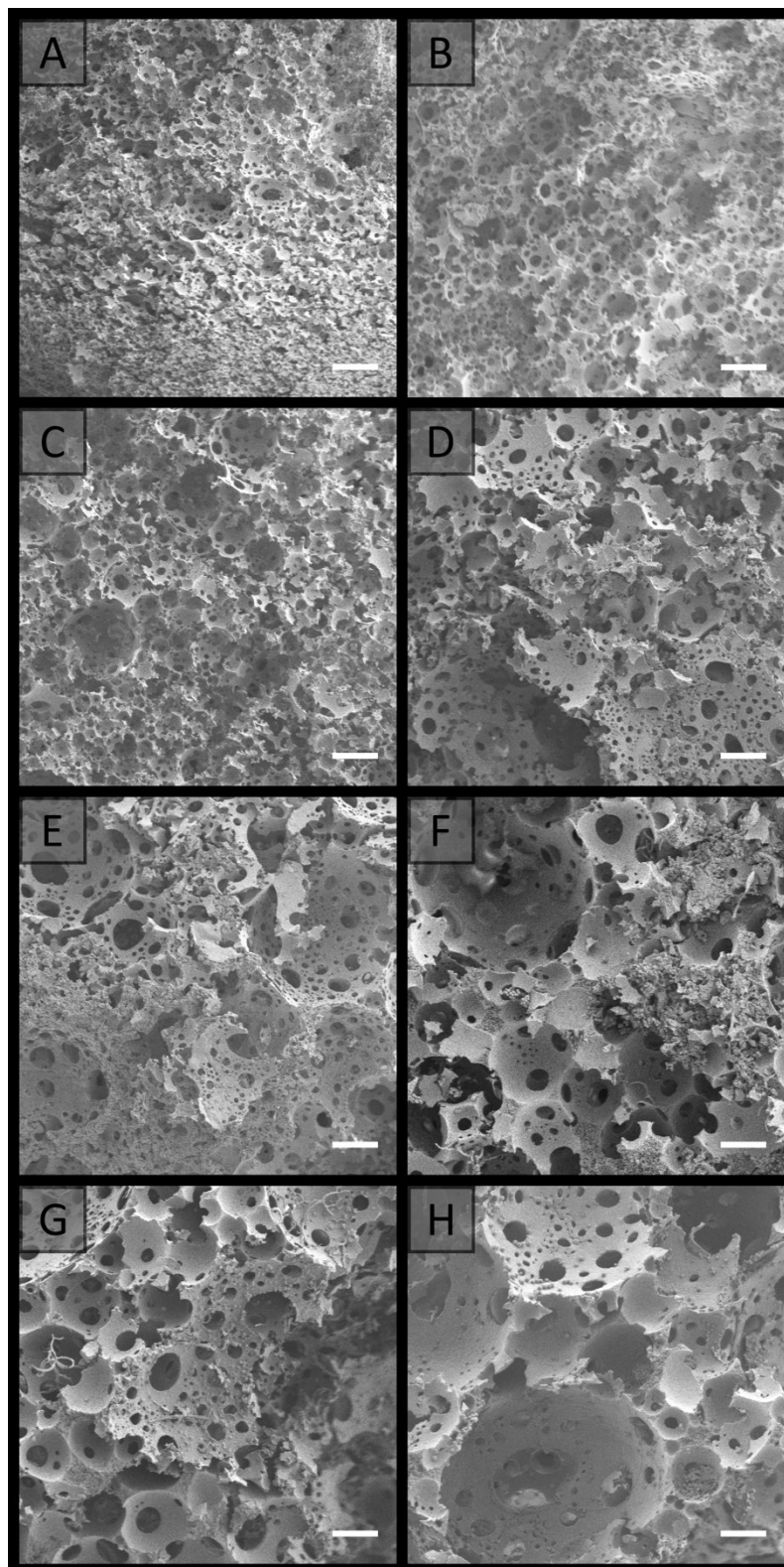
**Fig. S13** SEM images of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm, passed through 20 cm of 150  $\mu\text{m}$  i.d. capillary at different rates and cured. **A)** 10  $\mu\text{L}/\text{min}$ ; **B)** 25  $\mu\text{L}/\text{min}$ ; **C)** 50  $\mu\text{L}/\text{min}$ ; **D)** 100  $\mu\text{L}/\text{min}$ . Scale bar is 15  $\mu\text{m}$ . Images obtained at 500 $\times$  magnification.

## 5. Influence of Capillary Length



**Fig. S14** SEM images of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm and passed through different lengths of 250  $\mu\text{m}$  i.d. capillary and then cured. **A)** 5 cm; **B)** 10 cm; **C)** 20

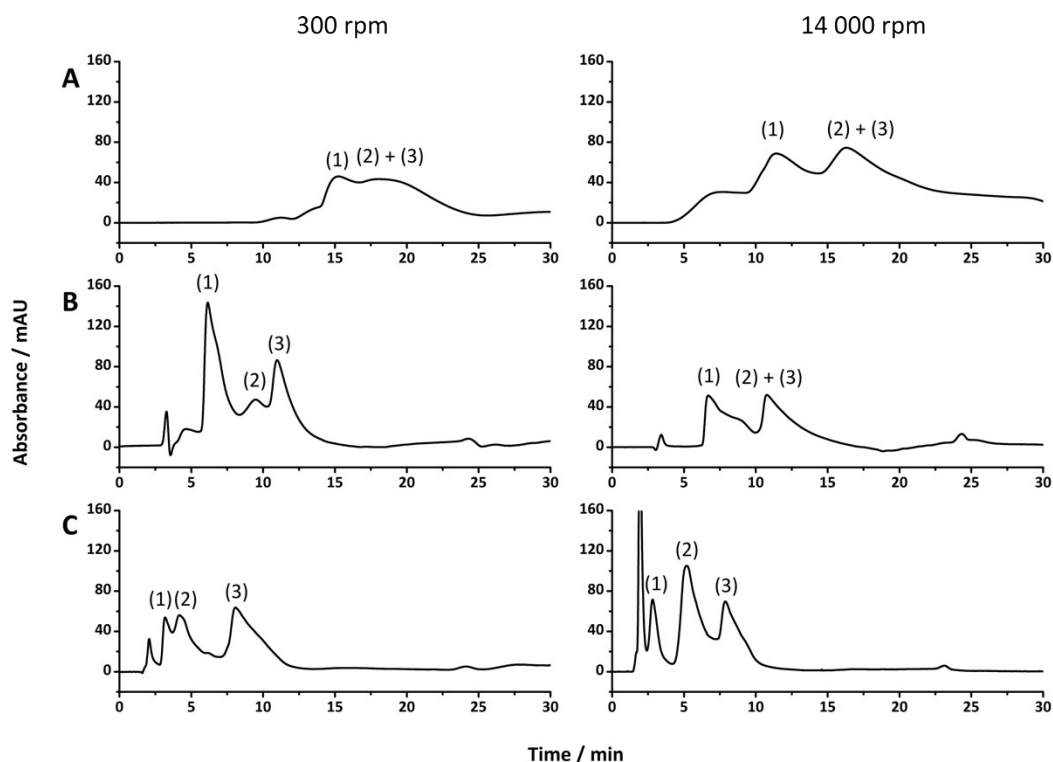
cm; **D**) 30 cm; **E**) 40 cm; **F**) 50 cm; **G**) 60 cm; **H**) Bulk. Scale bar is 15  $\mu\text{m}$ . Images obtained at 500 $\times$  magnification.



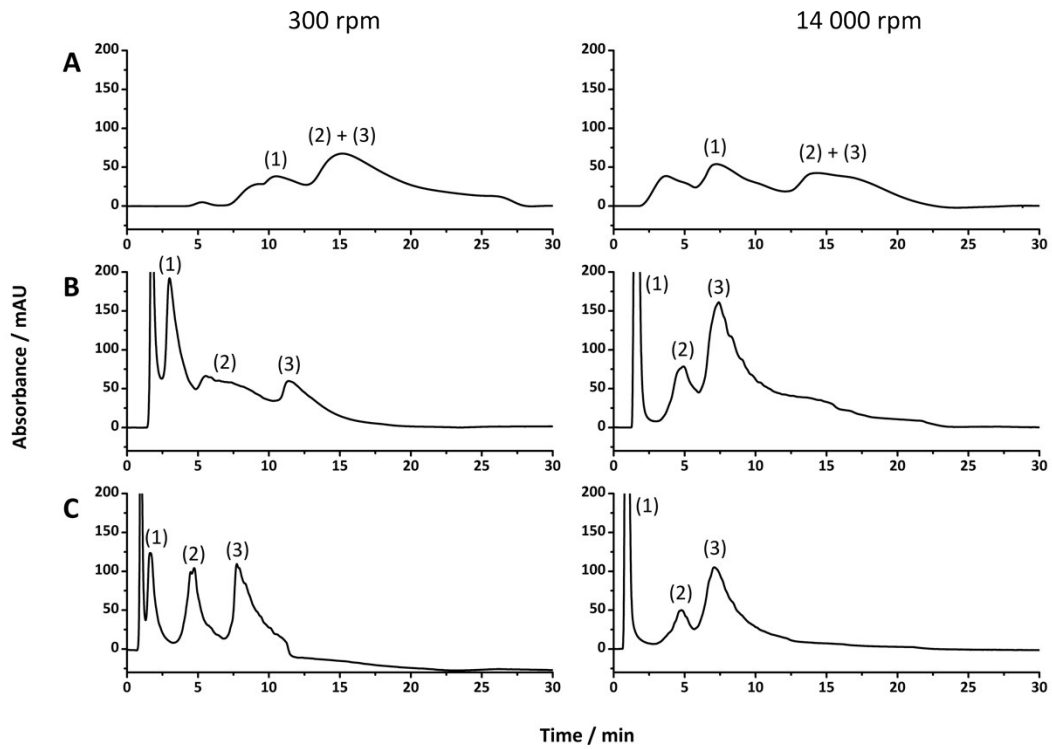
**Fig. S15** SEM images of poly(HIPE)s obtained from emulsions which had been emulsified at 300 rpm and passed through different lengths of 150  $\mu\text{m}$  i.d. capillary and then cured. **A**) 5 cm; **B**) 10 cm; **C**) 20

cm; **D**) 30 cm; **E**) 40 cm; **F**) 50 cm; **G**) 60 cm; **H**) Bulk. Scale bar is 15  $\mu\text{m}$ . Images obtained at 500 $\times$  magnification.

## 6. Chromatography

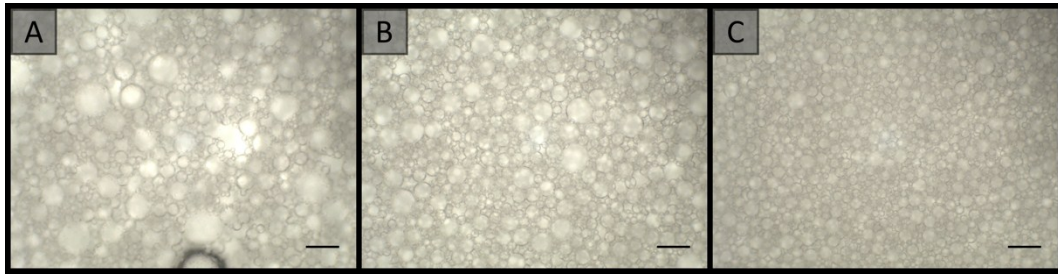


**Fig. S16** The separation of ribonuclease A (1), lysozyme (2) and  $\alpha$ -chymotrypsinogen A (3) under reversed-phase conditions. Conditions: 18 cm of different i.d. columns: **(A)** 540  $\mu\text{m}$  i.d., **(B)** 250  $\mu\text{m}$  i.d., **(C)** 150  $\mu\text{m}$  i.d., prepared with different emulsification energies. Eluent A was 0.1 vol% formic acid in Milli-Q  $\text{H}_2\text{O}$ , and eluent B was 0.1 vol% formic acid in acetonitrile; injection volume, 1  $\mu\text{L}$ ; protein concentration, 0.05 mg/mL for **(B)** and **(C)** and 0.3 mg/mL for **(A)**. Gradient: linear gradient 15 to 70% B in 15 min and then isocratic elution at 70% B for 5 min before returning to 15% B in 5 min; flow rate, 4.0  $\mu\text{L}/\text{min}$ . UV detection at 214 nm.

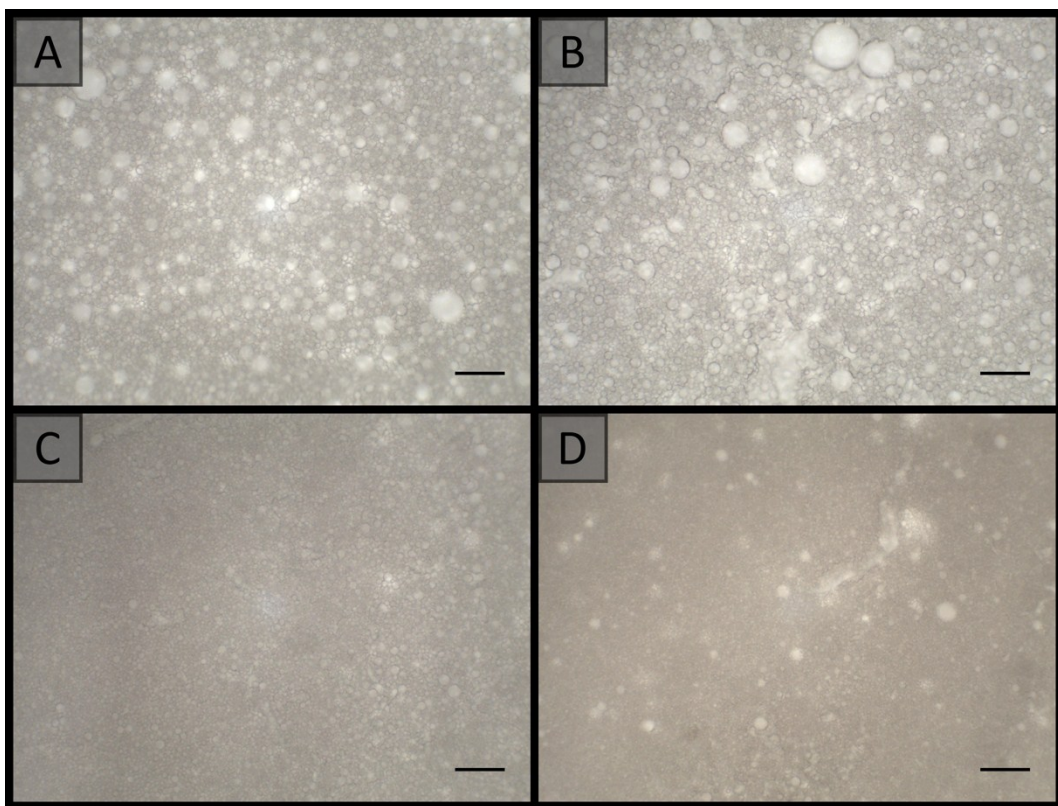


**Fig. S17** The separation of ribonuclease A (1), lysozyme (2) and  $\alpha$ -chymotrypsinogen A (3) under reversed-phase conditions. Conditions: 18 cm of different i.d. columns: **(A)** 540  $\mu\text{m}$  i.d., **(B)** 250  $\mu\text{m}$  i.d., **(C)** 150  $\mu\text{m}$  i.d., prepared with different emulsification energies. Eluent A was 0.1 vol% formic acid in Milli-Q  $\text{H}_2\text{O}$ , and eluent B was 0.1 vol% formic acid in acetonitrile; injection volume, 1  $\mu\text{L}$ ; protein concentration, 0.3 mg/mL. Gradient: linear gradient 15 to 50% B in 15 min and then isocratic elution at 50% B for 5 min before returning to 15% B in 5 min; flow rate, 8.0  $\mu\text{L}/\text{min}$ . UV detection at 214 nm.

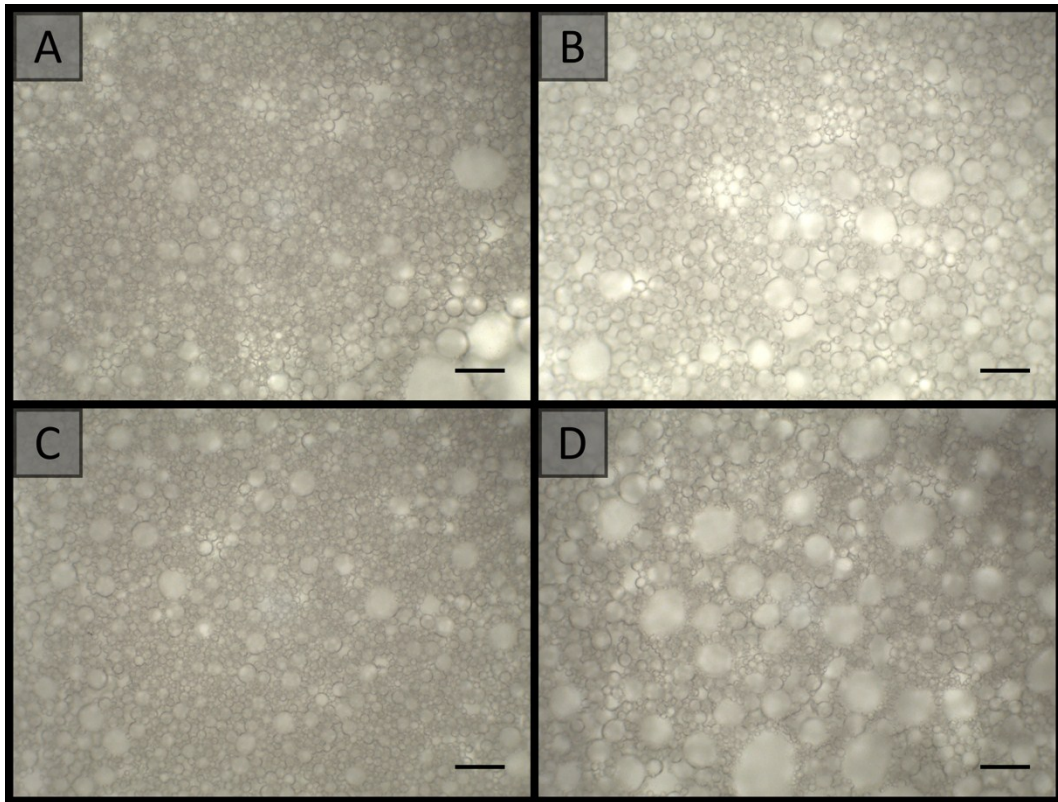
## 7. Optical Microscopy



**Fig. S18** Optical microscopy images of emulsions which had been emulsified at 300 rpm and passed through the syringe and/or needle. **A)** Bulk; **B)** Syringe; **C)** Syringe and needle. Scale bar is 50  $\mu\text{m}$ .

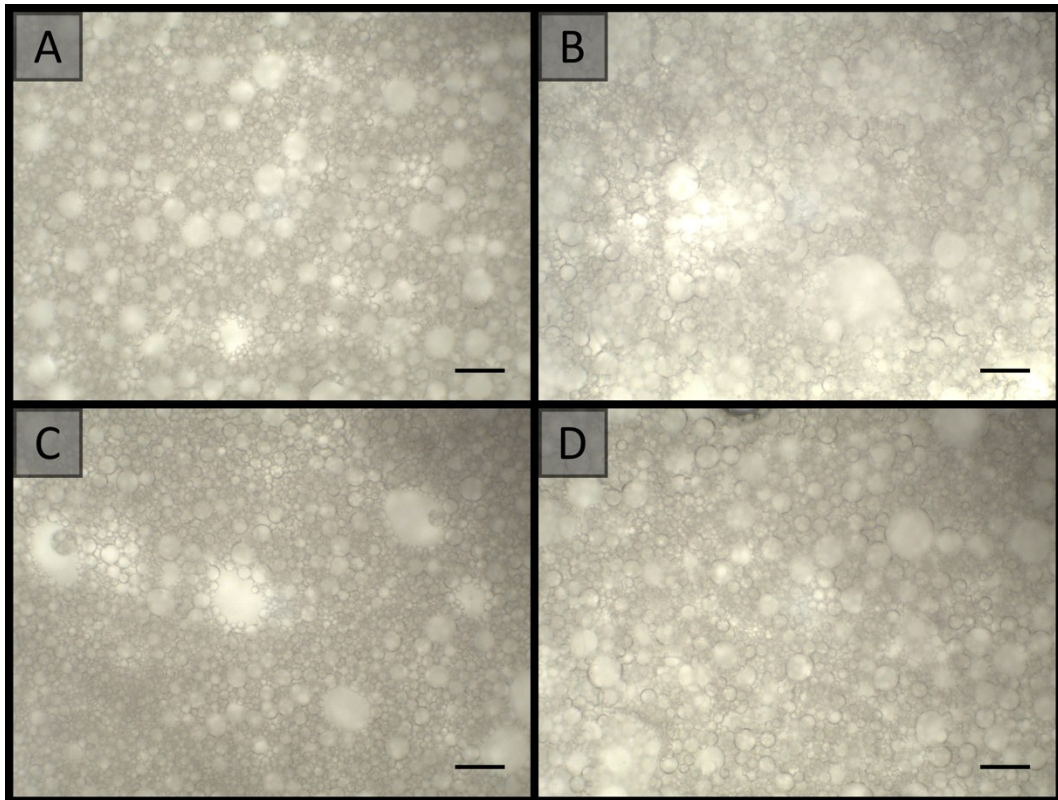


**Fig. S19** Optical microscopy images of emulsions which had been emulsified at 300 rpm and passed through 20 cm of various i.d. capillary columns: **A)** Bulk; **B)** 540  $\mu\text{m}$  i.d.; **C)** 250  $\mu\text{m}$  i.d.; **D)** 150  $\mu\text{m}$  i.d. Scale bar is 50  $\mu\text{m}$ .

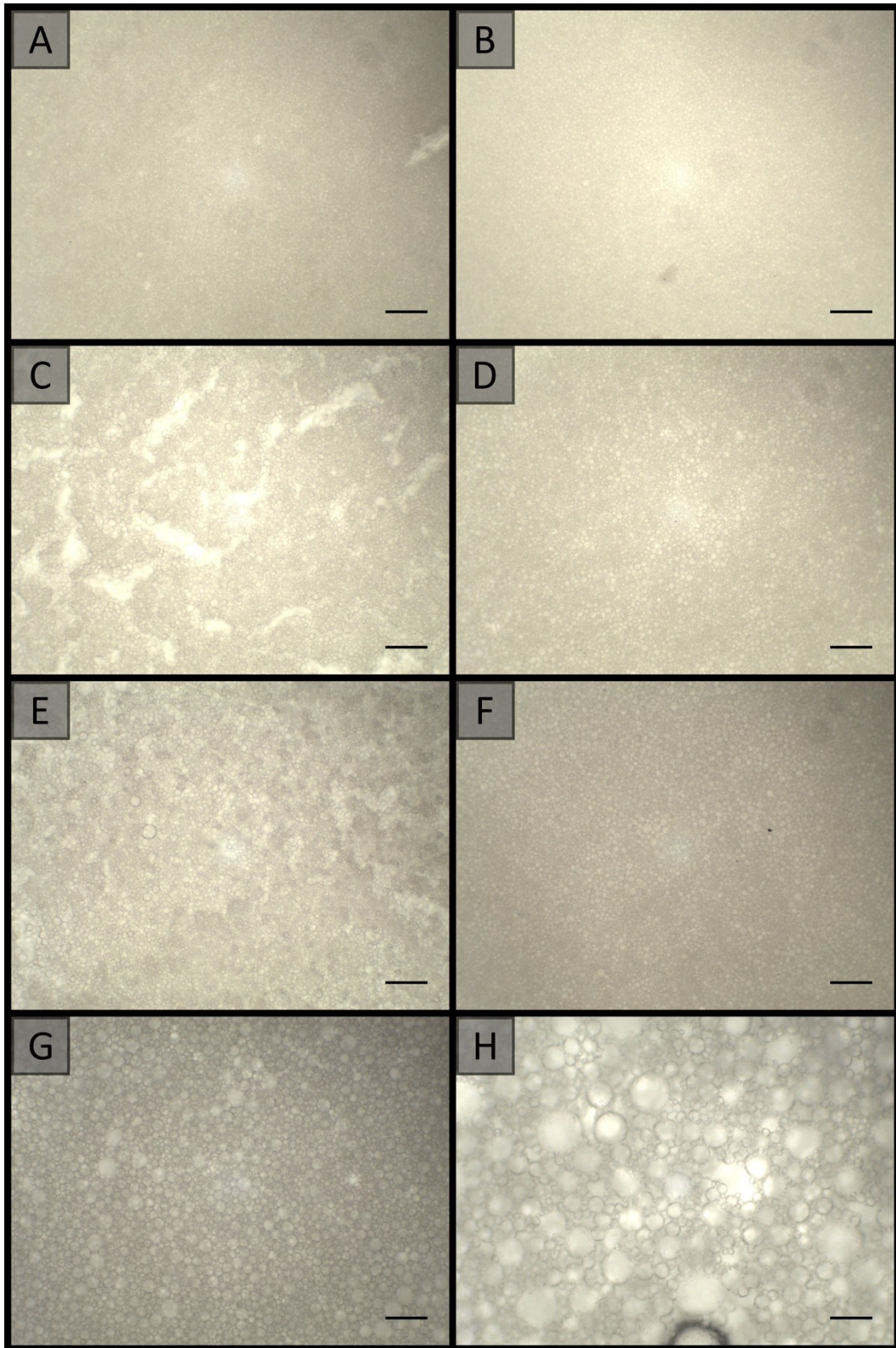


**Fig. S20** Optical microscopy of emulsions which had been emulsified at 300 rpm and passed through 20 cm of 250  $\mu\text{m}$  i.d. capillary at different rates. **A)** 10  $\mu\text{L}/\text{min}$ ; **B)** 25  $\mu\text{L}/\text{min}$ ; **C)** 50  $\mu\text{L}/\text{min}$ ; **D)** 100  $\mu\text{L}/\text{min}$ . Scale bar is 50  $\mu\text{m}$ .

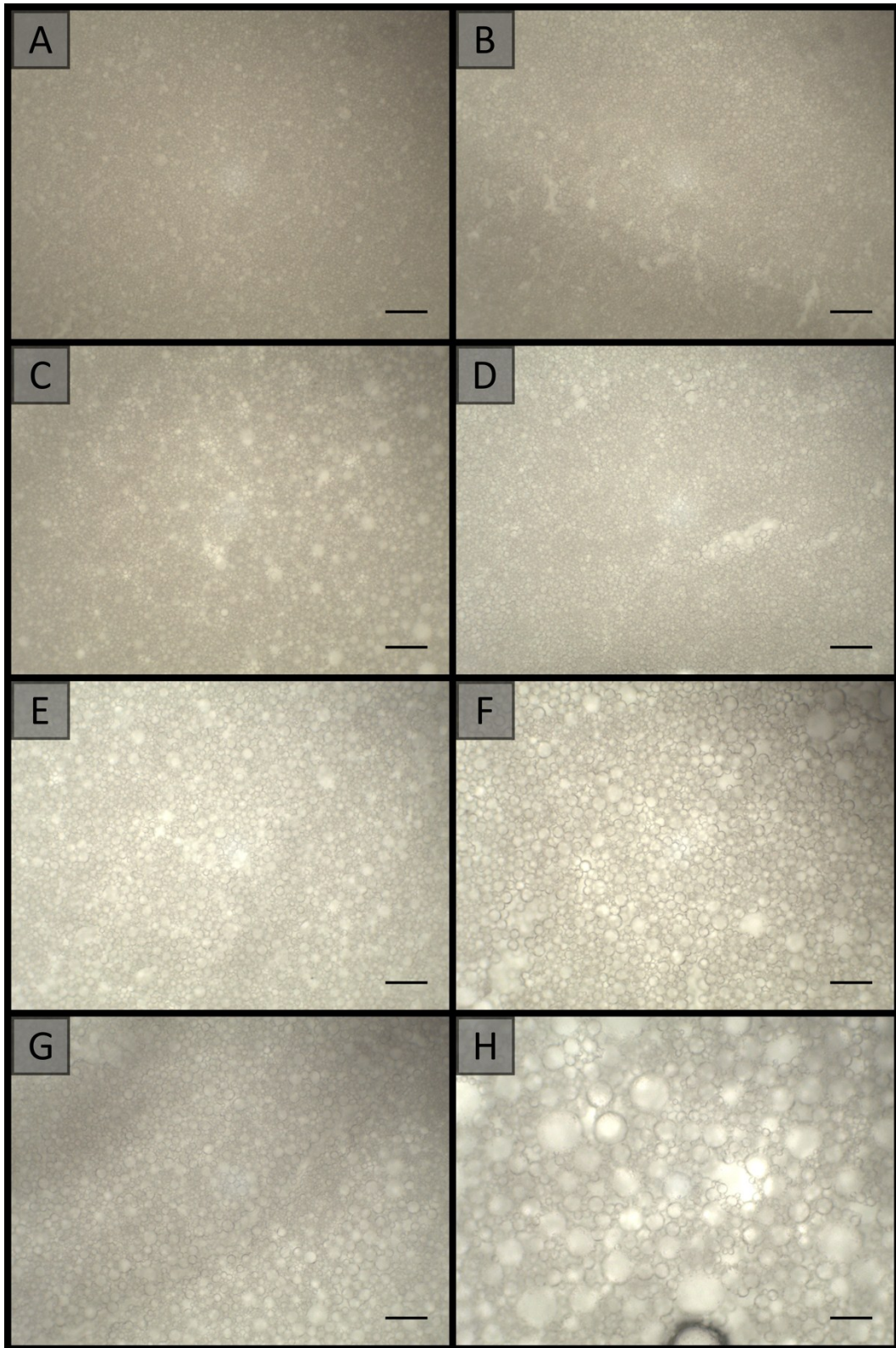




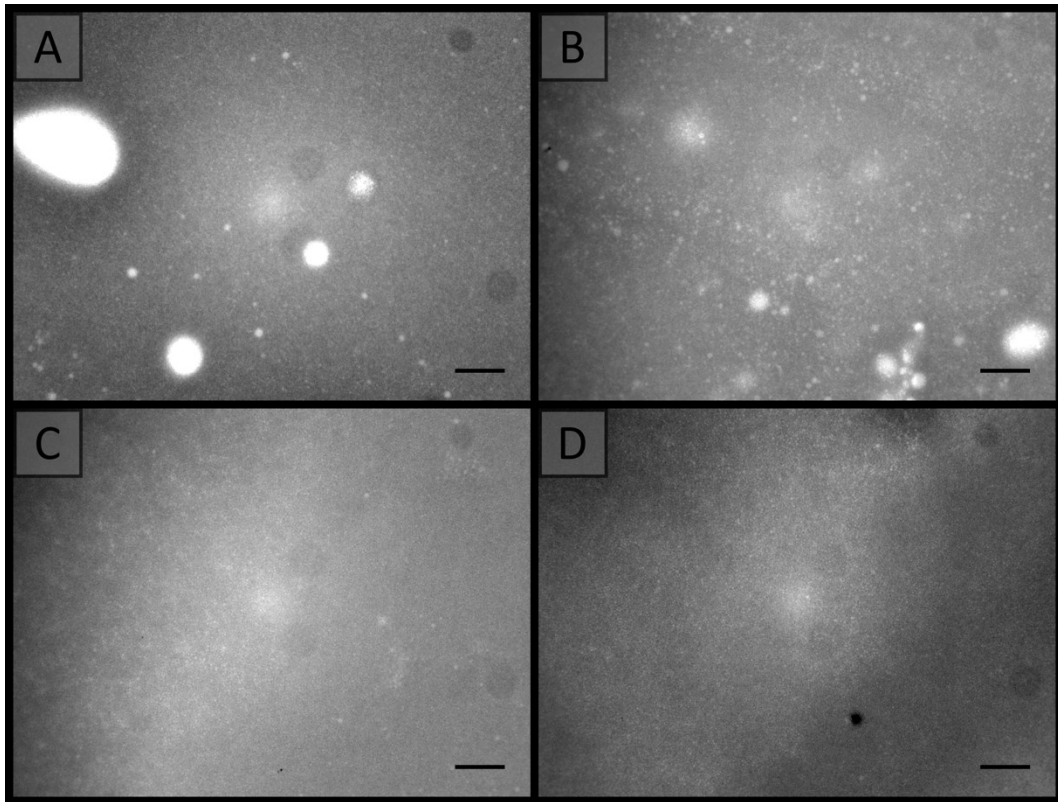
**Fig. S21** Optical microscopy of emulsions which had been emulsified at 300 rpm and passed through 20 cm of 150  $\mu\text{m}$  i.d. capillary at different rates. **A)** 10  $\mu\text{L}/\text{min}$ ; **B)** 25  $\mu\text{L}/\text{min}$ ; **C)** 50  $\mu\text{L}/\text{min}$ ; **D)** 100  $\mu\text{L}/\text{min}$ . Scale bar is 50  $\mu\text{m}$ .



**Fig. S22** Optical microscopy images of emulsions which had been emulsified at 300 rpm and passed through different lengths of 250  $\mu\text{m}$  i.d. capillary. **A)** 5 cm; **B)** 10 cm; **C)** 20 cm; **D)** 30 cm; **E)** 40 cm; **F)** 50 cm; **G)** 60 cm; **H)** Bulk. Scale bar is 50  $\mu\text{m}$ .



**Fig. S23** Optical microscopy images of emulsions which had been emulsified at 300 rpm and passed through different lengths of 150  $\mu\text{m}$  i.d. capillary. **A)** 5 cm; **B)** 10 cm; **C)** 20 cm; **D)** 30 cm; **E)** 40 cm; **F)** 50 cm; **G)** 60 cm; **H)** Bulk. Scale bar is 50  $\mu\text{m}$ .



**Fig. S24** Optical microscopy images of emulsions which had been emulsified at 14 000 rpm and passed through 20 cm of various i.d. capillary columns: **A)** Bulk; **B)** 540  $\mu\text{m}$  i.d.; **C)** 250  $\mu\text{m}$  i.d.; **D)** 150  $\mu\text{m}$  i.d. Scale bar is 50  $\mu\text{m}$ .