Bulk scale synthesis of monodisperse PDMS droplets above 3 μm and their encapsulation by elastic shells

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Supporting Information

'Magic cap' As mentioned in the experimental section, the samples prepared for the seeded growth study with $DMDES$, were exposed to styrene-butadiene capliners (SBC) that were produced by the company Wheaton[1] (product number 225290). When using the procedure for the preparation of these PDMS seed droplets, we discovered that samples only became monodisperse in the presence of these capliners. Samples that were closed with other caps, without styrene-butadiene liners, often led to polydisperse emulsions. As a result, it was expected that contaminants were released by the capliners that beneficially affected the size distribution of the emulsion. This was confirmed as monodisperse systems could still be obtained in the latter systems when the styrene-butadiene capliner had been added before

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addition of the monomer and had been closed off with another cap that did not affect the size distribution. This could also be achieved when only using the aqueous ammonia solution that had previously been in contact with the SBC for a period of 3 days. This indicated that capliner contaminants were soluble in an aqueous (ammonia) solution. Due to the solubility of the capliner pollutant in water, we could extract the capliner material by evaporating off the aqueous phase that had been in contact with the SBC for at least 24 hours. A fraction of this extracted material was then used for sample preparation. This sample had a foamy appearance, indicating surface activity, and resulted in monodisperse PDMS droplets that were found to have a droplet diameter of 5.6 μm and polydispersity of only 1.2 % as determined with SLS after 4 days of growth. The monodispersity confirmed that the capliner contaminants were indeed present in the extracted residue. These samples (11 mL) were prepared by mixing an aqueous ammonia solution (final concentration 22.7% v/v) and the $DMDES$ monomer (final concentration 9.1% v/v) on the rollerbank and keeping the samples tumbling during growth. Similar synthesis conditions, in absence of the capliner residue, resulted in extremely polydisperse samples with droplet sizes varying between 2 and 15 μm within one sample.

To identify the molecular composition of the beneficial contaminant, another fraction of the capliner residue was used for Nuclear Magnetic Resonance (NMR) and Mass-spectrometry (MS) analysis. The resulting spectra are shown in Figure S1. Both analysis methods indicated that at least the majority of the contaminants consisted of one (or more than one) type of molecule from the non-ionic Tergitol NP-X surfactant series,[2,3] with X denoting the number of ethylene glycol units of the PEG chain. Based on the main peak of 551 Da/atomic-charge in Figure S1B, experiments were conducted in which the non-ionic surfactant Tergitol NP-7 or NP-9 were added to the reaction mixtures at an overall concentration of 0.01 to 10.0 mM. Unfortunately, and surprisingly, these systems were still found to become polydisperse. As a result, the exact molecular composition of the capliner pollutant has not yet been positively identified. We can only speculate that it might be a contaminant that for instance

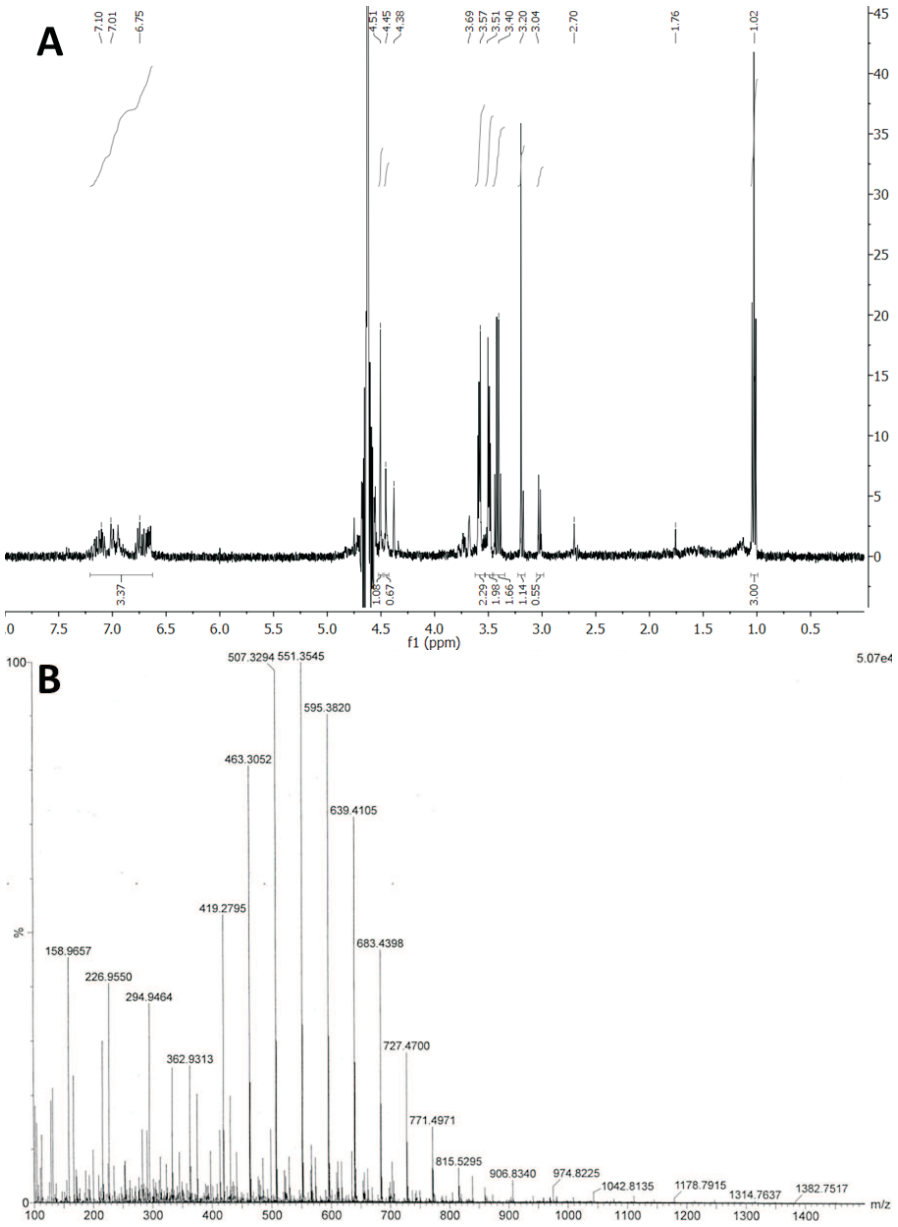

Figure S1: The ^{1}H-NMR-spectrum (A) and the Mass-spectrum (B) that were detected of the capliner residue. The ^{1}H NMR spectrum of the capliner residue was recorded on a Varian spectrometer operating at 400 MHz in D_2O and referenced against the signal of the residual protio impurity of the solvent (4.79 ppm). Electrospray ionization mass spectra were acquired using a Micromass LCT electrospray time-of-flight mass spectrometer. The capliner residue was dissolved in water and directly injected in the mass spectrometer, which used a mixture of acetonitrile/formic acid as the eluent.

would render droplets with a slightly higher surface charge. Extremely low amounts of material could (if they had this effect) already significantly impose an inter-droplet potential

that would be less inclined to aggregation. In the end this section can therefore only be seen as a warning: we are aware that small amounts of unknown chemicals might have favorably affected the monodispersity during the DMDES seeded growth study.

Table S1: The details of the monomer ($DMDES$) concentration and the final size and polydispersity of $PDMS$ droplets obtained from different methods of emulsion synthesis are shown in the table. All sizes and polydispersities were determined with SLS except for cyclohexane, pentane and iso-octane swollen $PDMS$ droplets for which optical microscopy analysis was used.

Method of droplet synthesis	$DMDES$ conc. %	Measured droplet size (μm)	Polydispersity %
Efficient initial mechanical mixing and no agitation during growth	6.8 (sample volume = 750 mL)	5.36	2.5
		3.94	2.5
		4.26	2.2
		4.10	1.9
	2.9 (sample volume = 720 mL)	2.40	1.6
	6.7 (sample volume = 30 mL)	2.80	1.9
		1.70	1.8
Pre-hydrolysis of $DMDES$	6.5	5.60 (30 min pre-hydrolysis)	2.0
		5.00 (30 min pre-hydrolysis)	1.9
		1.70 (24 h pre-hydrolysis)	2.9
		2.00 (24 h pre-hydrolysis)	2.9
Seeded growth - $DMDES$	9.0	3.48 (original/seed)	1.7
		8.00 (final size)	1.0
Seeded growth - hydrocarbon	4.1 (sample A)	2.9 (original/seed)	2.0
		5.4 (cyclohexane, 22h)	$\sim$ 5.5
		5.4 (pentane, 22h)	$\sim$ 5.5
	6.0 (sample B)	4.2 (original/seed)	2.1
		8.2 (cyclohexane, 22h)	$\sim$3.8
		4.9 (iso-octane, 22h)	$\sim$4.7
		- (hexadecane, 22h)	High
		- (OMCTS, 22h)	High
	6.7 (sample C)	3.2 (original/seed)	2.0
		5.5 (dyed cyclohexane, 6h)	$\sim$ 4.5

On a final note, we would like to note that not all SBC were as effective in generating monodisperse PDMS dispersions. Besides, we would like to stress that only the experiments conducted on seeded growth with the monomer $DMDES$ were exposed to these rubber liners. All other samples described in this paper, including all seeded growth studies with

second oils, were not exposed to these capliners and were therefore not subject to unknown chemicals as far as we are aware.

References

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(3) Shen, Z. X.; Thomas, J. J.; Siuzdak, G.; Blackledge, R. D. *Journal of Forensic Sciences* **2004**, *49*, 1028–1035.