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Supporting Information

Miniemulsion Photopolymerization in a Continuous Tubular Reactor: Particle Size Control via Membrane Emulsification

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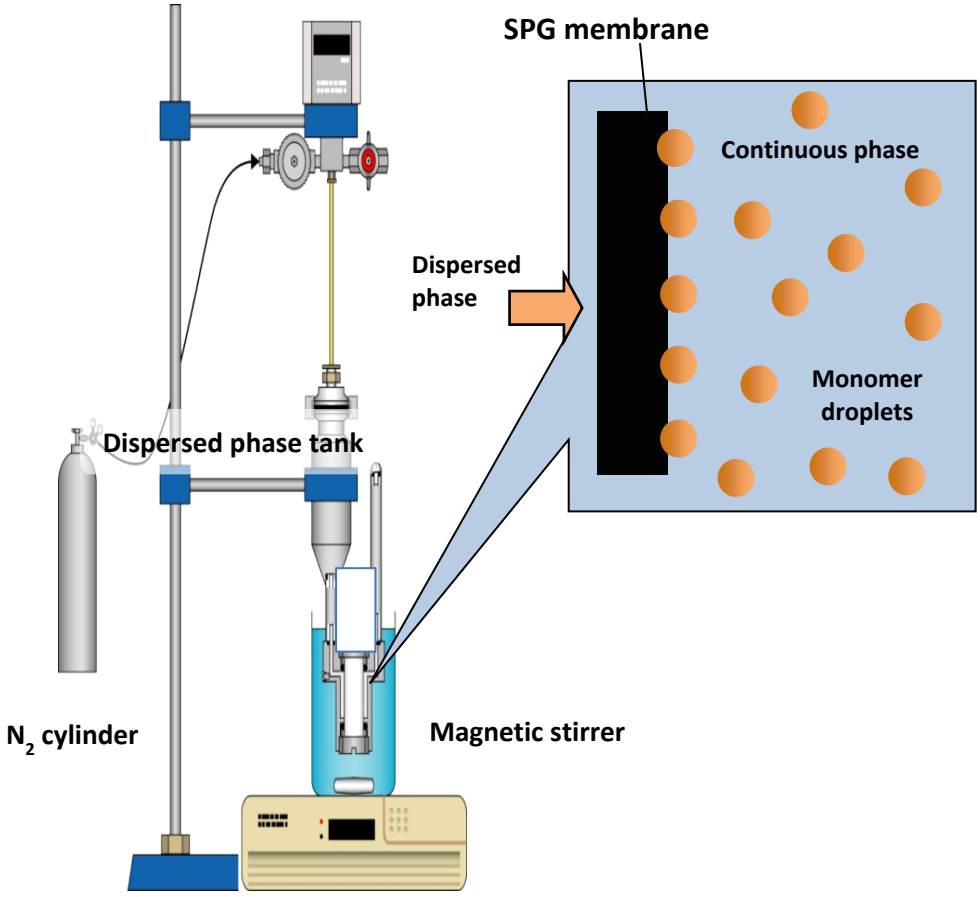

Scheme. S1. Schematic illustration of SPG membrane emulsification. Reprinted (adapted) with permission from ref.[45] Copyright 2017 Royal Society of Chemistry.

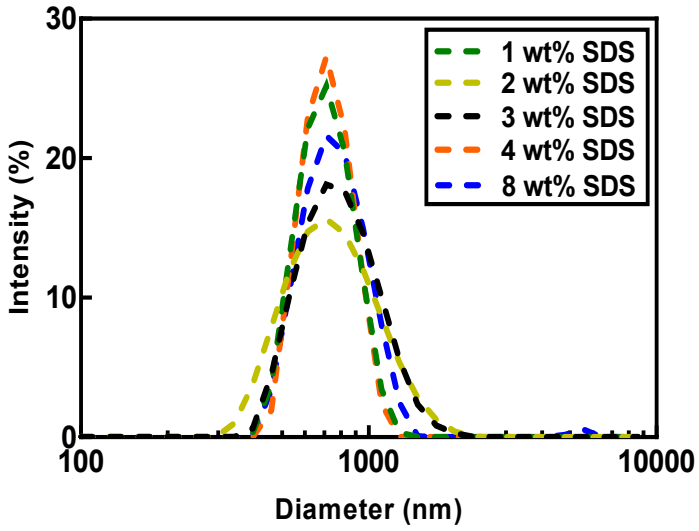

Fig. S1. Droplet size distribution for pore size 300 nm with varying SDS concentration 1 to 8 wt% and 0.01 M TPO (Table 1; Run F1-F5).

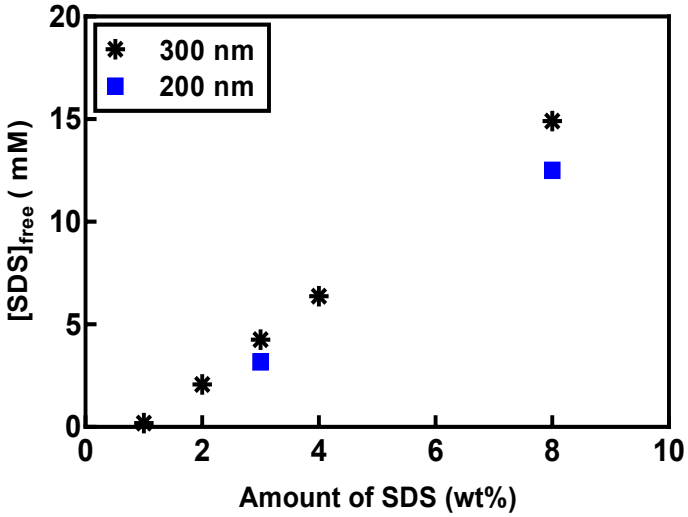

Fig. S2. Concentration of free SDS in the aqueous phase after completion of the emulsification as function of initial SDS amount for pore size 300 nm (Table 2, Run F1-F5) and 200 nm (Table 2, Run F6-F7).

Calculation of Free Surfactant Concentration

The surfactant concentrations studied were ranging from 1 to 8 wt%. The total interfacial area was calculated for each surfactant concentration using initial droplet diameters measured via DLS using the following formulae:

$$A\,(interfacial\,area) = N_d \cdot \pi \cdot D^2$$

Where, $N_d =$ number of monomer droplets and $D =$ avg. droplet diameter.

$$N_d = \frac{m_M}{m_d} \quad \text{and} \quad m_d = \rho_M \frac{4}{3}\pi r^3$$

Where, $m_M =$ mass of monomer, $m_d =$ mass of droplet, $\rho_M =$ density of monomer and $r = D/2$

From the obtained interfacial area (A), the number of SDS molecules at the interface "N_{SDS}" was calculated using:

$$N_{SDS} = A \cdot \Gamma_{cmc}$$

Where, Γ_{cmc} is the surface conc. of SDS at interface and is equal to $4.17 \times 10^{-10}\, mol \cdot cm^{-2}$.[47]

To obtain the amount of free surfactant, the value obtained from step 2 was subtracted from the actual surfactant amount used.

Comments: The above calculations are based on a surface concentration of SDS at a styrene water interface as reported by Chang et al.[47] Table 2 presents the results of these calculations. Average droplet diameter used in above calculation were measured via DLS, also reported in Table 2 in main text.

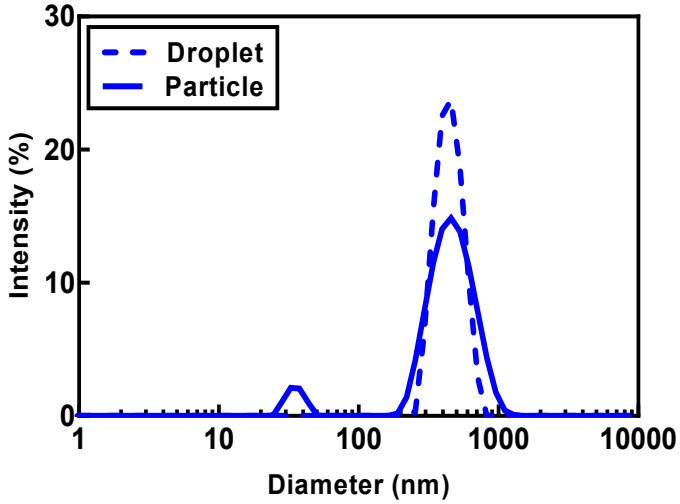

Fig. S3. Size distribution for pore size 200 nm with 8 wt% SDS and 0.01 M TPO (Table 1; Run B17; $D_{z,\ particle}$ = 346 nm and PDI = 0.85) photopolymerized in batch. Dotted line: Droplets (before polymn.); Full lines: Particles (after polymn.).

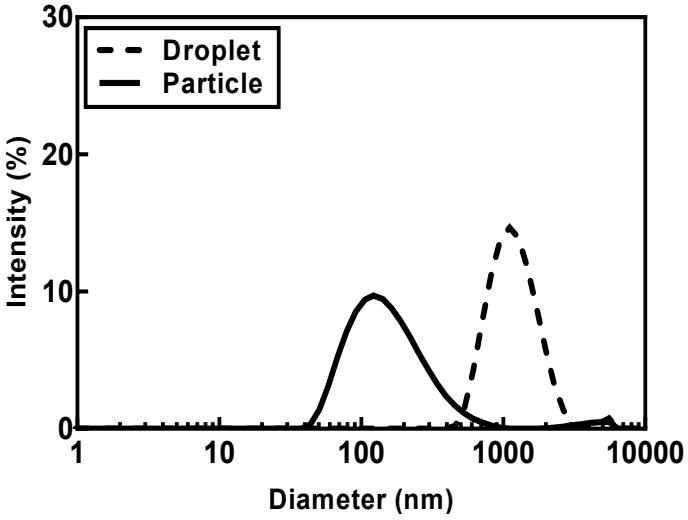

Fig. S4. Size distribution for pore size 400 nm with 3 wt% SDS and 20 wt% NaCl (Table 1; Run F13; $D_{z,\ particle}$ = 160 nm and PDI = 0.49). Dotted line: Droplets (before polymn.); Full lines: Particles (after polymn.)

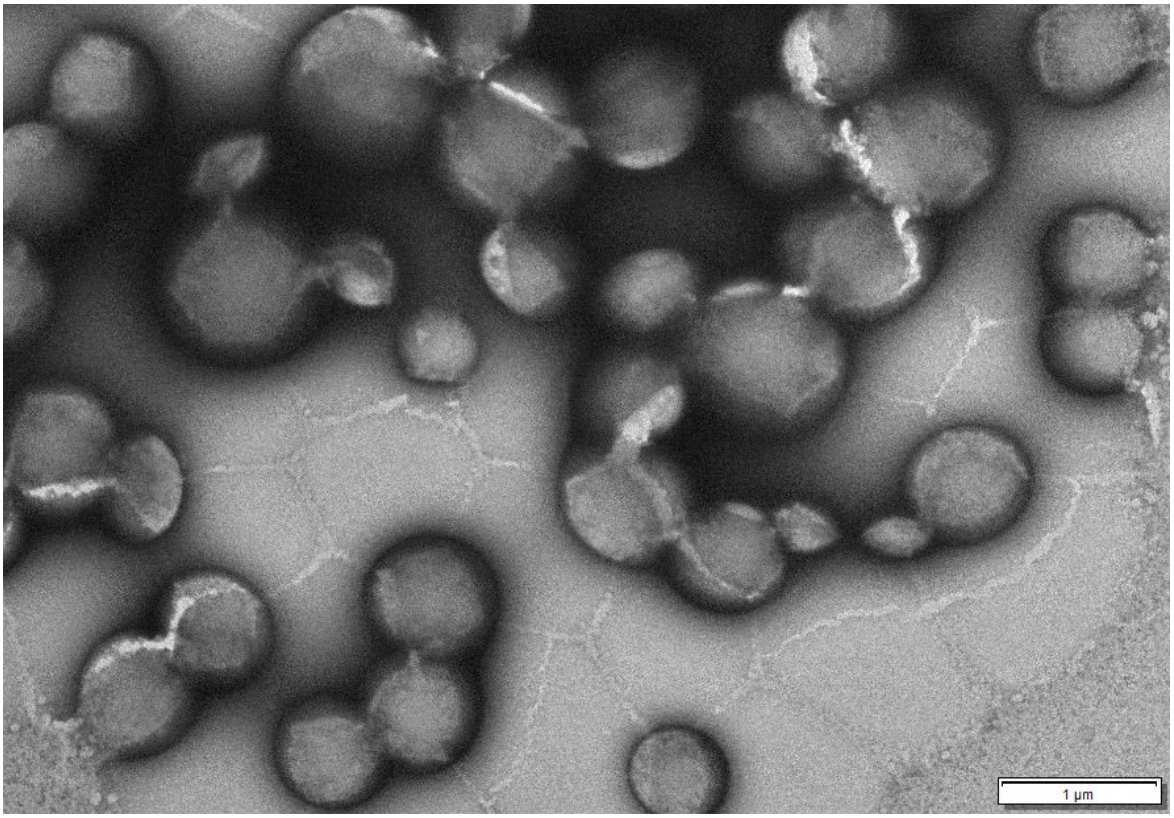

Fig. S5. TEM image of polymer particles for pore size 400 nm with 3 wt% SDS and 10 mol % HQ as aqueous phase radical scavenger (Table 1; Run F14).

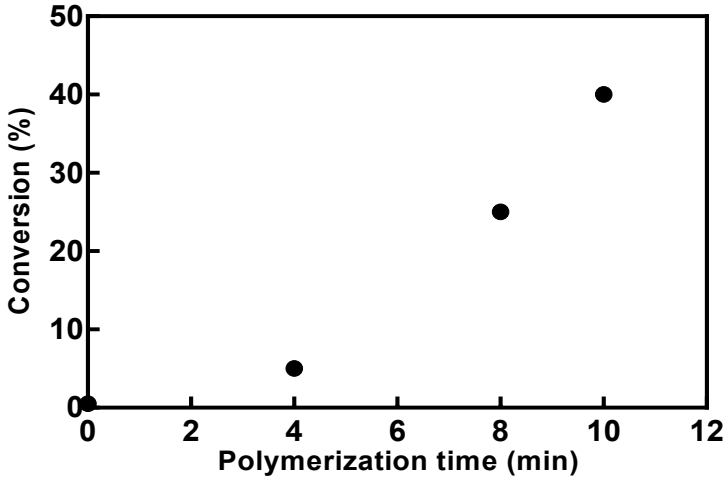

Fig. S6. Conversion as function of polymerization time for pore size 400 nm using 10 mol% HQ and 3 wt% SDS (Table 1; Run F14).

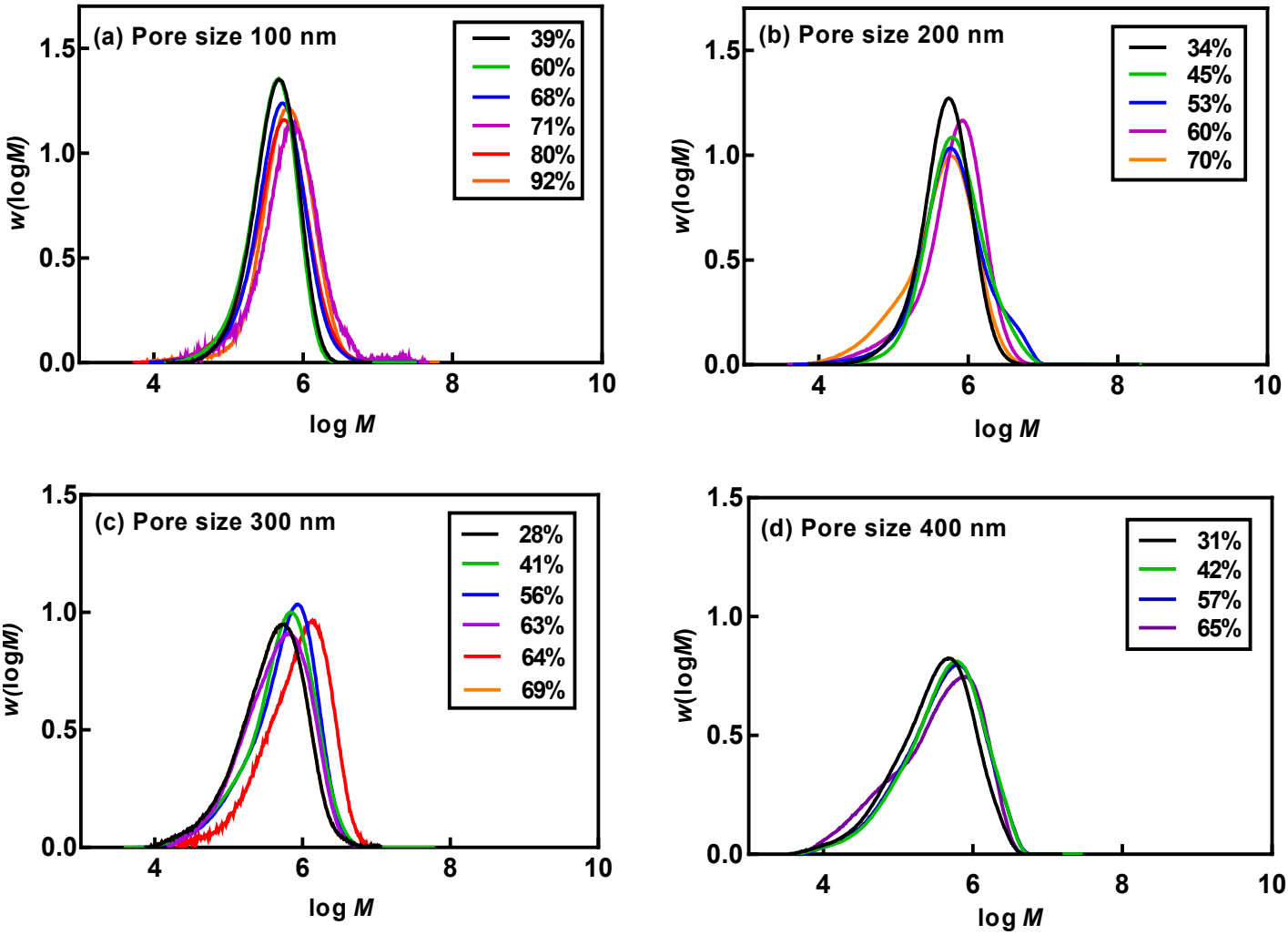

Fig. S7. Molecular weight distributions for photoinduced polymerization for pore size (a) 100 (Run F16) (b) 200 (Run F9) (c) 300 (Run F15) and (d) 400 (Run F12) nm.

Table S1. Summary of Photopolymerization of SPG membrane emulsified emulsions in continuous flow reactor.[a]

Run	Pore size (nm)	D_z[b] (nm)	PdI [b]	D_z[b] (nm)	PDI[b]	α[c](%)	M_n[d] (× 10^5) g/mol
		Droplets		Particles			
				223	0.034	39	3.0
				211	0.079	60	2.7
				218	0.035	68	3.0
F16	100	227	0.041				

				223	0.041	71	3.60
				220	0.123	80	3.8
				212	0.014	92	3.5
F9	200	415	0.04	399	0.084	34	3.2
				382	0.094	45	4.0
				370	0.103	53	3.0
				394	0.08	60	3.21
				422	0.168	70	1.99
F15	300	758	0.116	688	0.140	28	2.45
				688	0.111	41	3.71
				674	0.372	56	1.99
				714	0.291	63	2.79
				788	0.088	64	2.77
				772	0.37	69	1.99
F12	400	935	0.119	909	0.243	31	1.78
				814	0.244	42	1.37
				835	0.18	57	2.31
				873	0.284	65	1.93

[a] Monomer droplets were prepared with 100-400 nm pore size with 0.01 mol/L of TPO and 6 wt% solid contents, polymerized at room temperature under visible radiation (violet, λ_{max} = 405 nm)

[b] Z-average diameter and polydispersity index analysed from DLS;

[c] Monomer conversion were determined via gravimetric calculation.

[d] Number average molecular weight measured by GPC.