Supporting Information

Polymerization of Electric Field-Centered Double Emulsion Droplets to Create Polyacrylate Shells

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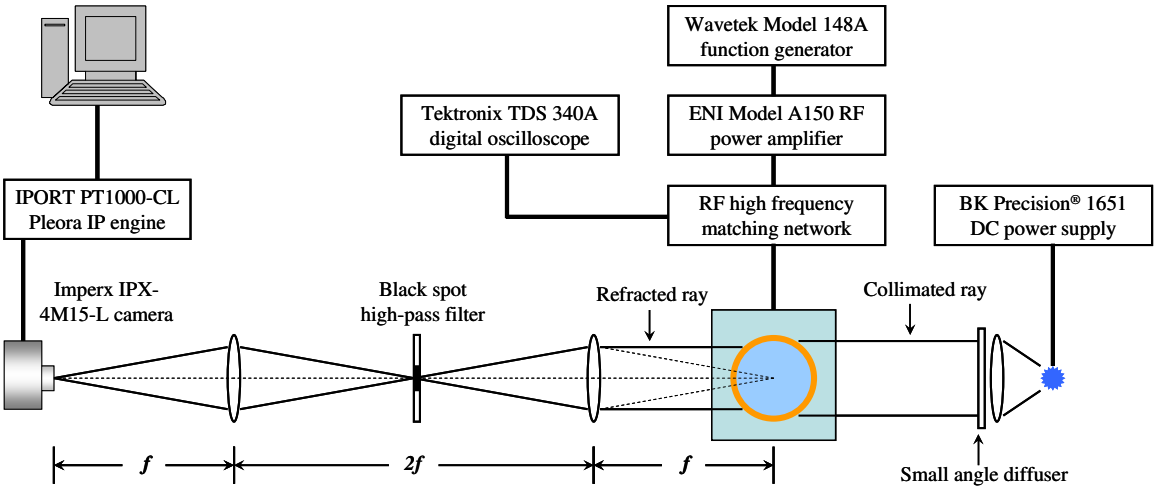
1. Schematic of the droplet centering setup.



Scheme S1. Setup used for droplet centering experiments.

2. Estimate of the maximum temperature change in the outer droplet (prepolymer solution) that could occur during the exothermic polymerization reaction.

The calculation below estimates the maximum change in the temperature of a 16.5 µL droplet consisting of 25 v/v% tripropylene glycol diacrylate (TPGDA) and 75 v/v% *N,N*-dimethylacetamide (DMA). We assume that all the monomer polymerizes, both double bonds react, and no heat is transferred to the surrounding medium (*i.e.,* adiabatic condition). The volumes of the TPGDA and DMA are assumed to be additive. The small amount of photoinitiator present in the droplet was neglected in the ΔT calculation.

The relevant physical properties of the components are as follows.

TPGDA density: 1.355 g/mL (BASF tech. info. sheet for Laromer® TPGDA)
TPGDA heat capacity C_P: 1.774 J·g^{-1}•K^{-1} (*op. cit.*)
TPGDA molecular weight: 1.0355 mg/mmol
DMA density: 0.937 g/mL (Sigma-Aldrich website)
DMA heat capacity: 2.016 J·g^{-1}•K^{-1} (CRC Handbook of Chemistry and Physics)

An exact value for the enthalpy of polymerization ($\Delta H°_{polymeriz.}$) of tripropylene glycol diacrylate (TPGDA) could not be found in the literature. As proxy, we used the $\Delta H°_{polymeriz.}$ of methyl acrylate, which is -78 J/mmol,[1] and included a factor of two to account for the two double bonds in the diacrylate.

$$\Delta H_{reaction} = 2\Delta H^{o}_{polymeriz.} \cdot mmol\text{TPGDA} = 2(\text{-}78 \text{ J/mmol}) \cdot 0.0142 \text{ mmol} = \text{-}2.22 \text{ J}$$

$$\Delta T = \frac{-\Delta H}{m_{\text{TPGDA}} C_{P_{\text{TPGDA}}} + m_{\text{DMA}} C_{P_{\text{DMA}}}} = 72°$$

3. Microscope images of poly(propyleneglycol diacrylate) shells.

Several poly(propylene-glycol diacrylate) shells were polymerized from centered DE droplets using low intensity UV light and were recovered intact. Shown below are wide-field microscope images of one of them.

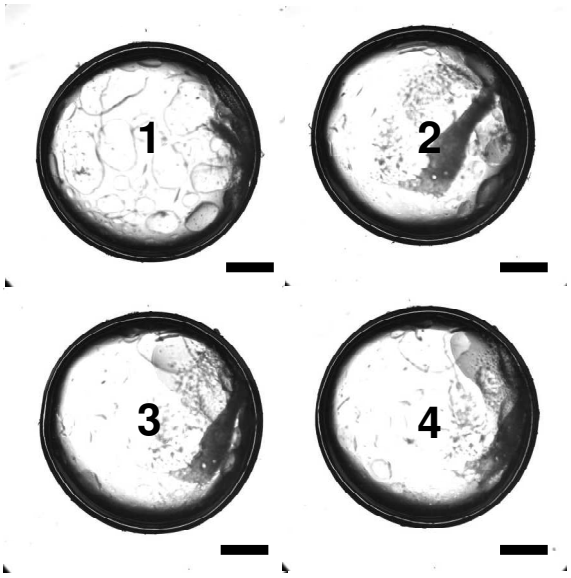


Figure S1. Four wide-field microscope images of a rotated ~4.6 mm poly(propylene-glycol diacrylate) shell. The average measured sphericity of the inner and outer surfaces are 99.3 ± 0.7% and 98.6 ± 0.2%, respectively. The average shell nonconcentricity *NC* is 7.9 ± 2.0%. Scale bars are 1 mm.

4. DMA/TPGDA/Silicone Oil Solubility Study

The maximum solubility of DMA, TPGDA, and 25 v/v% TPGD (in DMA solvent) in 50, 100, 350 and 1000 cS silicone oil are shown below in Table S1. The maximum percentage of DMA, TPGD, or 25 v/v% TPGD that partitions into the silicone was determined in the following manner. A 2.5 mL screw capped vial was filled with 1 mL of DMA, TPGDA, or 25 v/v% TPGD and 1 mL of one silicone oil. The liquids were vigorously shaken by hand for 20 s and then left to phase separate for 3 days. After 3 days, 650 μL $CDCl_3$ was mixed with ~25 μL liquid aliquots taken from the phase separated top and bottom layers. The samples were then subject to ^{1}H nuclear magnetic resonance spectroscopy (^{1}HNMR) on a Bruker ARX400 spectrometer. All the signals for each liquid in the spectrum were integrated to determine the partition percentages of each liquid in a layer.

The results from Table S1 show that ~5 % DMA and ~4.5% TPGDA partition into the silicones when the pure liquids are used. When 25 v/v% TPGDA solution is emulsified with the silicone oils, between 4-5% DMA and 0.5-1.7% TPGDA transfer into the silicone oils. In the 1.7 % case, the sampled oil layer was cloudy due to incomplete phase separation of the TPGDA and DMA. This likely contributed to the anomalously high TPGDA percentage in

the oil. To verify this, a control experiment was performed by carefully layering 15 mL of 25 v/v% TPGD on top of 20 mL 350 cS silicone oil in a 100x100 mm glass petri dish. Oil samples were collected at 15 and 30 mins and analyzed by ^{1}HNMR. Both sampling times are longer than the time our DE droplets spend in the presence of the ambient oil and inner 350 cS silicone oil droplet. The average percentage TPGDA transferred to the oil layer from this experiment was found to be 0.6 % (Table S1). This value is roughly equivalent to the amounts of TPGDA transferred to the other silicone oils after emulsification, and verifies that the cloudiness in the 350 cS oil layer three days after emulsification was due to remaining dispersed TPGDA

Table S1. Approximate partition percentages for DMA, TPGDA and 25 v/v% TPGDA into different viscosity silicone oils.[a,b]

Entry	Silicone oil viscosity	DMA	TPGDA	25 v/v% TPGDA in DMA
1	50 cS	0.4/5.1	2.9/4.5	0.4/4.2/0.5
2	100 cS	1.6/5.0	0.5/4.4	1.0/4.7/0.7
3	350 cS	2.6/5.5	0.9/4.6	0.5/5.1/1.7 (0.6)[c]
4	1000 cS	0/4.3	0.5/4.3	0.3/4.2/0.6

[a] Silicone oil (1 mL) and DMA, TPGDA, or 25 v/v% TPGDA (1 mL) were shaken for 20 s and the mixture allowed to phase separate for 3 days. ^{1}HNMR was run on 25 µL aliquots from each separated layer and the partition percentages of each liquid component were determined by integrating the signals for each liquid in the spectrum and then setting the sum of all integrals to 100%.

[b] Blue numbers represent the percent silicone oil in DMA, TPGDA, or 25 v/v% TPGDA; red and green numbers represent the percent DMA and TPGDA, respectively, in the silicone oil phase.

[c] Partition percentage of TPGDA in the silicone oil when 25 v/v% TPGDA (15 mL) was layered on 350 cS silicone oil (20 mL) for 30 min in a 100x10 mm glass petri dish.

5. Comments on the irradiation and curing conditions

The irradiation and curing parameters selected for these proof-of-principle experiments were determined empirically by exposing droplets of prepolymer solution in ambient silicone oils to both high and low intensity UV light for various times. After allowing the droplets to cure in the dark for ~ 3 min after irradiation, they were physically removed to check whether the shells had polymerized enough to harden. In our centering/polymerization experiments we followed the same procedure; after UV irradiation and the ~3 min curing in the dark we attempted to physically remove the shell to see whether it was hardened. When shells where not fully cured the top of the shell would often burst while the bottom half remained intact. This is due in part to the anisotropic irradiation used to initiate polymerization.

6. Movie Descriptions

Movie 1 (Sped up 4×): Electric-field driven centering and subsequent anisotropic polymerization of a ~4.6-mm diameter DE droplet irradiated with low-intensity UV light. The DE droplet is suspended at a silicone oil gradient that was allowed to form over the course of one day. By tracking the faint white caustic ring of the inner droplet, the centering progress of the inner droplet, prior to shell polymerization, can be followed. In this

experiment, the centered DE droplet is irradiated twice with ~20-35 mW/cm^2 UV light (for 20 s, followed by a 52 s break, and then for 5 additional s) to ensure the shell fully cured.

Movie 2 (Sped up 4×): Electric-field driven centering and subsequent anisotropic polymerization of ~4.6-mm diameter DE droplet irradiated with high-intensity UV light. The DE droplet is suspended at a silicone oil gradient that was allowed to form over the course of one day. By tracking the faint white caustic ring of the inner droplet, the centering progress of the inner droplet, prior to shell polymerization, can be followed. In this experiment, the centered droplet is irradiated with ~90-100 mW/cm^2 UV light for 25 s, which results in shell elongation and rupture.

Movie 3 (Sped up 4×): Electric-field driven centering and subsequent anisotropic polymerization of ~4.6-mm diameter DE droplet by irradiating for 30 s with ~20-35 mW/cm^2 UV light. In this case, the DE droplet is suspended at the100/1000 cS silicone oil interface of a freshly layered silicone oil gradient. Again, the faint white caustic ring of the inner droplet can be used to track the centering progress of the inner droplet prior to shell polymerization. The dark strip in the background arises from the difference in the refractive index of the 100 and 1000 cS silicone oil layers of the gradient. The striations are a consequence of disturbing the oil interface while pipetting the DE droplet.

Additional References

[1] G. Odian, *Principles of Polymerization*, 4th ed., Wiley & Sons, Inc., NY, **2004**.