Supporting Information

Living crystallisation-driven self-assembly of polyester-based 1D and 2D particles of controlled size as oil-in-oil Pickering particles

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Experimental section

Materials and instruments

Chemicals were purchased from Sigma-Aldrich. The ε-caprolactone monomer was dried over CaH_2 for 24 h. The monomer was purified by distillation under reduced pressure before storing under an inert atmosphere of N_2.

Nuclear magnetic resonance spectroscopy

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300, DPX-400 or HD500 spectrometer.

Glove box

Air-free work was conducted in the nitrogen atmosphere of a Mbraun MB Unilab Pro SP or Mbraun MB-01 equipped with a solvent filter.

Size exclusion chromatography (SEC)

SEC measurements were performed in $CHCl_3$ on an Agilent 1260 Infinity II multi-detector GPC/SEC system fitted with RI, ultraviolet (UV, λ = 309 nm), and viscometer detectors. The polymer was eluted through an Agilent guard column (PLGel 5 µM, 50 × 7.5 mm) and two Agilent mixed-C columns (PLGel 5 µM, 300 × 7.5 mm) using $CHCl_3$ (buffered with 0.5% NEt_3) as the mobile phase (flow rate = 1 mL min^{-1}, 40 °C). Number average molecular weights (M_n), weight average molecular weights (M_w) and dispersities ($Đ_M = M_w/M_n$) were determined using Agilent GPC/SEC software (vA.02.01) against a 15-point calibration curve (M_p = 162 - 3,187,000 g mol^{-1}) based on poly(styrene) standards (Easivial PS-M/H, Agilent). Molecular weights (M_n), weight average molecular weights (M_w) are given in g mol^{-1}.

$LogP_{oct}$/SA Analysis.

Octanol-water partition coefficients ($LogP_{oct}$) were calculated for oligomeric models in Materials Studio 2020, using an atom-based approach (ALogP98 method) for all molecular models containing C, H, N, and O atoms.[1] $LogP_{oct}$ calculations were normalized by solvent accessible surface area (SA) using Materials Studio 2020.[1] First, single oligomers were subjected to a Geometry Optimization procedure using the Forcite Molecular Dynamics (MD) module with a COMPASS II force field. The force field contains information on important parameters, like preferred bond lengths, bond angles, torsion angles, partial charges, and van der Waals radii that influence the conformation. To minimize energy and determine a preferred conformation, these simulations ran until the energy of the oligomer decreased below predetermined convergence criteria (1×10^{-4} kcal mol^{-1} energy convergence, 0.005 kcal mol^{-1}/Å force convergence, and 5×10^{-5} Å displacement convergence). Second, these SA values

represent the Connolly surface area created by an algorithm that rolls a ball over the surface of the oligomer. To ensure the SA values are meaningful in the context of octanol-water partition coefficients ($LogP_{oct}$), the probe had a 1.4 Å radius to match the size of a water molecule. Third, to monitor variations in surface area calculations as the n-mer size increased, oligomers were annealed for 200 cycles using a sinusoidal temperature ramp (300 – 700 K) to maximize variability in SA values. After averaging SA values for cycles 100, 150 and 200, the standard deviation ranged from 0.4 - 2.7% with an average of 1.2%. Oligomeric models contained appropriate ratios of PCL and P*n*DMA units to mimic experimental conditions.

Differential scanning calorimetry (DSC)

Determination of the DSC curves was carried out using a STARe system DSC3 with an auto-sampler (Mettler Toledo, Switzerland). Disc shapes measuring 5 mm in diameter and 0.4 - 0.6 mm in thickness weighing 5 - 10 mg of polymer. Sample discs were positioned in 40 µL aluminium pans. Thermograms obtained with a heating rate of 10 °C min^{-1} were recorded from -100 - 100 °C with a 10 °C min^{-1} heating and cooling rate over two cycles. The glass transition temperature (T_g) was determined by the minimum of the first derivative in the second heating cycle of DSC.

Transmission electron microscopy (TEM)

TEM imaging was performed on a JEOL JEM-1400 microscope operating at an acceleration voltage of 80 kV. Samples were diluted with *n*-octane after 1 week of ageing (0.1 mg mL^{-1}) prior to analysis. Samples were drop cast onto formvar-coated copper grids and dried overnight. TEM samples were positively stained by exposure to ruthenium (VIII) oxide vapour for 7 minutes at 20 °C prior to analysis. The ruthenium (VIII) oxide was prepared as follows: ruthenium (IV) oxide (0.30 g) was added to water (50 g) to form a black slurry. Sodium periodate (2.0 g) was added and stirred for 1 minute prior to use.[2]

Atomic force microscopy (AFM)

AFM imaging was performed on a JPK Nanowizard 4 system at room temperature in the supplied acoustic enclosure and vibration isolation using Nanosensor PPP-NCHAuD tips with a force constant of around 42 $N{\cdot}m^{-1}$. For data acquisition and handling Nanowizard Control and Data Processing Software V.6.1.117 in QI mode with a setpoint of *25 nN* was used. Samples were prepared on freshly cleaved mica by drop-casting a solution of 0.1 $mg{\cdot}mL^{-1}$ sample in octane, allowing to dry, then washing with heptane and allowing to dry overnight.

Light microscope

Emulsions were imaged using a Leica DMIL LED microscope equipped with a Leica MC170 HD colour camera. 7 µL of the sample was added on a glass slide and covered with a Menzel-Gläser 20 × 20 mm # 0 cover slip before imaging immediately. Magnification: 40 or 20 x.

Surface tension

The surface tension between the solvents were measured using a KRÜSS DSA25S drop-shape analyser. The shape of pendant DMF or acetonitrile drops, immersed in octane or assembly solution, was recorded and analysed by the Laplace equation of capillarity to determine the DMF- or acetonitrile-octane interfacial tension.

Experimental procedures

Synthesis of chain transfer agent (CTA)/ROP initiator: 2-cyano-5-hydroxypentan-2-yl ethyl carbonotrithioate (CHPET)

Synthesis of CHPET was conducted following a previously reported method.[3] ^{1}H NMR (400 MHz, $CDCl_3$, 299 K, ppm) δ = 3.75 (t, J = 6.1 Hz, 2H), 3.36 (q, J = 7.4 Hz, 2H), 2.36 – 2.06 (m, 2H), 1.92 (s, 3H), 1.92 - 1.83 (m, 2H), 1.38 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm) δ = 217.4, 119.6, 61.8, 47.0, 35.8, 31.3, 27.9, 24.9, 12.8.

Synthesis of poly(ε-caprolactone)$_{50}$ (PCL_{50})

In a nitrogen-filled glove box, diphenyl phosphate (0.035 g, 0.140 mmol) in dry toluene (3.5 mL) and CHPET (0.035 g, 0.140 mmol) in dry toluene (6.323 mL) were added to ε-caprolactone (1.037 mL, 9.823 mmol). The solution was stirred at room temperature for 6 h, and then precipitated into excess diethyl ether at 0 °C for three times and collected *via* Buckner filtration before drying under reduced vacuum over P_2O_5 for 2 days (0.807 g). ^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm) δ = 4.05 (t, J = 6.7 Hz, 106H), 3.64 (t, J = 6.5 Hz, 2H), 3.33 (q, 2H), 2.30 (t, J = 7.5 Hz, 106H), 2.13 – 1.91 (m, 2H), 1.88 (s, 3H), 1.73 – 1.56 (m, 218H), 1.46 – 1.30 (m, 110H). SEC (0.5% NEt_3 in $CHCl_3$, λ = 309 nm, PS standard) M_n = 10.5 kg mol^{-1}, $Đ_M$ = 1.07.

Synthesis of poly(ε-caprolactone)$_{50}$-block-poly(n-decyl methacrylate)$_{155}$ (PCL_{50}-b-$PnDMA_{155}$)

PCL_{50} macro-CTA (0.05 g, 0.009 mmol), *n*-decyl methacrylate (filtered through basic alumina, 0.496 g, 2.190 mmol), AIBN (14.40 µL of a 10.00 mg mL^{-1} solution) and toluene (filtered through basic alumina, 1.889 mL) were mixed in a pre-dried ampoule. The homogenous solution was degassed *via* three freeze-pump-thaw cycles and the ampoule back filled with nitrogen. The ampoule was clamped in a pre-heated oil bath at 70 °C for 18 h. The ampoule was removed from the oil bath and held in an ice bath for 10 minutes, whilst exposed to air, before the solution was precipitated into methanol (0 °C) three times. The product was collected and dried *in vacuo*. ^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm) δ = 4.06 (t, J = 6.7 Hz, 50H), 3.91 (s, 155H), 2.30 (t, J = 7.5 Hz, 50H), 1.84 (d, J = 29.8 Hz, 137H), 1.71 – 1.52 (m, 292H), 1.28 (s, 1289H), 1.02 (s, 87H), 0.89 (t, J = 6.3 Hz, 406H). SEC (0.5% NEt_3 in $CHCl_3$, λ = 309 nm, PS standard) M_n = 38.9 kg mol^{-1}, $Đ_M$ = 1.16.

Crystallisation-driven self-assembly (CDSA) of PCL-based block copolymers

Block copolymers and assembly solvent were added to a 7 mL vial at a concentration of 5 mg mL^{-1}. The resultant solution was heated at 80 °C for a period of 8 h. After allowing the solution to cool overnight, the samples were aged for 2 weeks at ambient temperature prior to being analysed.

Living-CDSA of PCL-based block copolymers

Polydisperse cylindrical micelles of PCL_{50}-*b*-P*n*DMA_{155} in *n*-octane (0.5 mg mL^{-1}) were sonicated (7 × 30 minute cycles) using a sonicating bath cooled to 0 °C. After seed formation, a volume of PCL_{50}-*b*-P*n*DMA_{155} and PCL_{50} polymer solution in $CHCl_3$ (20 mg mL^{-1} total, 10 mg mL^{-1} wrt PCL_{50}-*b*-P*n*DMA_{15}) was added to a diluted sample of the seed solution (0.01 mg mL^{-1} in *n*-octane) and aged for 2 days. The unimers-to-seed ratio was controlled by the volume of polymer solution that was added to the seed

solution. AFM images of the platelets were analysed by ImageJ software, where at least 100 particles were counted for each sample to obtain the platelet area.

Emulsion formation

Platelet solution concentration was altered to achieve desired % w/w by removing solvent was a specified volume of assembly solution by air flow, then redispersing in a volume of octane to provide the targeted concentration. The solution was left to redisperse for an hour, then vortexed for 5 seconds to ensure full redispersion. DMF was added directly to the particle solutions and vortexed for 30 seconds before imaging. Emulsion images were analysed by ImageJ software, where at least 100 droplet diameters were counted for each sample to obtain the average droplet diameter.

Short cylinder formation

Polydisperse cylindrical micelles of PCL_{50}-*b*-P*n*DMA_{155} in *n*-octane (0.5 mg mL^{-1}) were sonicated (3 × 30 minute cycles) using a sonicating bath cooled to 0 °C.

Supplementary Figures and Tables

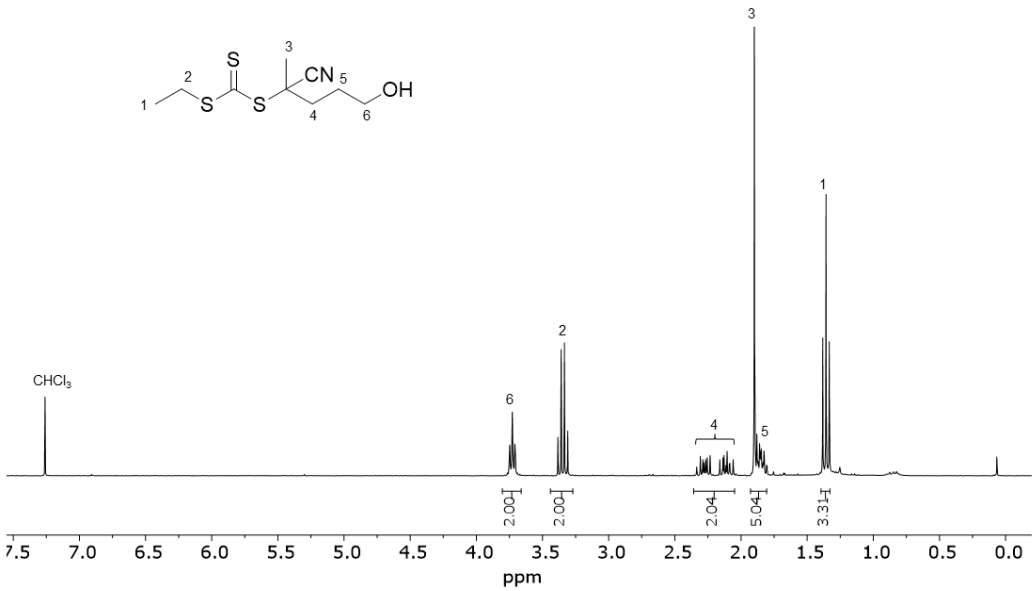


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of 2-cyano-5-hydroxypentan-2-yl ethyl carbonotrithioate

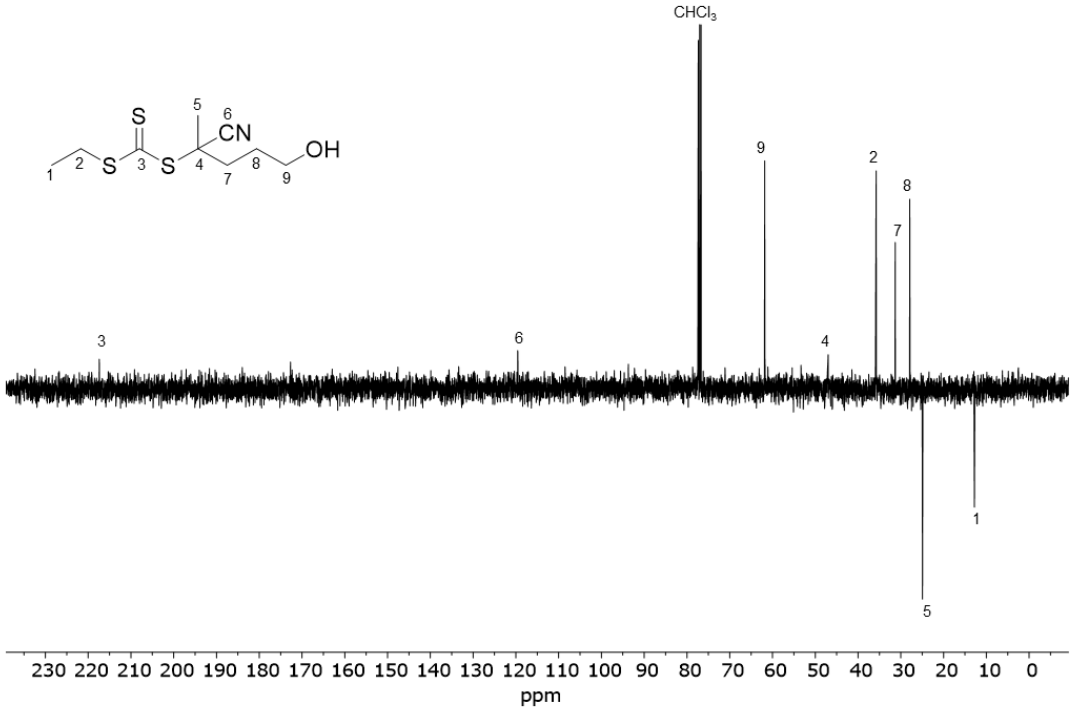
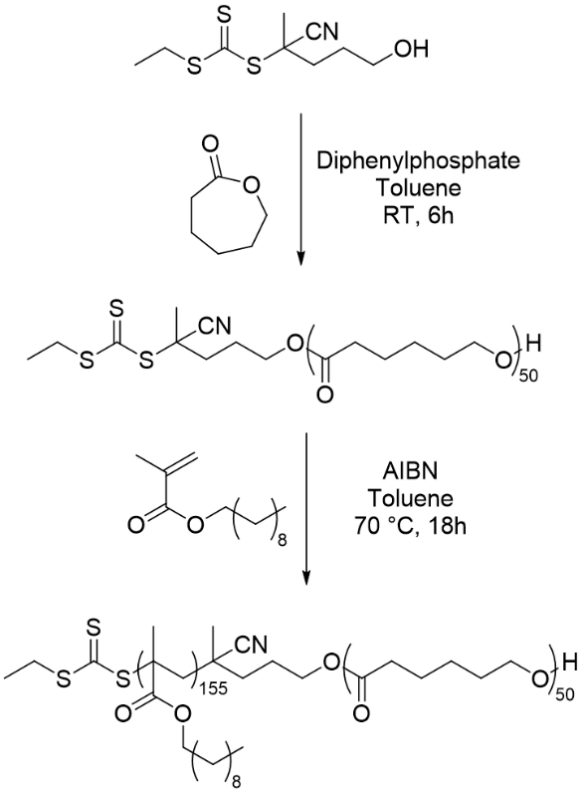


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of 2-cyano-5-hydroxypentan-2-yl ethyl carbonotrithioate



Scheme 1. Synthesis of PCL_{50}-*b*-P*n*DMA_{155} through the ring opening polymerisation of ε-caprolactone and RAFT polymerisation of *n*-decyl methacrylate

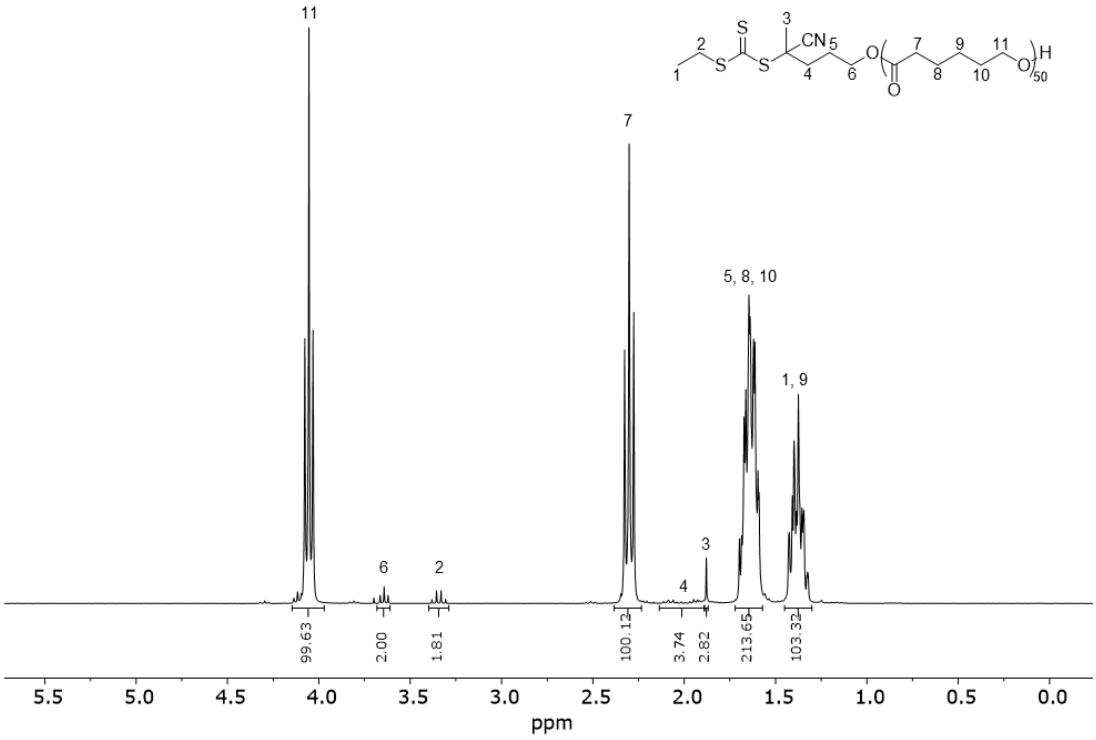


Figure S3. ^1H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of PCL_{50}

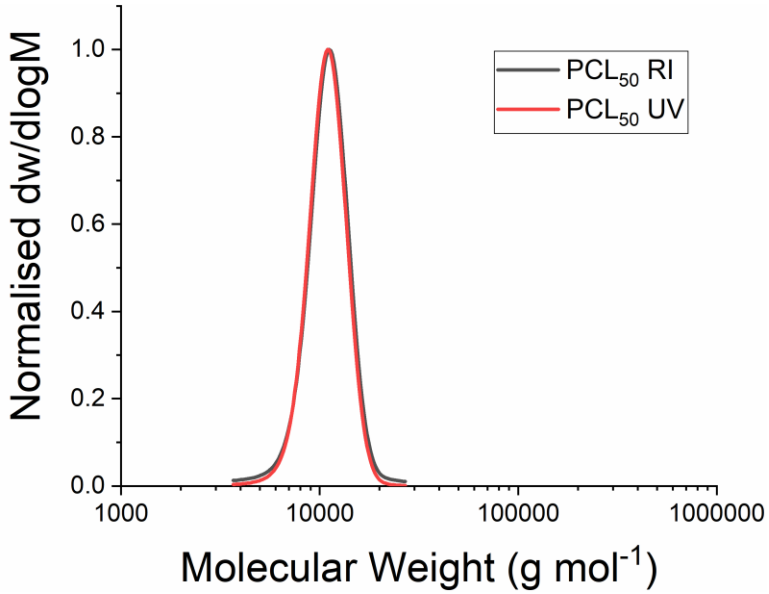


Figure S4. Size exclusion chromatography analysis (RI and UV, λ = 309 nm) of PCL_{50} in $CHCl_3$ calibrated against PS standards.

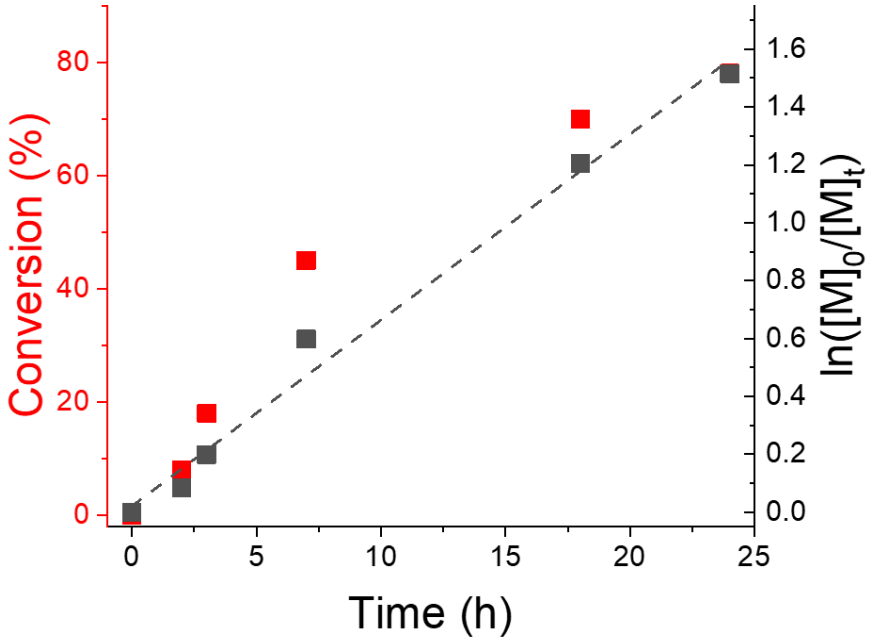


Figure S5. Conversion and ln of initial monomer concentration by monomer concentration ($ln([M]_0/[M]_t)$) against time for the RAFT polymerisation of *n*DMA.

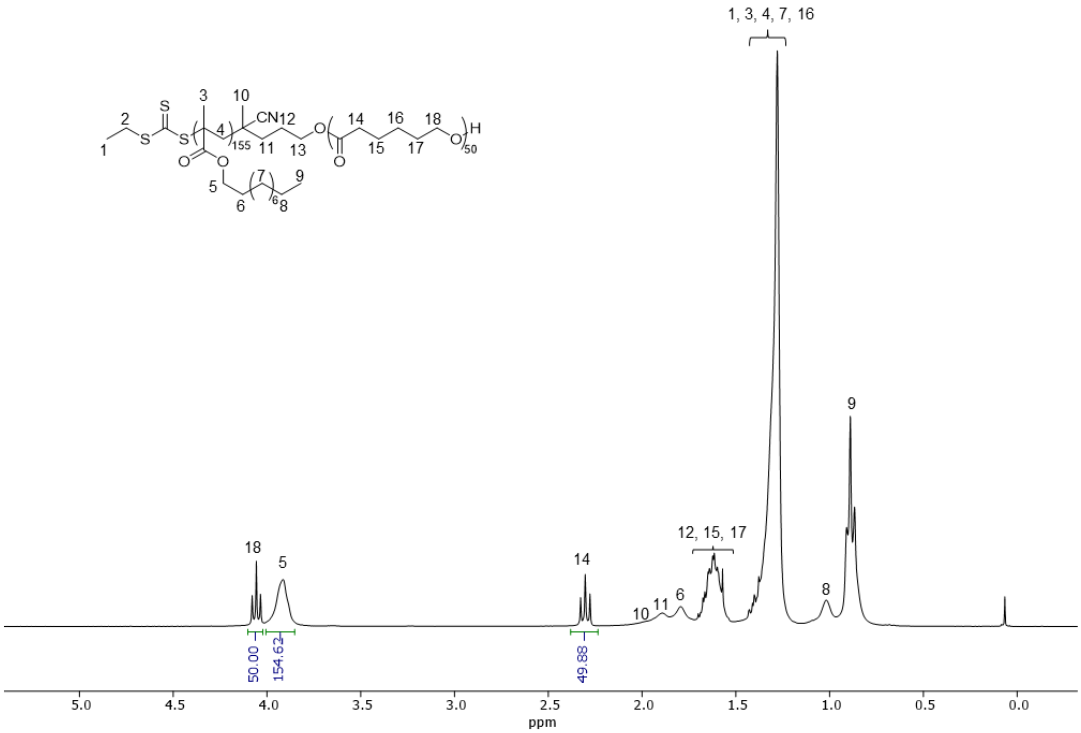


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of PCL_{50}-*b*-P*n*DMA_{155}

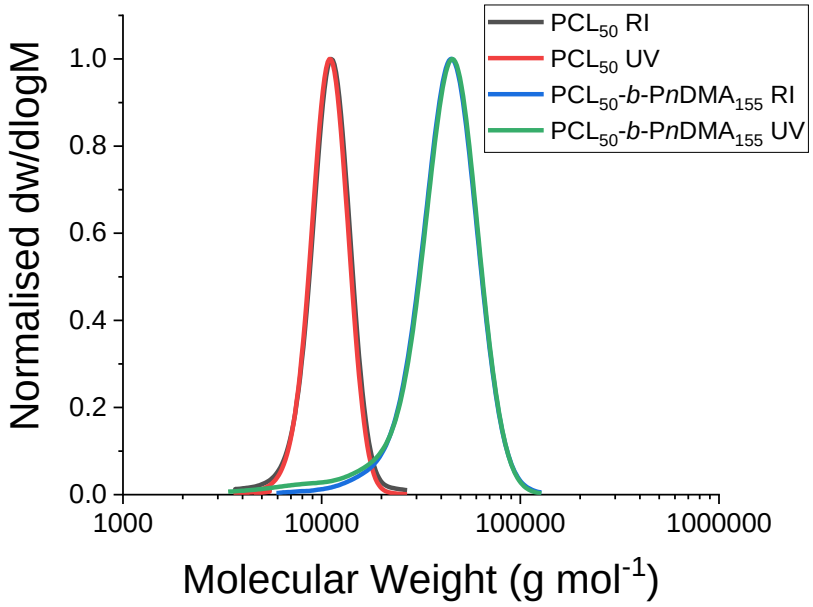


Figure S7. Size exclusion chromatography analysis (RI and UV, λ = 309 nm) of PCL_{50} and PCL_{50}-*b*-P*n*DMA_{155} in $CHCl_3$ calibrated against PS standards.

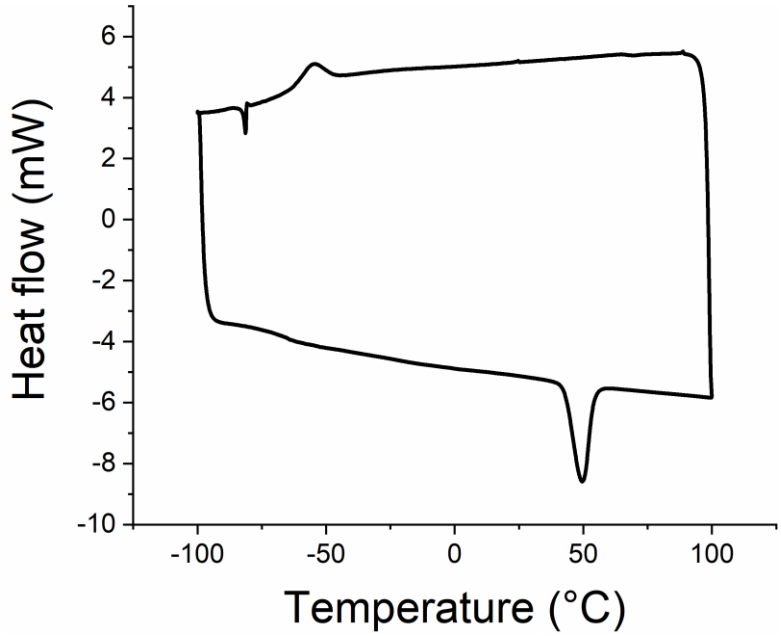


Figure S8. Differential scanning calorimetry analysis of PCL_{50}-*b*-P*n*DMA_{155}, heating rate 10 °C s^{-1}

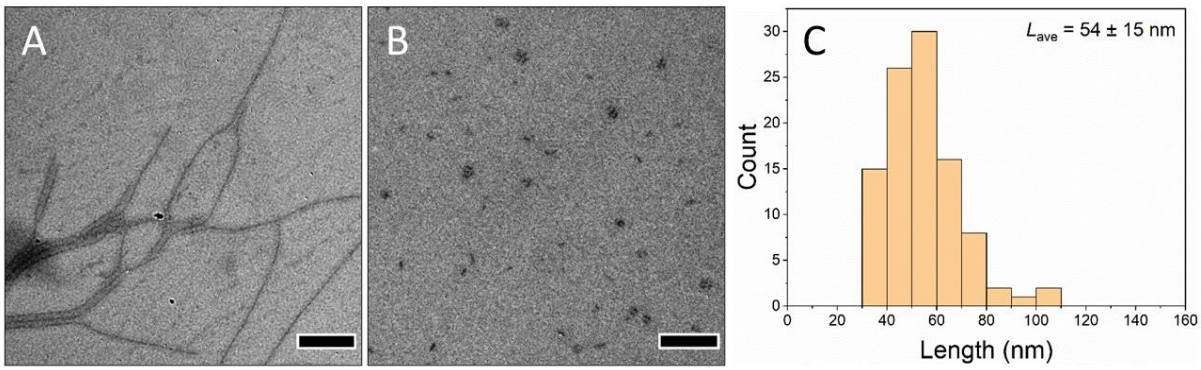


Figure S9. Transmission electron microscope (TEM) images of (A) cylindrical particles of PCL_{50}-*b*-P*n*DMA_{155} in octane, and (B) seed particles from the sonication of cylinders. (C) distribution of seed particle lengths.

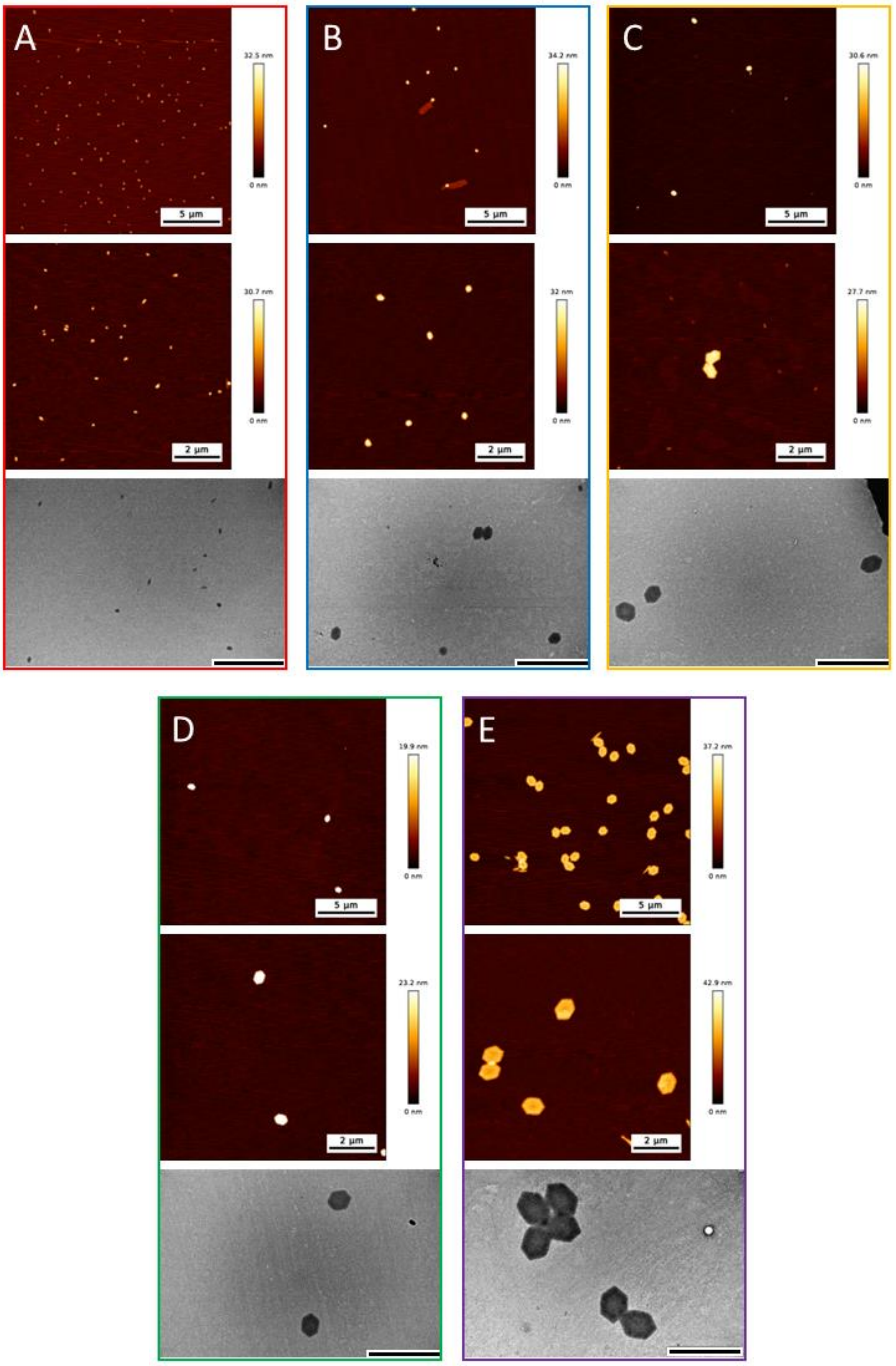


Figure S10. AFM and TEM images of 2D platelets from addition of PCL_{50} and PCL_{50}-*b*-P*n*DMA_{155} to seed particles at m_{unimer}/m_{seed} ratios (A) 1, (B) 10, (C) 25, (D) 40, and (E) 100. All scale bars in TEM images = 2 µm

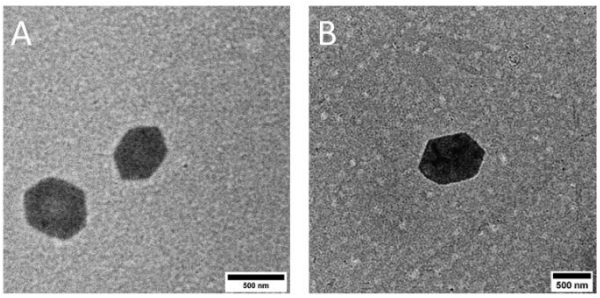


Figure S11. TEM images of platelets with m_{unimer}/m_{seed} ratio = 25 (A) at assembly concentration, (B) after redispersion at 1% w/w in octane

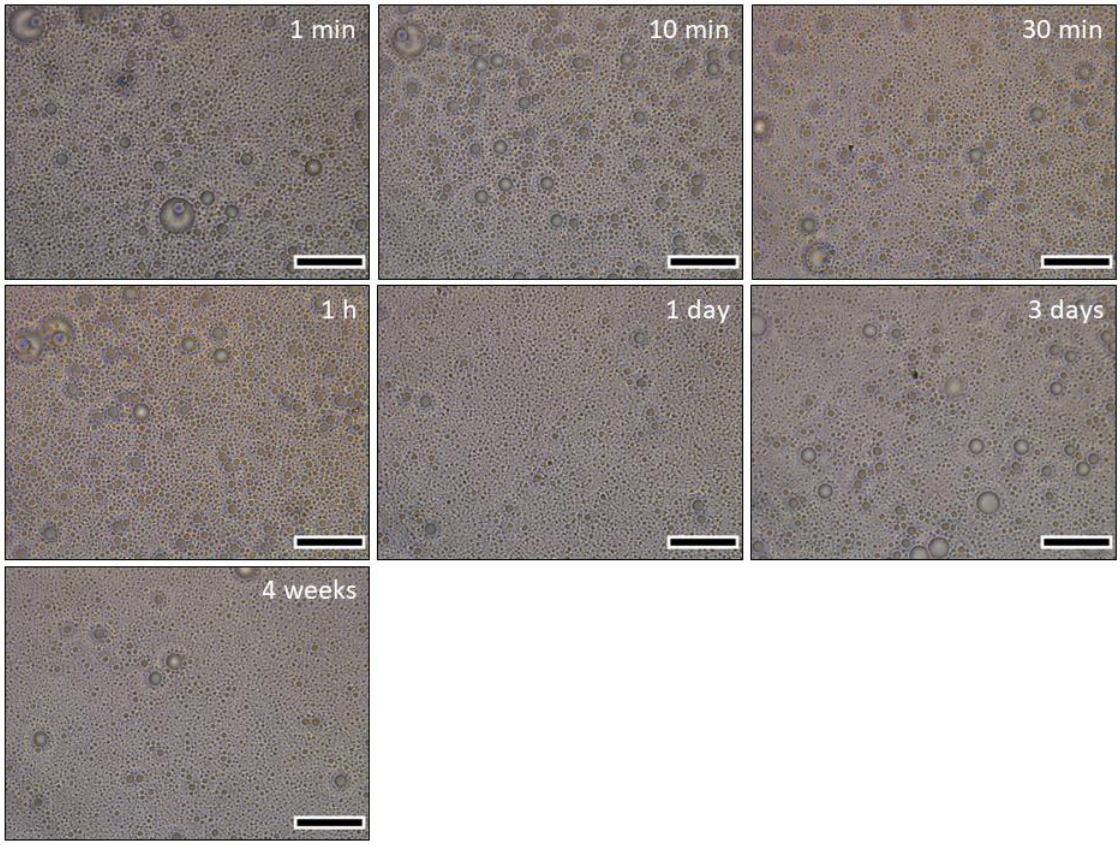


Figure S12. Microscope images between 1 minute and 4 weeks of emulsion of DMF/octane 1/5 using P25 as emulsifier at 1% w/w platelet concentration. All scale bars = 50 µm

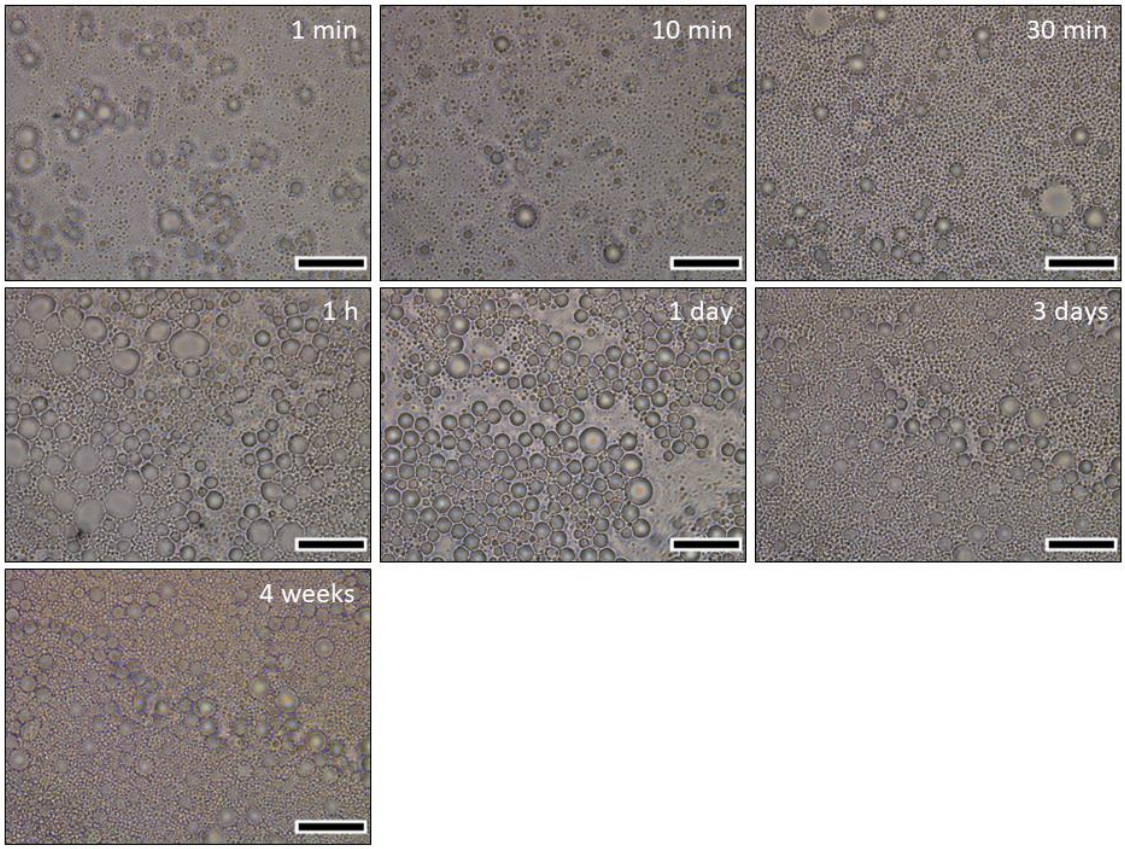


Figure S13. Microscope images between 1 minute and 4 weeks of emulsion of DMF/octane 1/5 using P100 as emulsifier at 1% w/w platelet concentration. All scale bars = 50 µm

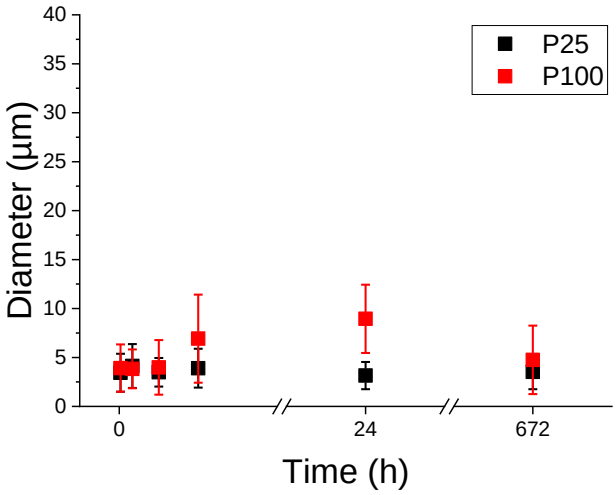


Figure S14. Droplet sizes of DMF/octane 1/5 v/v stabilised by P25 and P100 at 1% w/w particle concentration over time.

Table S1. Droplet diameters of emulsions stabilised by P25 and P100 at 1% w/w over time. 100 droplets counted for each measurement.

Time	Diameter (µm)	
	P25	P100
1 min	3.4 ± 1.9	3.9 ± 2.4
10 mins	4.1 ± 2.2	3.8 ± 2.0
30 mins	3.5 ± 1.5	4.0 ± 2.8
1 h	3.9 ± 2.0	6.9 ± 4.5
24 h	3.2 ± 1.4	8.9 ± 3.5
72 h	3.8 ± 2.4	5.2 ± 2.9
4 weeks	3.5 ± 1.8	4.8 ± 3.5

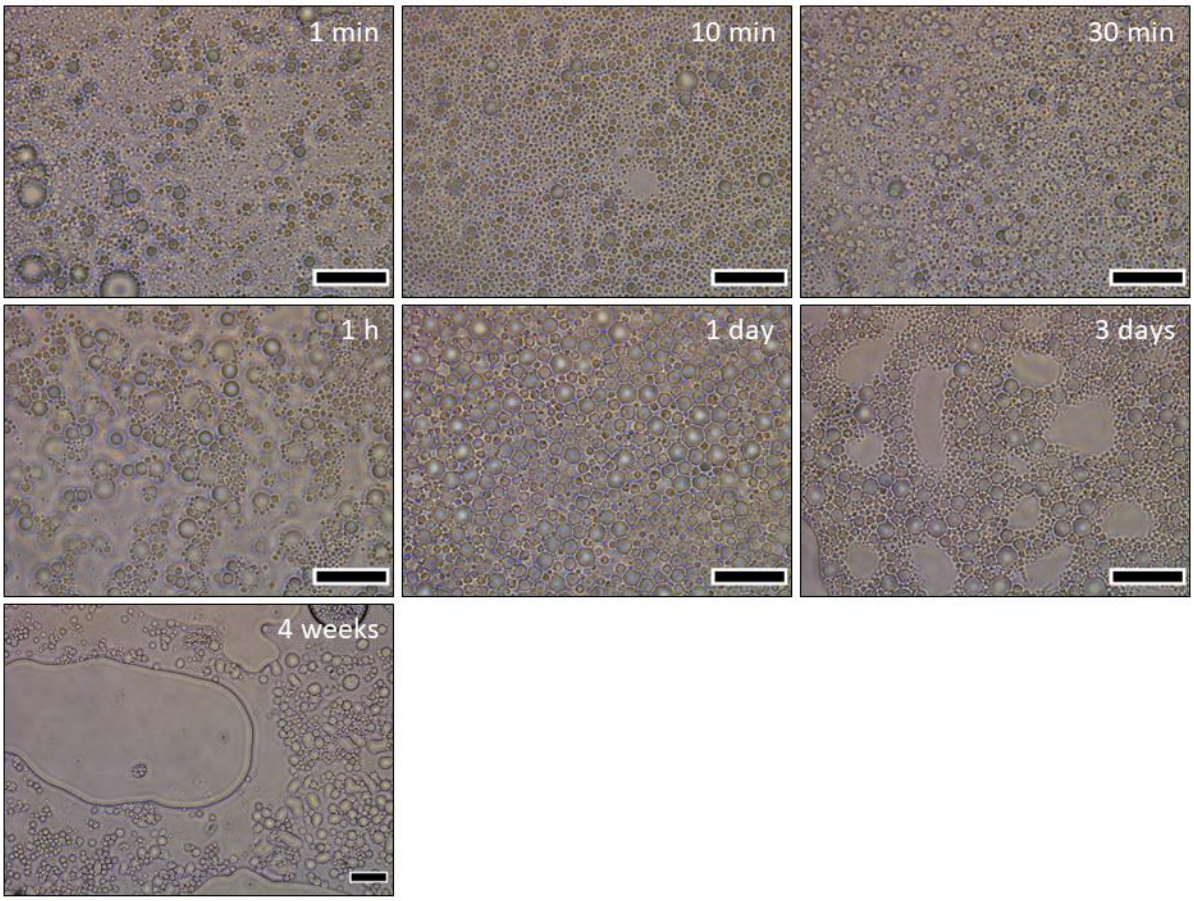


Figure S15. Microscope images between 1 minute and 4 weeks of emulsion of DMF/octane 1/5 using P25 as emulsifier at 0.2% w/w platelet concentration. Scale bars = 50 µm

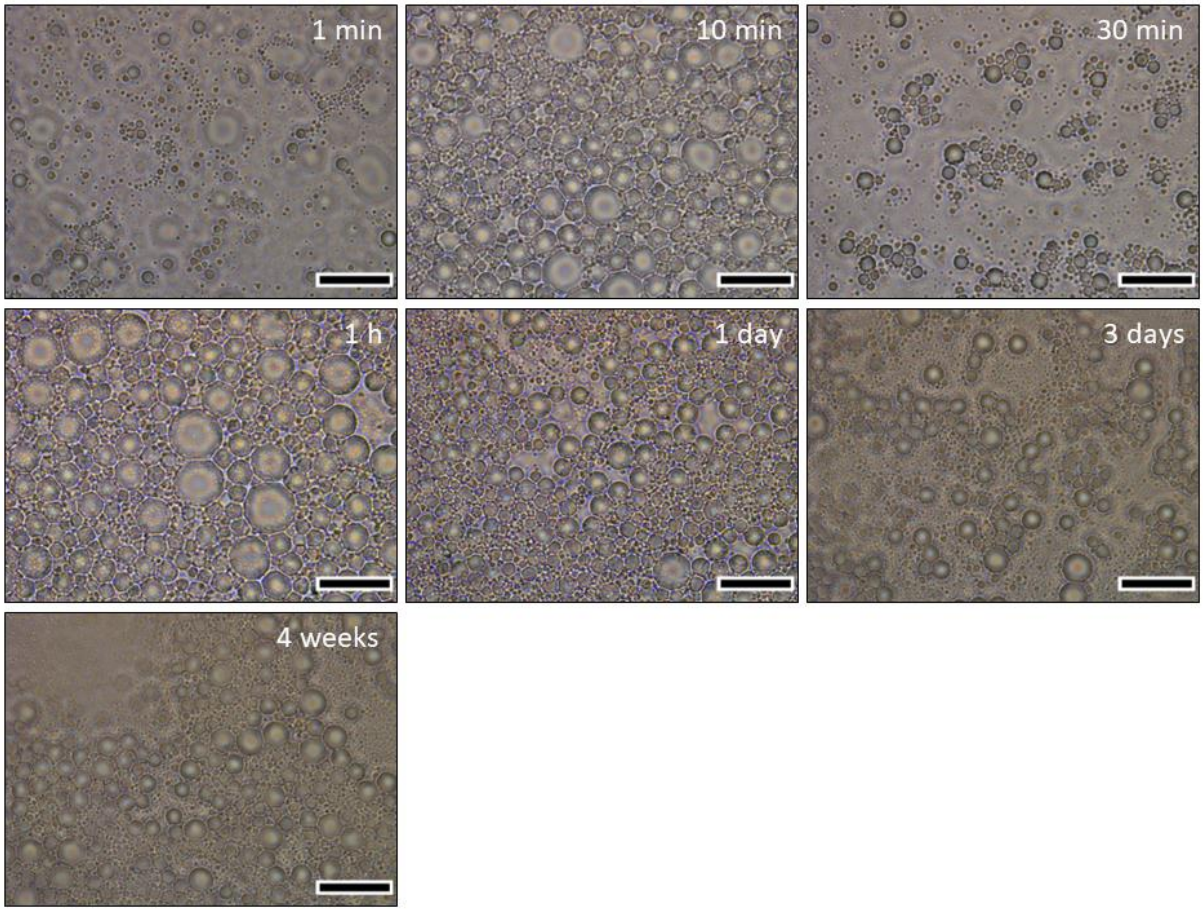


Figure S16. Microscope images between 1 minute and 4 weeks of emulsion of DMF/octane 1/5 using P100 as emulsifier at 0.2% w/w platelet concentration. Scale bars = 50 µm

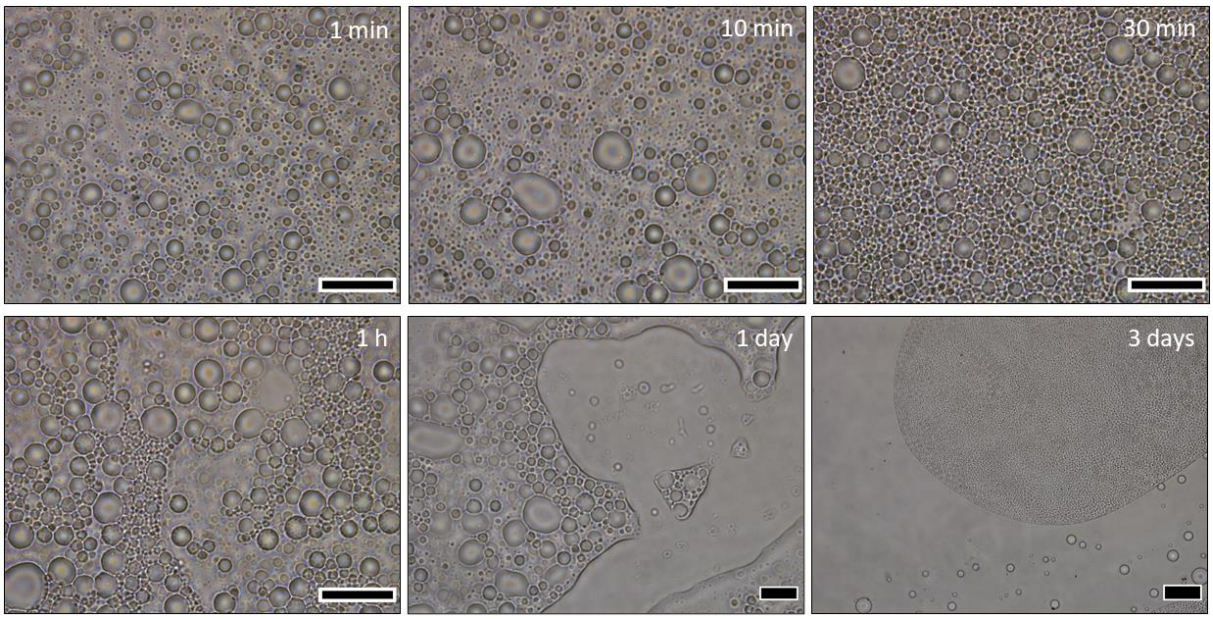


Figure S17. Microscope images between 1 minute and 3 days of emulsion of DMF/octane 1/5 using P100 as emulsifier at 0.1% w/w platelet concentration. Scale bars = 50 µm

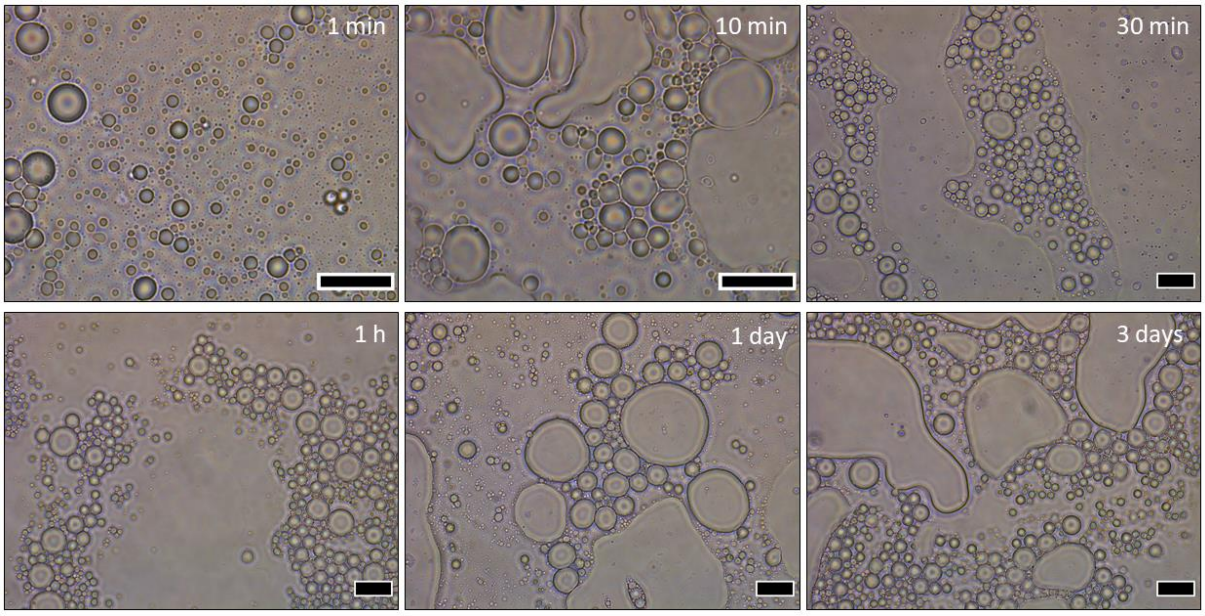


Figure S18. Microscope images between 1 minute and 3 days of emulsion of DMF/octane 1/5 using P25 as emulsifier at 0.1% w/w platelet concentration. Scale bars = 50 µm

Table S2. Droplet diameters of emulsions stabilised by P25 and P100 at 0.2 and 0.1% w/w over time. 100 droplets counted for each measurement.

Time	Diameter (µm)			
	P25		P100	
	0.2% w/w	0.1% w/w	0.2% w/w	0.1% w/w
1 min	3.7 ± 3.6	6.0 ± 5.2	4.5 ± 2.5	5.3 ± 3.6
10 mins	4.1 ± 2.5	11.2 ± 12.6	9.9 ± 5.5	6.6 ± 5.7
30 mins	3.7 ± 1.8	-	6.0 ± 3.2	6.3 ± 3.3
1 h	6.2 ± 3.4	-	13.4 ± 7.1	9.3 ± 3.8
24 h	9.1 ± 3.4	-	8.2 ± 4.1	16.8 ± 19.1
72 h	11.0 ± 11.2	-	6.6 ± 4.3	-
4 weeks	-	-	8.5 ± 5.3	-

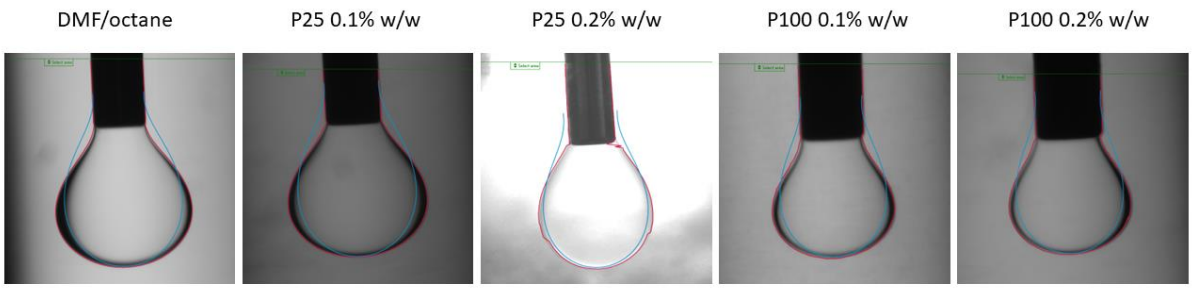


Figure S19. Drop shape analysis of a droplet of DMF in octane, and into self-assembly solutions of P25 and P100 at 0.1 and 0.2% w/w in octane

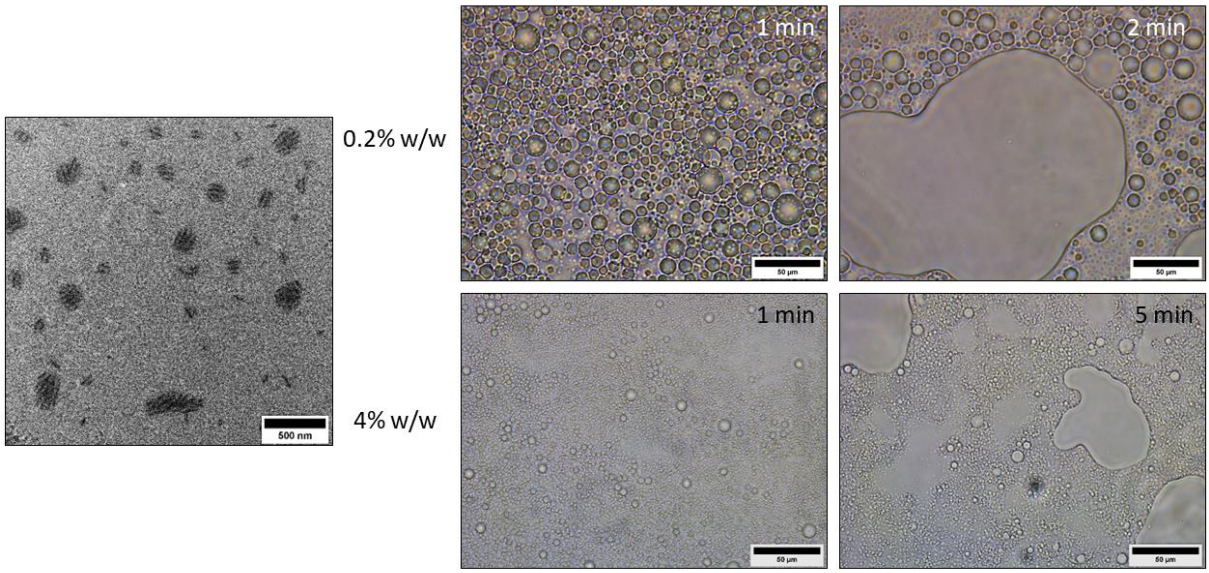


Figure S20. TEM image of short cylindrical micelles of PCL_{50}-*b*-P*n*DMA_{155} in octane. Microscope images of DMF/octane 1/5 v/v using short cylinders as emulsifier at 0.2% w/w and 4% w/w particle concentration. TEM scale bar = 500 nm. Emulsion images scale bars = 50 µm

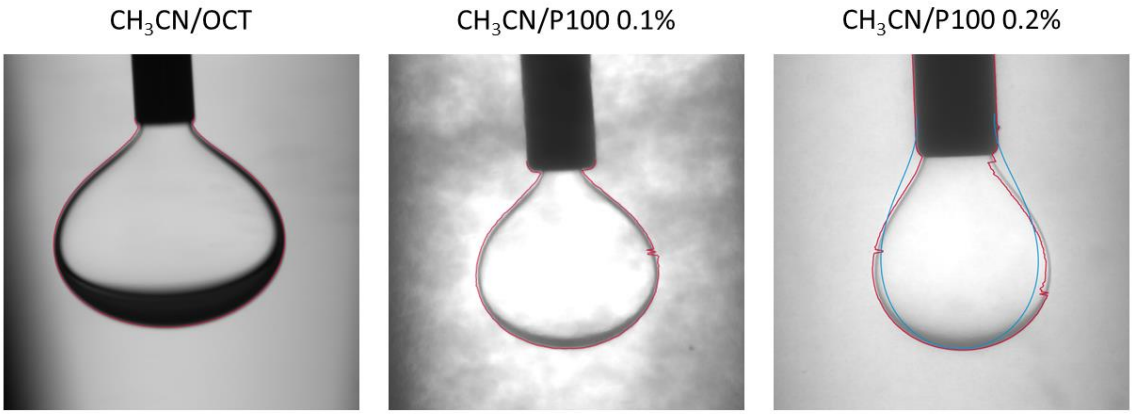


Figure S21. Drop shape analysis of a droplet of CH_3CN in octane (left), into 0.1% w/w P100 in octane (centre), and 0.2% w/w P100 in octane (right).

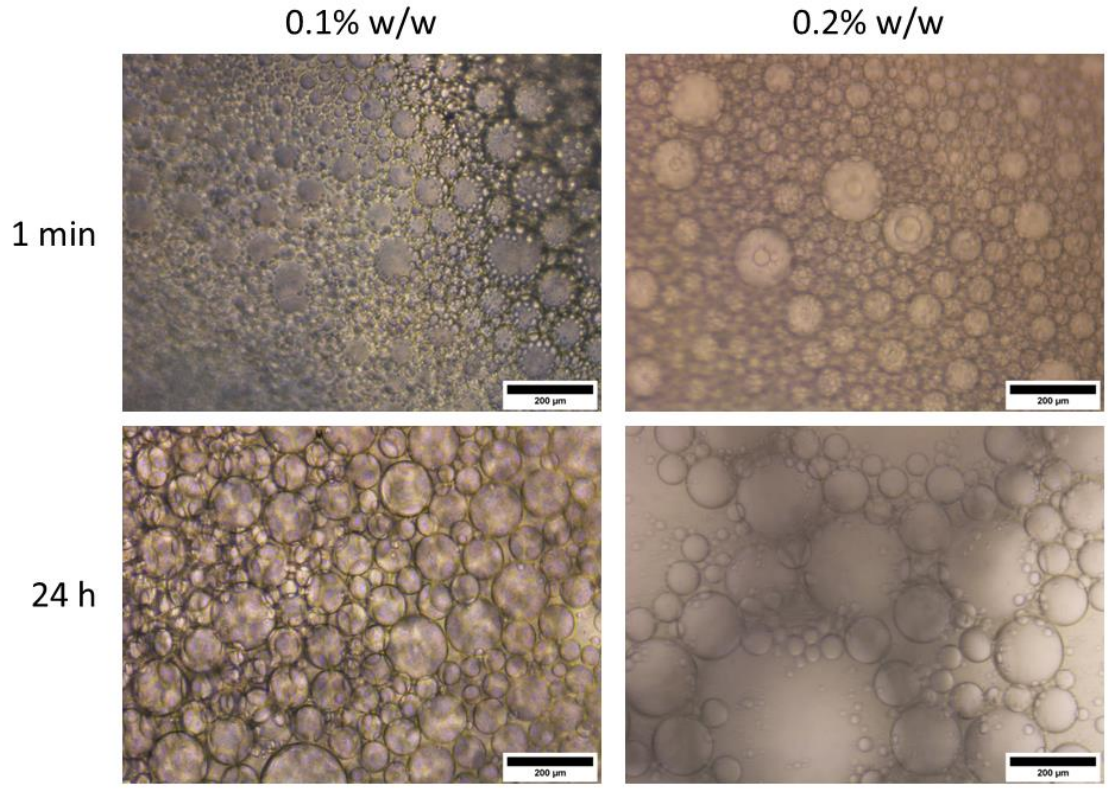


Figure S22. Microscope images between ACN/octane 1/5 v/v using P100 as an emulsifier at 0.1% w/w and 0.2% w/w particle concentration after 1 min and 24 h post vortex. Emulsion images scale bars = 200 µm

References

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2. L. A. Fielding, M. J. Derry, V. Ladmiral, J. Rosselgong, A. M. Rodrigues, L. P. D. Ratcliffe, S. Sugihara and S. P. Armes, *Chem. Sci.*, 2013, **4**, 2081-2087.
3. M. C. Arno, M. Inam, Z. Coe, G. Cambridge, L. J. Macdougall, R. Keogh, A. P. Dove and R. K. O'Reilly, *J. Am. Chem. Soc.*, 2017, **139**, 16980-16985.