Electronic supplementary information

ω-Unsaturated methacrylate macromonomers as reactive polymeric stabilizers in mini-emulsion polymerization

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Table S1 Recipes for the mini-emulsion polymerization series of benzyl methacrylate and hexadecane as hydrophobe with poly(*n*-butyl methacrylate-*block*-[methacrylic acid-*co*-methyl methacrylate]) as stabilizer.

	Reaction code				
	1.25% w/w	**2.5% w/w**	**5% w/w**	**7.5% w/w**	**10% w/w**
Macromonomer/ g	0.1007	0.2008	0.3995	0.6008	0.7997
Water/ g	32.00	32.0	32.0	32.0	32.0
Benzyl Methacrylate/ g	7.6010	7.6025	7.6061	7.5952	7.5980
Hexadecane/ g	0.4313	0.4170	0.4028	0.4166	0.4083
AIBN/ g	0.0106	0.0119	0.0113	0.0108	0.0131

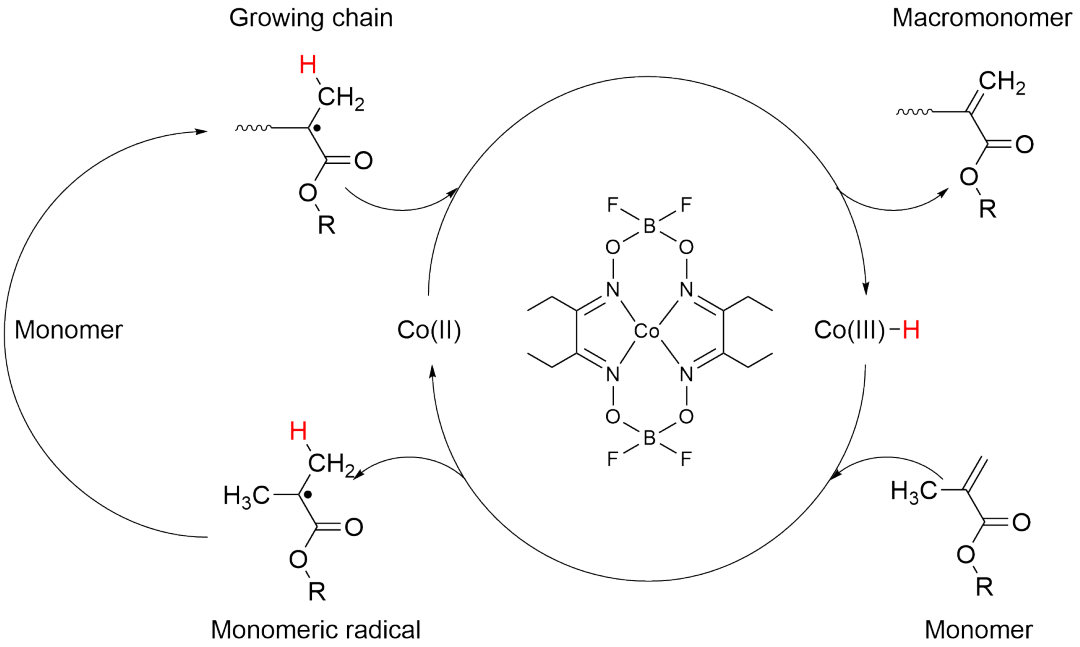
Table S2 Parameters used to calculate the surface free energy for poly(benzyl methacrylate) films.

Substance	**[a]Contact angle/ °**	**Surface tension/ mN.m^{-1}**	**Polar part/ mN.m^{-1}**	**Dispersive part/ mN.m^{-1}**
Ethylene glycol	60.25 ± 0.49	47.7	21.3	26.4
Water	85.12 ± 1.23	72.8	51	21.8
Hexadecane	3.40	27.6	0	27.6

[a] Contact angle was measured by sessile drop technique using Young-Laplace fitting method.

Table S3 Small-angle X-ray scattering (SAXS) parameters used for the fitting of sphere form factor and Hayter-Penfold Rescaled Mean Spherical Approximation (RMSA) structure factor to macromonomer micelles.

Scale	1
Background	6.14×10^{-3}
SLD sample/ 10^{-6} Å^{-2}	9.69
SLD solvent/ 10^{-6} Å^{-2}	9.43
Volume fraction	3.63×10^{-2}
Charge/ e	10
Temperature/ K	303
Salt concentration/ M	0.01
Dielectric constat	76.546
Distribution of radius (log)	0.37
Sphere radius/ nm	**13.255**
Chi^2/Npts	**1.719**



Scheme S1 Synthesis of ω-unsaturated methacrylate macromonomers by catalytic chain transfer polymerisation (CCTP) with bis[(difluoroboryl)diethylglyoximato]cobalt(II) (CoEtBF) as catalyst.

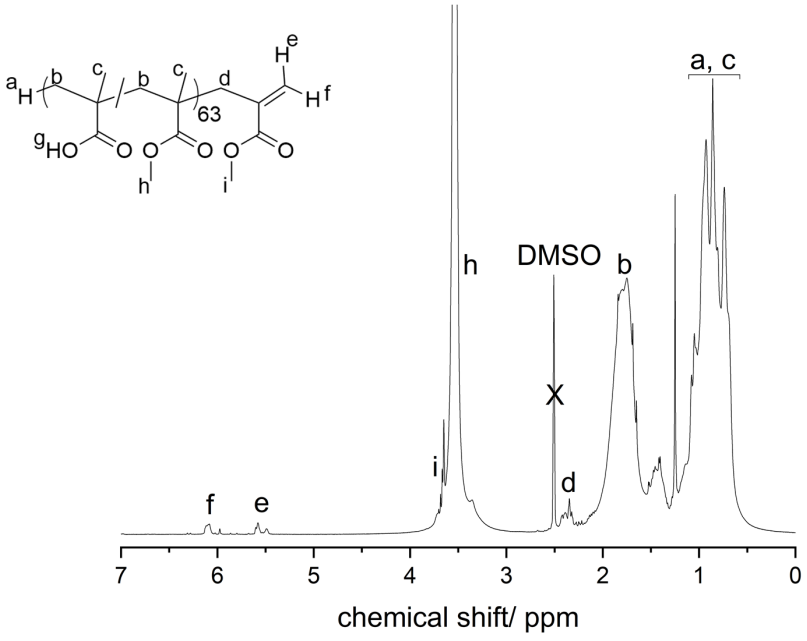


Figure S1 ^{1}H NMR spectrum for poly(methacrylic acid-*co*-methyl methacrylate).

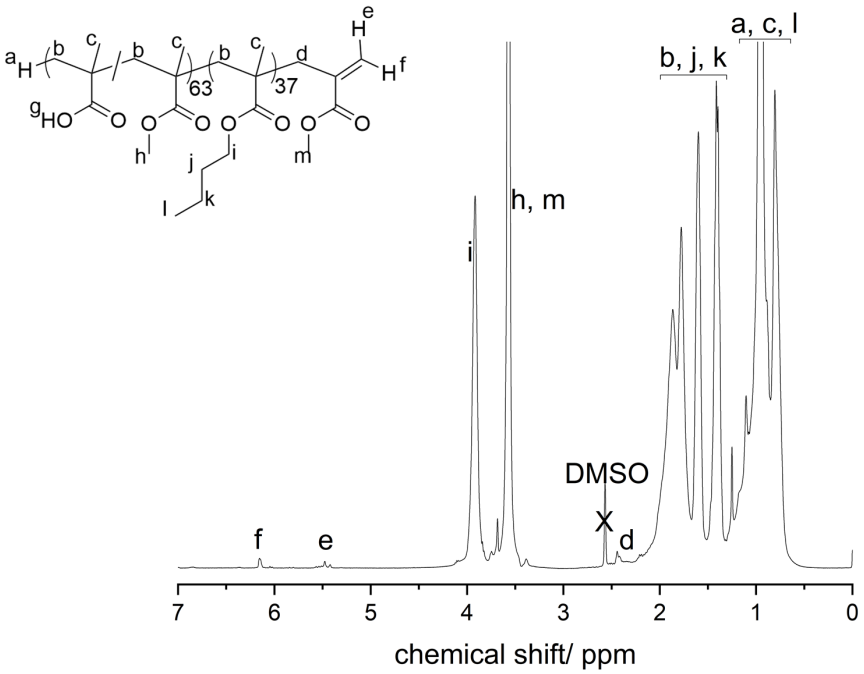


Figure S2 ^{1}H NMR spectrum for poly(*n*-butyl methacrylate-*block*-[methacrylic acid-*co*-methyl methacrylate]).

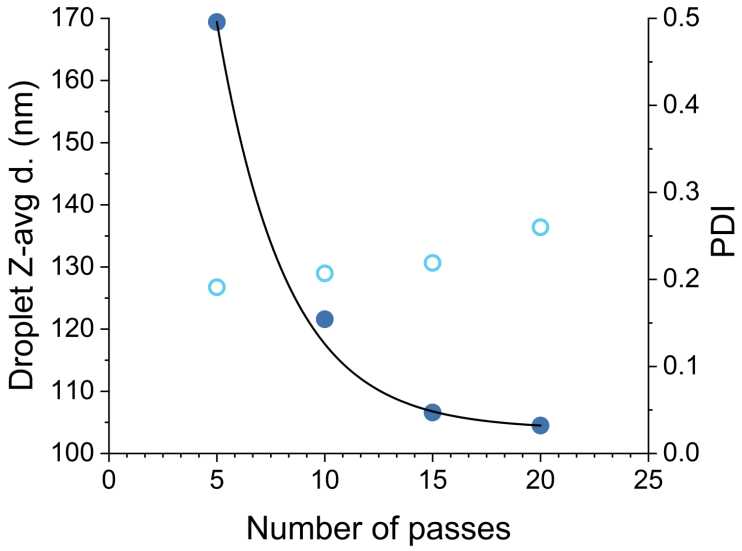


Figure S3 Z-average droplet diameter and PDI measure by DLS of SDS stabilized hexadecane mini-emulsion after 5, 10, 15 and 20 passes through a high-pressure homogenizer with value pressure 12.5 kPsi.

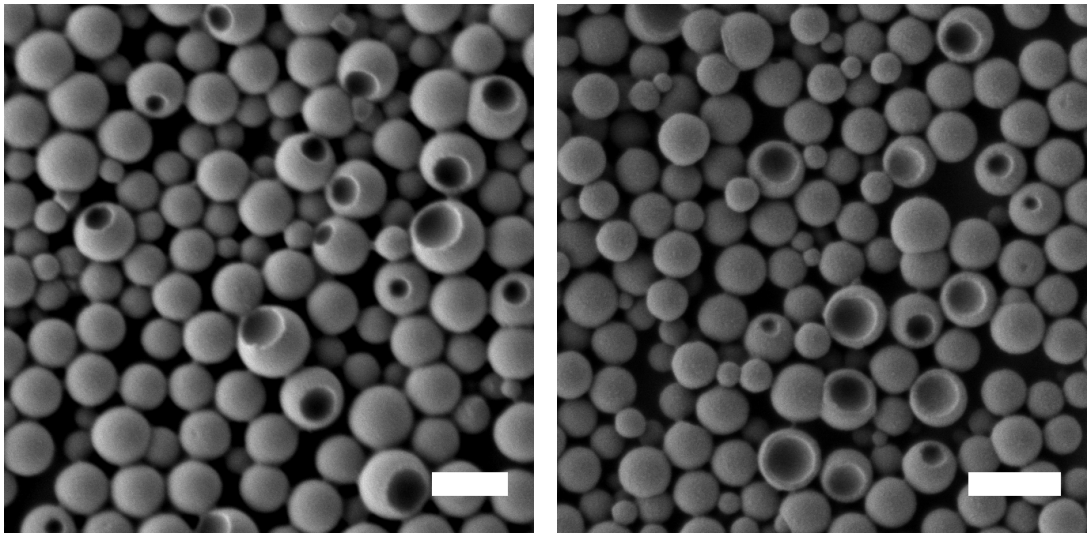


Figure S4 High magnification SEM images of reactions MM-1.25% (left) and MM-2.5% (right) showing a range of dimple sizes. Both scale bars are 250 nm.

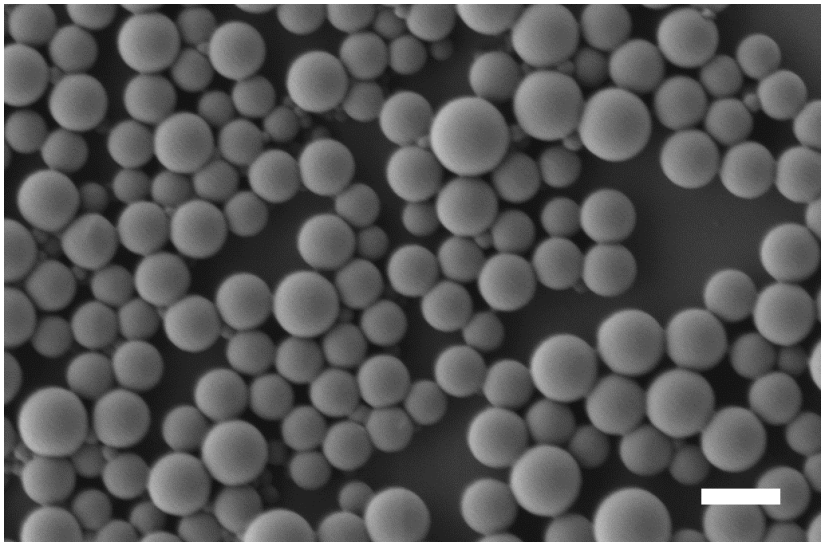


Figure S5 Scanning electron microscopy image of poly(benzyl methacrylate) particles with 5% w/w octadecyl methacrylate as hydrophobe and 1.25 wt% macromonomer stabilizer. Scale bar is 300nm.

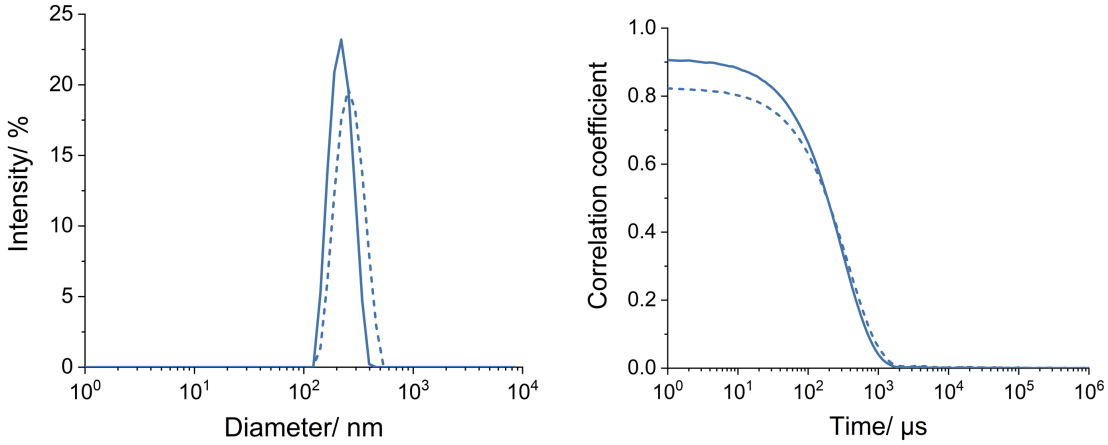


Figure S6 DLS data for a mini-emulsion benzyl methacrylate with 5% w/w octadecyl methacrylate as hydrophobe and 1.25 wt% macromonomer stabilizer. Intensity weight size distributions (left) and correlograms (right) are shown. Mini-emulsion droplet data shown as dashed lines, final particle data shown as solid lines.

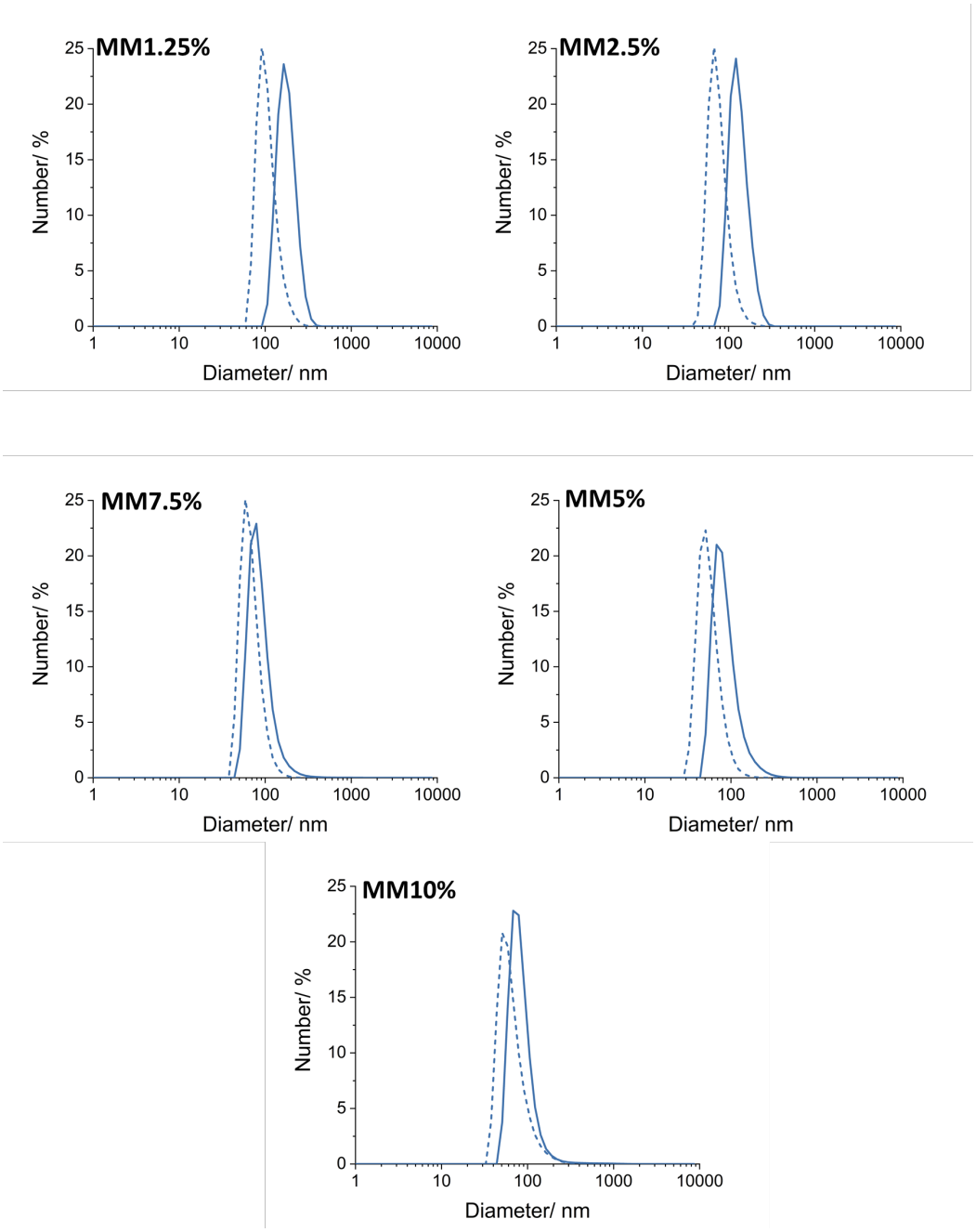


Figure S7 Number weighted size distributions of poly(benzyl methacrylate) mini-emulsion monomer droplets and particles at full conversion. Droplet distributions are shown in dashed lines, particle distributions are shown as solid lines.

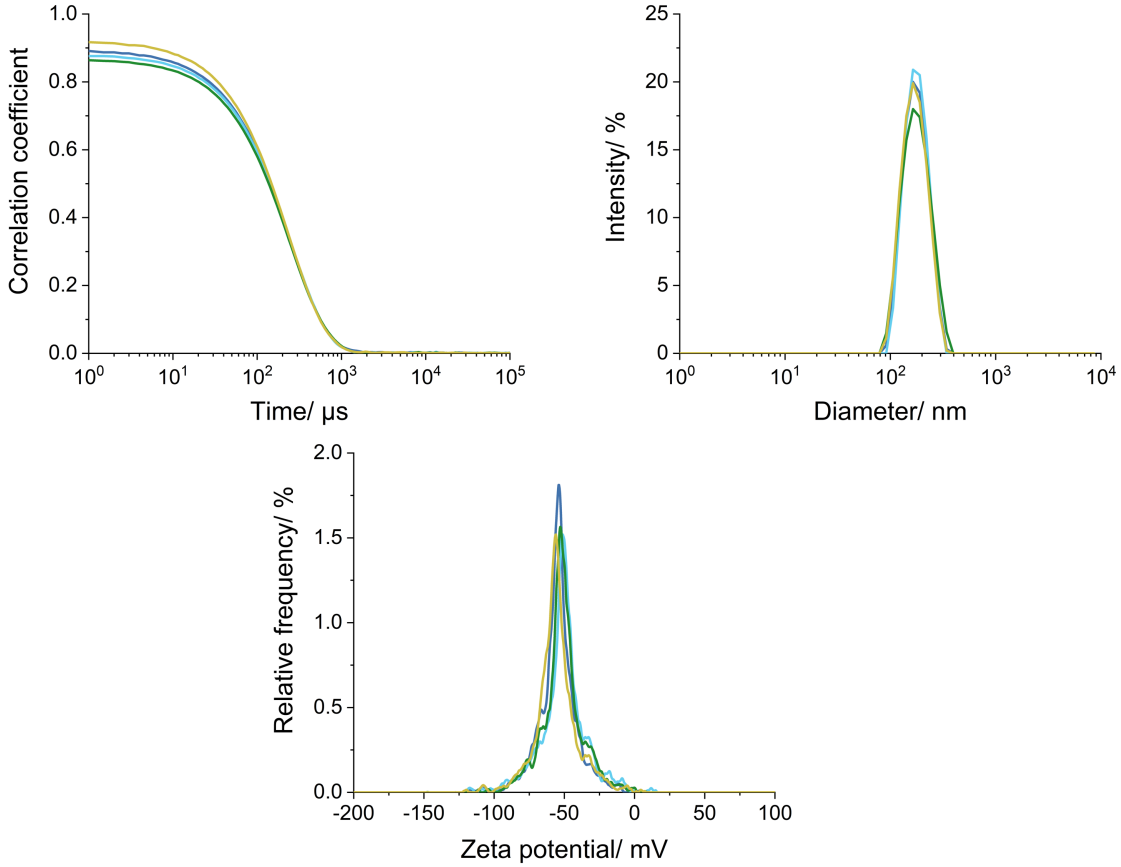


Figure S8 (Top left) DLS analysis producing correlograms and (top right) particle size distributions of poly(benzyl methacrylate) particles after 0 days (dark blue), 7 days (light blue), 14 days (green) and 21 days (yellow) dialysis against deionized water (≥15 MΩ). (Bottom) Zeta potential spectrum of poly(benzyl methacrylate) particles after 0 days (dark blue), 7 days (light blue), 14 days (green) and 21 days (yellow) dialysis against deionized water (≥15 MΩ).

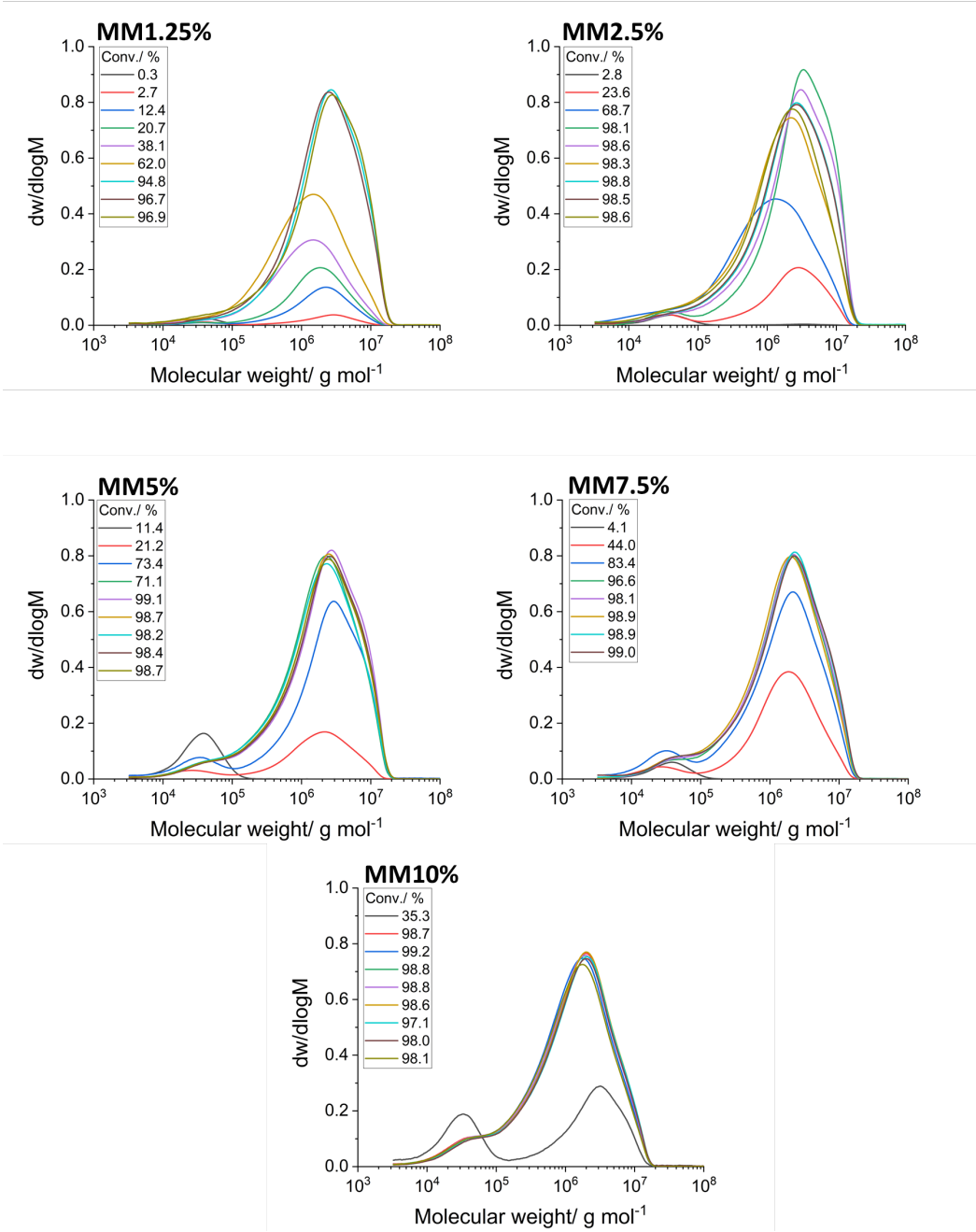


Figure S9 Molecular weight distribution (GPC, THF) for macromonomer stabilized benzyl methacrylate mini-emulsion polymerizations. Percentage cumulative monomer of the reaction when each sample was taken is show in the inset legends. The distributions have been normalised to cumulative monomer conversion.