SUPPLEMENTARY INFORMATION

Droplet Nucleation in Miniemulsion Thiol-Ene Step Photopolymerization

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Fig. S1. ¹H NMR spectra in DMSO-d⁶ of a EDDT-DAP miniemulsion (20 w% monomer phase content) containing 10 mM of DBHQ (radical inhibitor) as a function of storage time (in the dark and at ambient temperature). t = 0 is the first measurement just after ultrasonication.



Fig S2. Variation of backscattering signal (Δ BS) in the middle of the measuring vial as a function of storage time of an EDDT-DAP monomer miniemulsion (monomer content: 5 wt%) prepared using different hexadecane (HD) concentrations.



Fig. S3. ¹H NMR spectra in DMSO-d⁶ during a EDDT-DAP miniemulsion photopolymerization for different irradiation times. Monochromatic irradiation at 385 nm, $I = 3.7 \text{ mW cm}^{-2}$



Fig. S4. Series of SEC traces during an EDDT-DAP miniemulsion photopolymerization. Monochromatic irradiation at 385 nm, I = 3.7 mW cm⁻²



Fig S5. Droplet stability of an EDDT-DAP miniemulsion having a monomer weight fraction of 1 wt%. (A) Temporal evolution of z-average diameter (DLS analysis with time interval of 5 min for 12 h). The result shows that the droplet size is unchanged over a period of 12h; (B) Backscattering signal (BS) as a function of sample height for different storage times (Turbiscan analysis at ambient temperature); (C) Variation of BS as a function of storage time, t = 0 is the time just after ultrasonication.



Fig S6. TEM pictures of EDDT-DAP latexes obtained by miniemulsion photopolymerization using TPO-Li (**A**) and TPO (**B**) as radical photoinitiator.