# Supporting information:

# Shedding Light on Surfactant-Free Emulsion Polymerization

Erika Paola Fonseca Parra,[a] Jean-Luc Six,[a] and Khalid Ferji*[a]

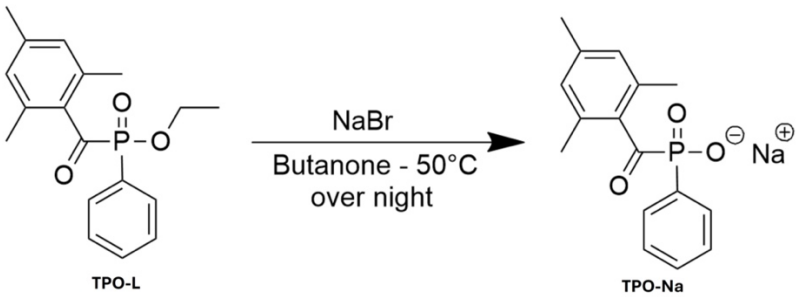
Corresponding author:

Dr. Khalid FERJI

Laboratoire de Chimie Physique Macromoléculaire

1 rue Grandville, Nancy 54001 France

khalid.ferji@univ-lorraine.fr




**Scheme S1.** Synthesis of TPO-Na from TPO-L.

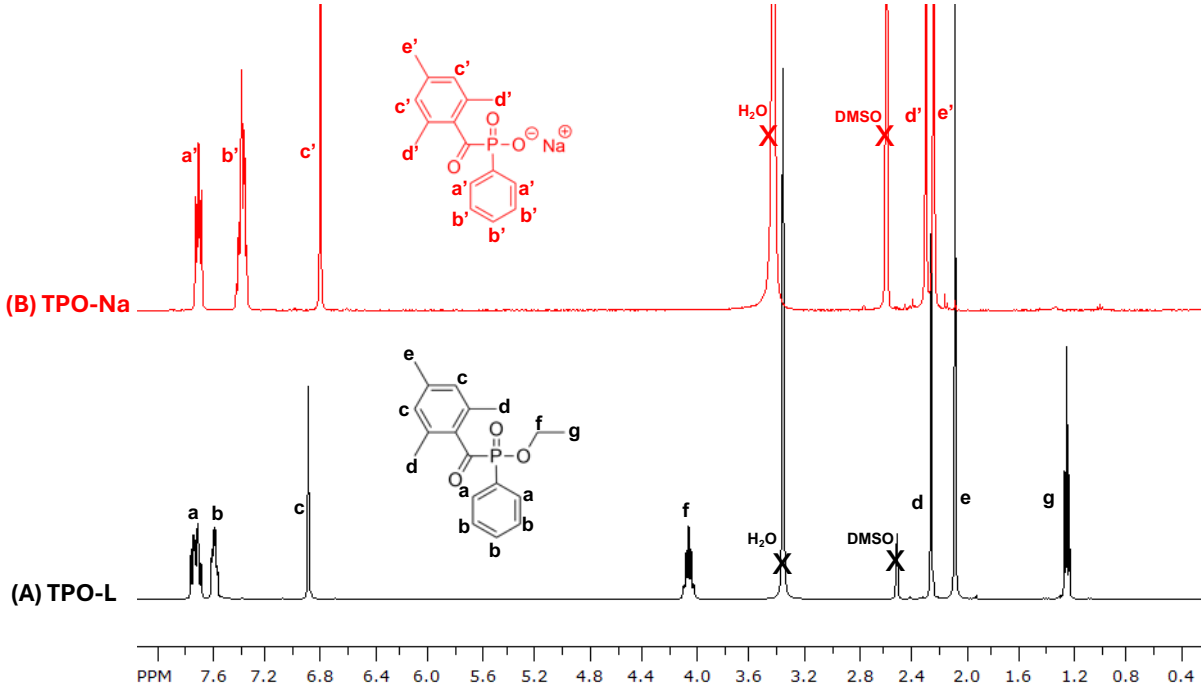



**Fig. S1.** $^{1}$H NMR spectra of (A) TPO-L and (B) TPO-Na in DMSO-$d_6$.

**Table S1.** Experimental conditions used in SFEP of GlyMA at room temperature under 405 nm (30 mW) irradiation.

| Samples | SC[a] | R[b] | $V_{GlyMA}$ (µL) | TPO-Na (µL)[c] | $H_2O$ (mL) |
|---|---|---|---|---|---|
| P-0.08GlyMA10 | 10% | 0.08‰ | 700 | 13 | 6.2 |
| P-0.1GlyMA10 | | 0.1‰ | 700 | 16 | 6.2 |
| P-0.2GlyMA10 | | 0.2‰ | 700 | 32 | 6.2 |
| P-0.5GlyMA10 | | 0.5‰ | 700 | 79 | 6.2 |
| P-0.66GlyMA10 | | 0.66‰ | 700 | 106 | 6.2 |
| P-1GlyMA10 | | 1‰ | 700 | 159 | 6.1 |
| P-2.5GlyMA10 | | 2.5‰ | 700 | 397 | 5.9 |
| P-5GlyMA10 | | 5‰ | 700 | 794 | 5.5 |
| P-1GlyMA20 | 20% | 1‰ | 1860 | 454 | 7.5 |
| P-1GlyMA50 | 50% | 1‰ | 2791 | 681 | 2.3 |

[a] solids content.
[b] $R = (n_{TPO\text{-}Na}/n_{GlyMA}) \times 1000$
[c] volume of diluted TPO-Na solution in the water withdrawn from a stock solution (10 mg/mL)

**Fig. S2.** Experimental setup of SFEP of GlyMA at room temperature under 405 nm (30 mW) irradiation using a light source (Opto-Spectrum Generator L12194-00-39-070).

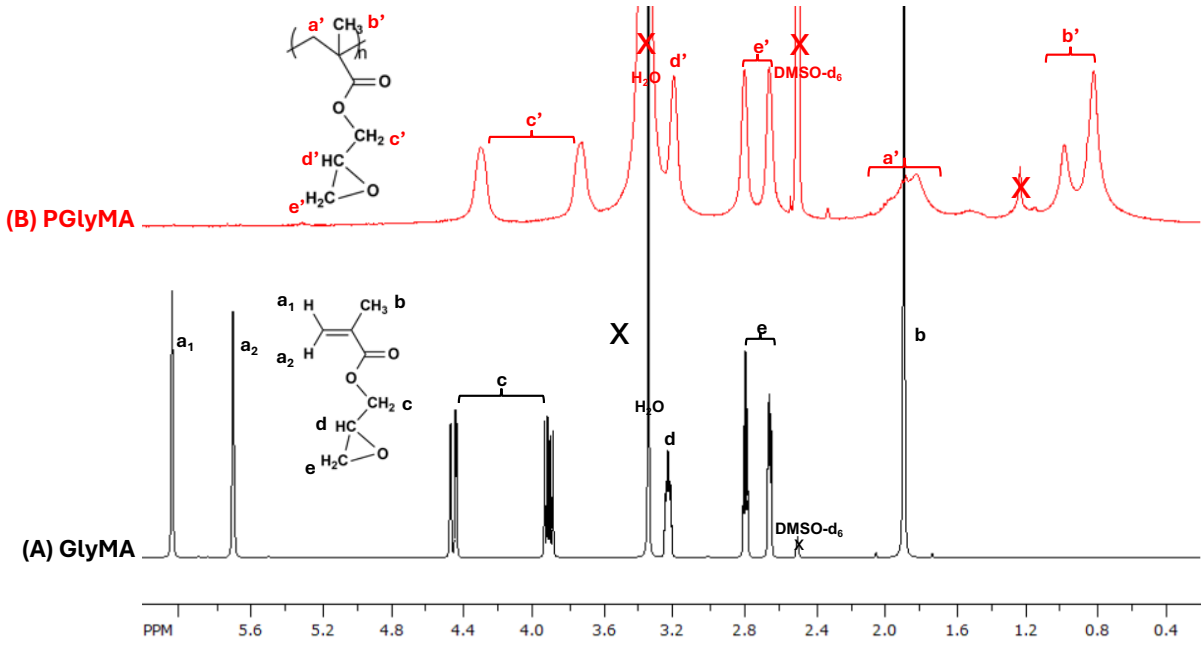



**Fig. S3.** $^{1}$H NMR spectra in DMSO-$d_6$ of (A) GlyMA and (B) PGlyMA prepared *via* SFEP of GlyMA at room temperature under 405 nm in water. R= 1‰, SC= 10% w/w.

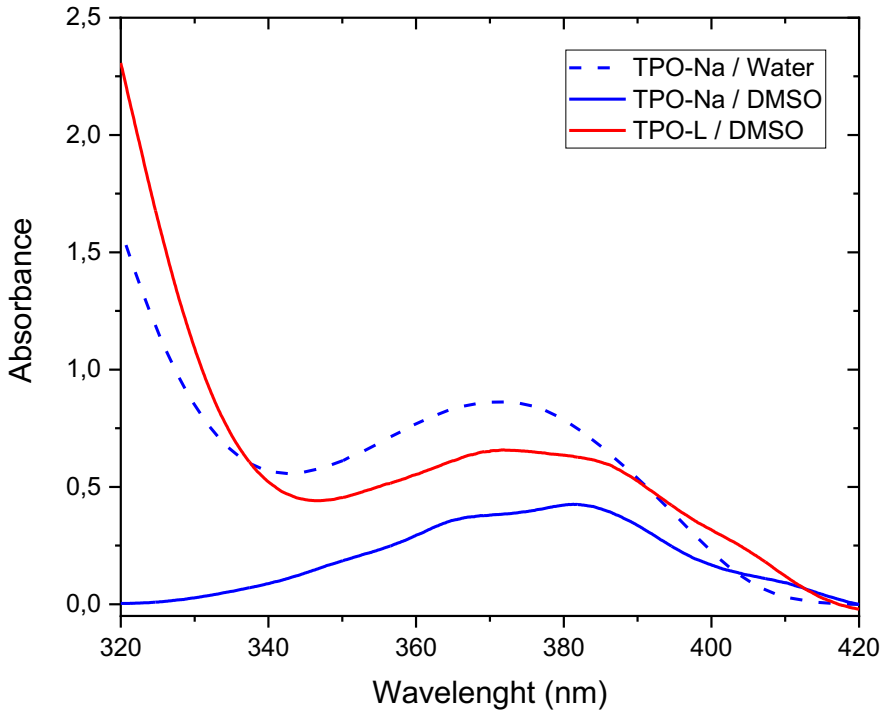



**Fig. S4.** UV-absorption spectra of TPO-L (Red curve) and TPO-Na (Blue curve) in DMSO (Solid) and Water (Dashed).

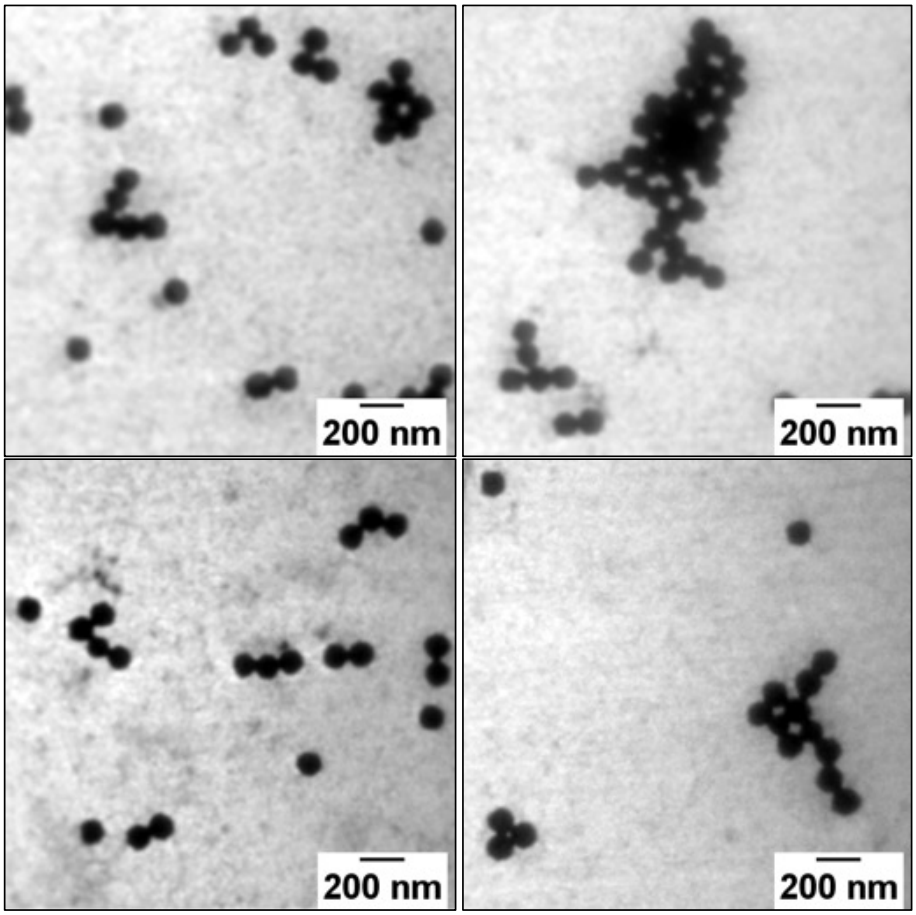



**Fig. S5.** Surfactant-free latex prepared *via* SFEP of GlyMA at 60°C (T-20GlyMA2.2) using R=20‰ and SC=2.2% w/w in water.

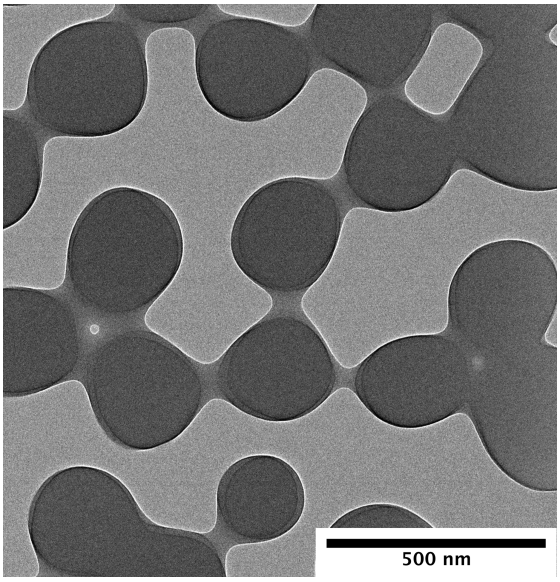



**Fig. S6.** High resolution TEM image of latex prepared *via* SFEP of GlyMA at RT under 405 nm irradiation.

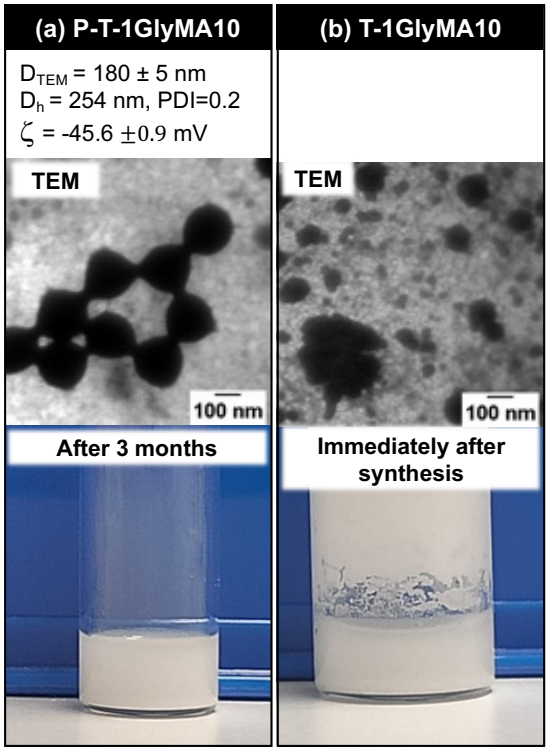
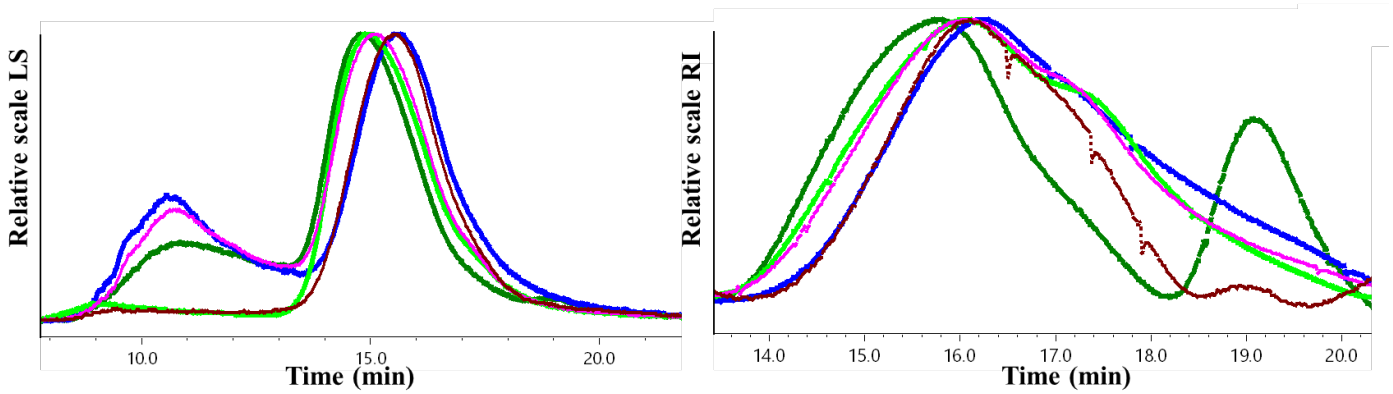


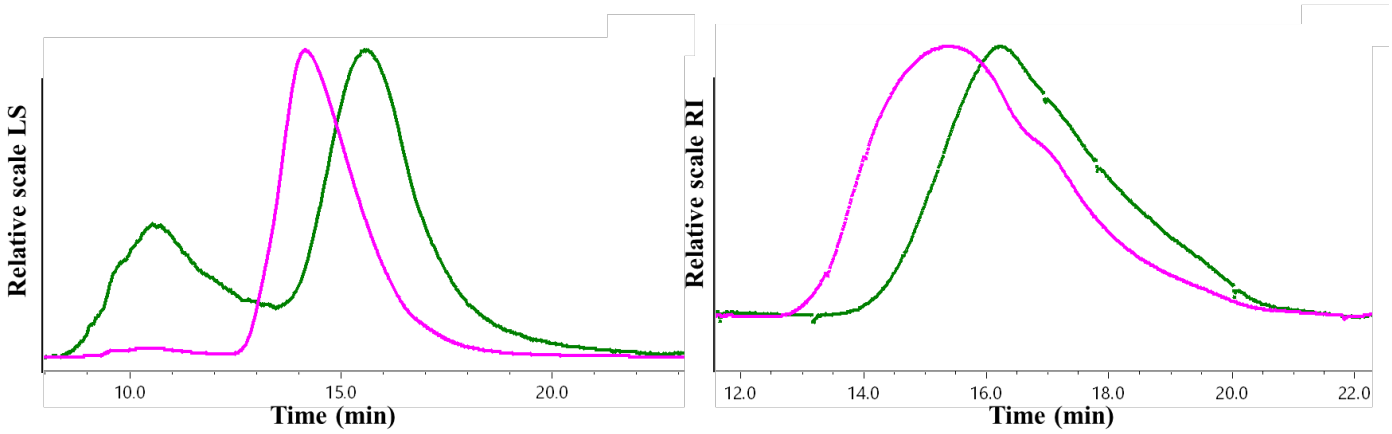

**Fig. S7.** Surfactant-free latex prepared *via* SFEP of GlyMA at 60°C, SC=10% w/w and R=1 ‰ in water (a) using TPO-Na under 405 nm (P-T-1GlyMA10), (b) and using KPS (T-1GlyMA10).


**Fig. S8.** Surfactant-free latex prepared *via* SFEP of GlyMA at RT SC=10% w/w and R=1 ‰ in water using TPO-L under 405 nm (P(TPO-L)-1GlyMA10).




| Experiments | 0.2GlyMA10 | 0.5GlyMA10 | 0.67GlyMA10 | 1GlyMA10 | 2.5GlyMA10 |
|---|---|---|---|---|---|
| $\overline{Mn}$ (kg/mol) | 327 | 237 | 201 | 164 | 610 |
| Đ | 1.4 | 1.9 | 1.8 | 1.5 | 1.4 |

**Fig. S9.** SEC chromatograms of PGlyMA synthesized *via* photo-SFEP of GlyMA under 405 nm irradiation with a solid content (SC) of 10% at various R values. Detection was performed using light scattering (LS) and refractive index (RI) detectors in THF ($\overline{M_n}$ estimated using dn/dc = 0.084 mL/g).




| Experiments | 1GlyMA10 | 1GlyMA20 |
|---|---|---|
| $\overline{Mn}$ (kg/mol) | 164 | 280 |
| Đ | 1.5 | 2.6 |

**Fig. S10.** SEC chromatograms of PGlyMA synthesized *via* photo-SFEP of GlyMA under 405 nm irradiation using R=1‰ at different solids content. Detection was performed using light scattering (LS) and refractive index (RI) detectors in THF ($\overline{M_n}$ estimated using dn/dc = 0.084 mL/g).

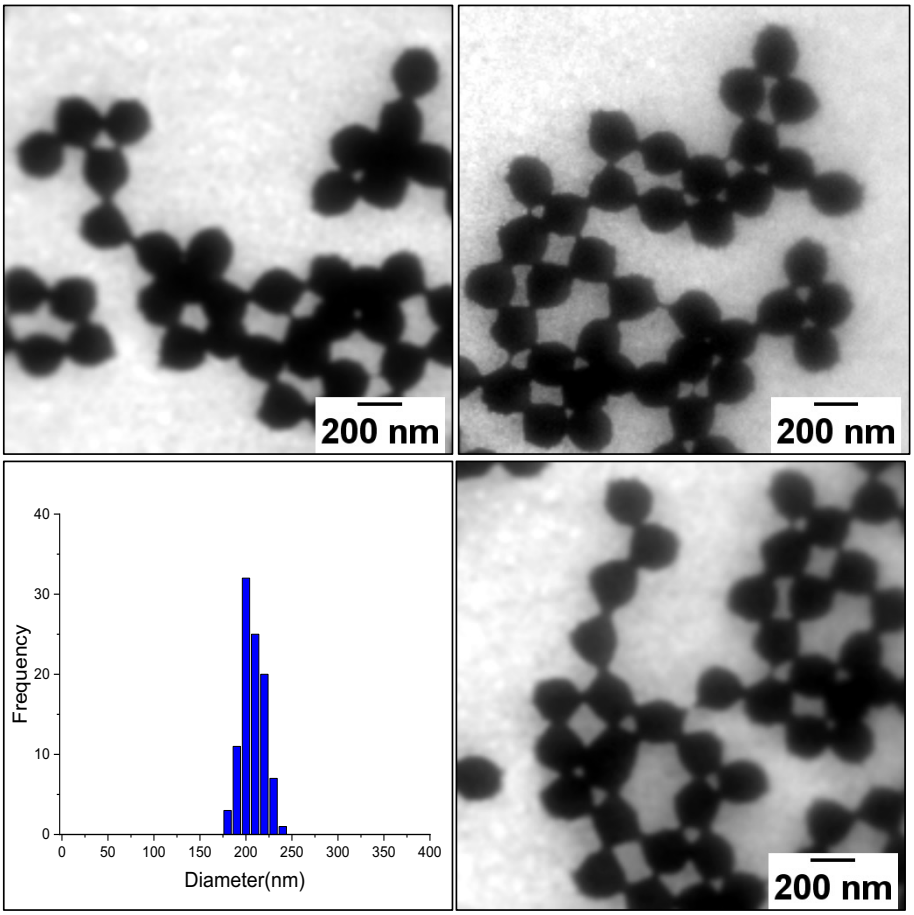



**Fig. S11.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-0.1GlyMA10) using R=0.1‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

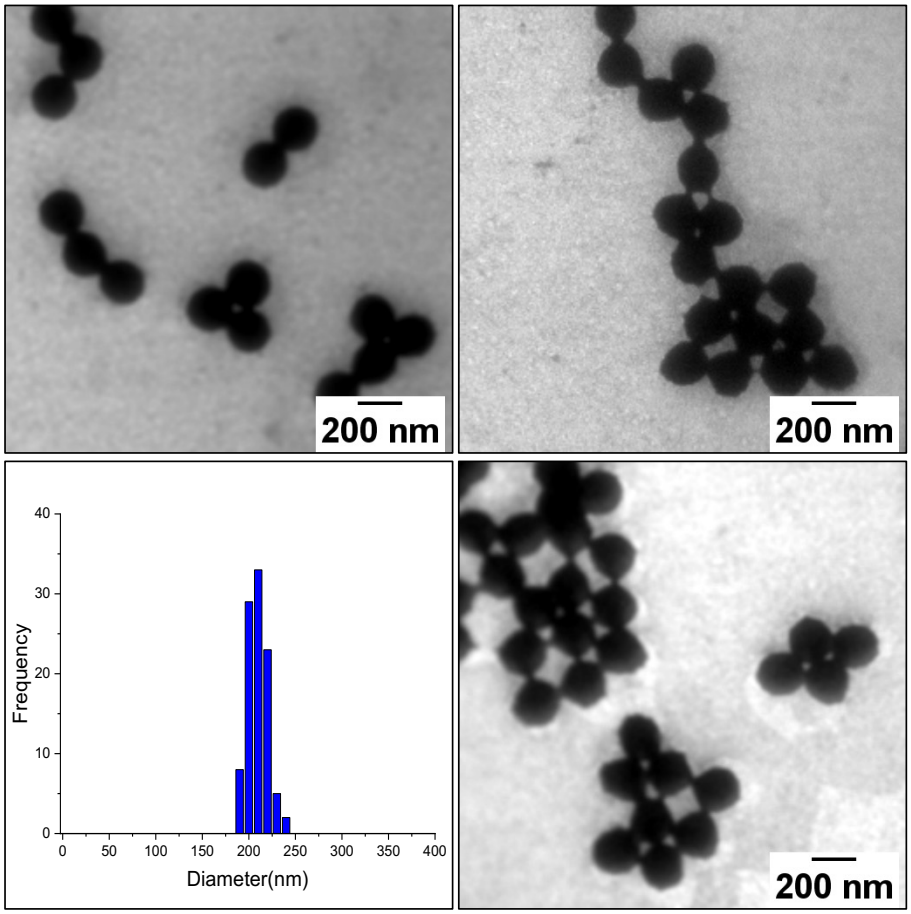



**Fig. S12.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-0.2GlyMA10) using R=0.2‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

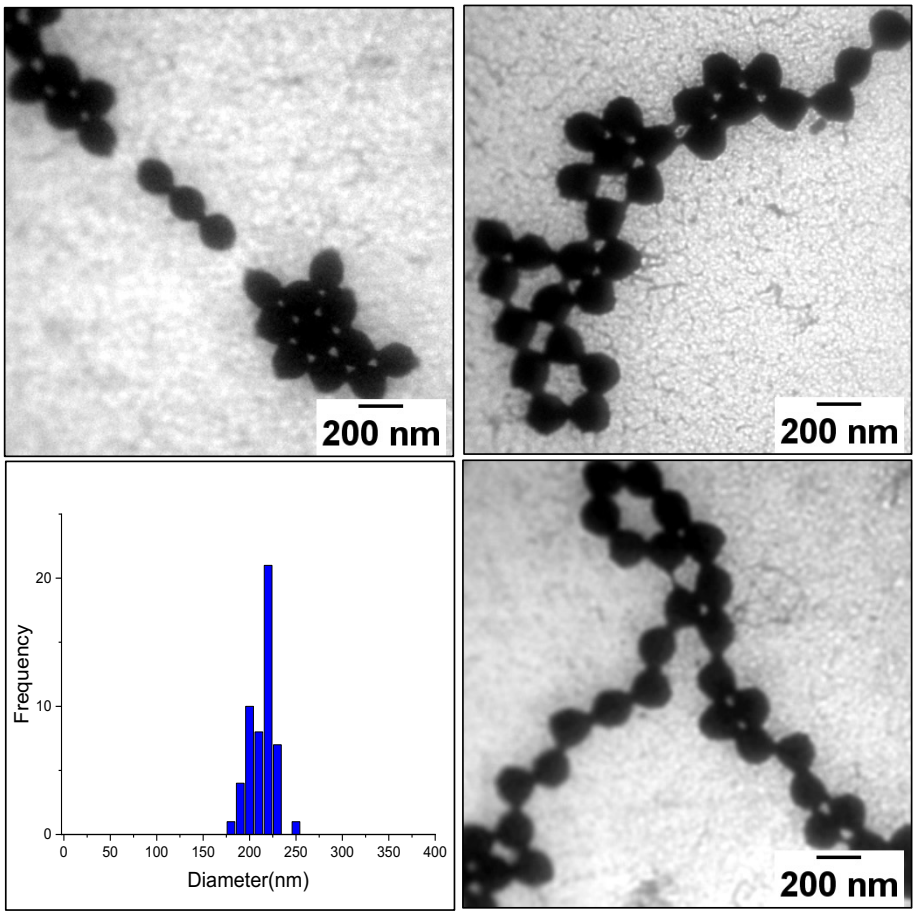



**Fig. S13.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-0.5GlyMA10) using R=0.5‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

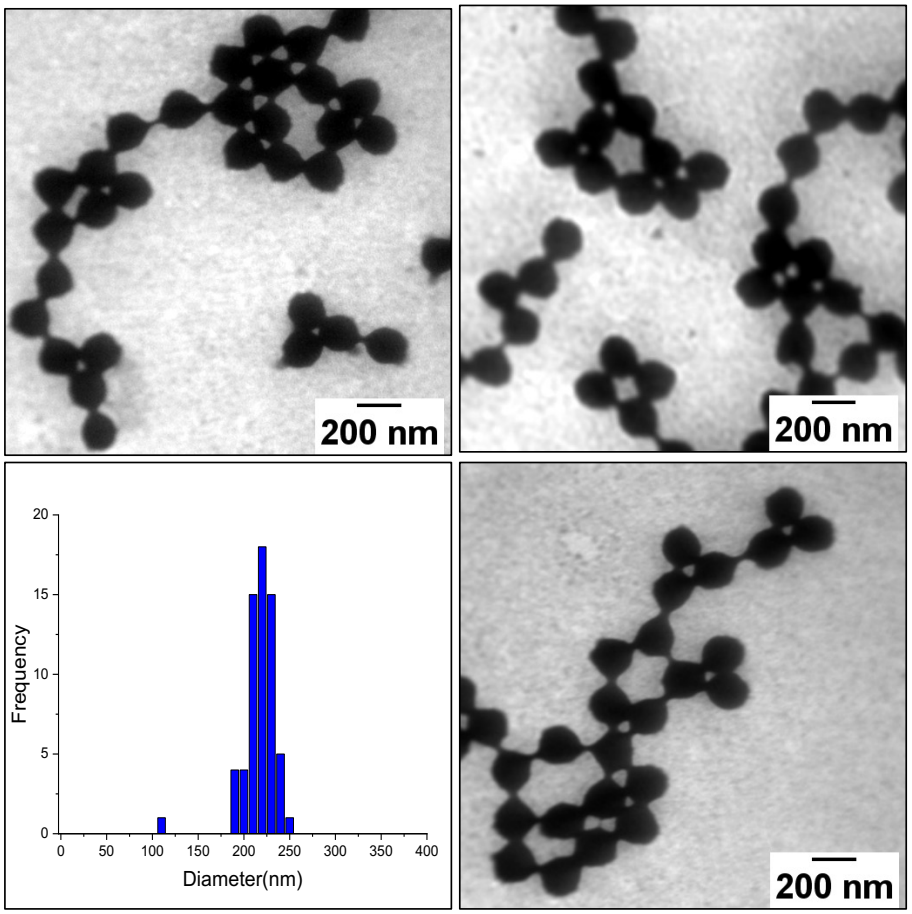



**Fig. S14.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-0.67GlyMA10) using R=0.67‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

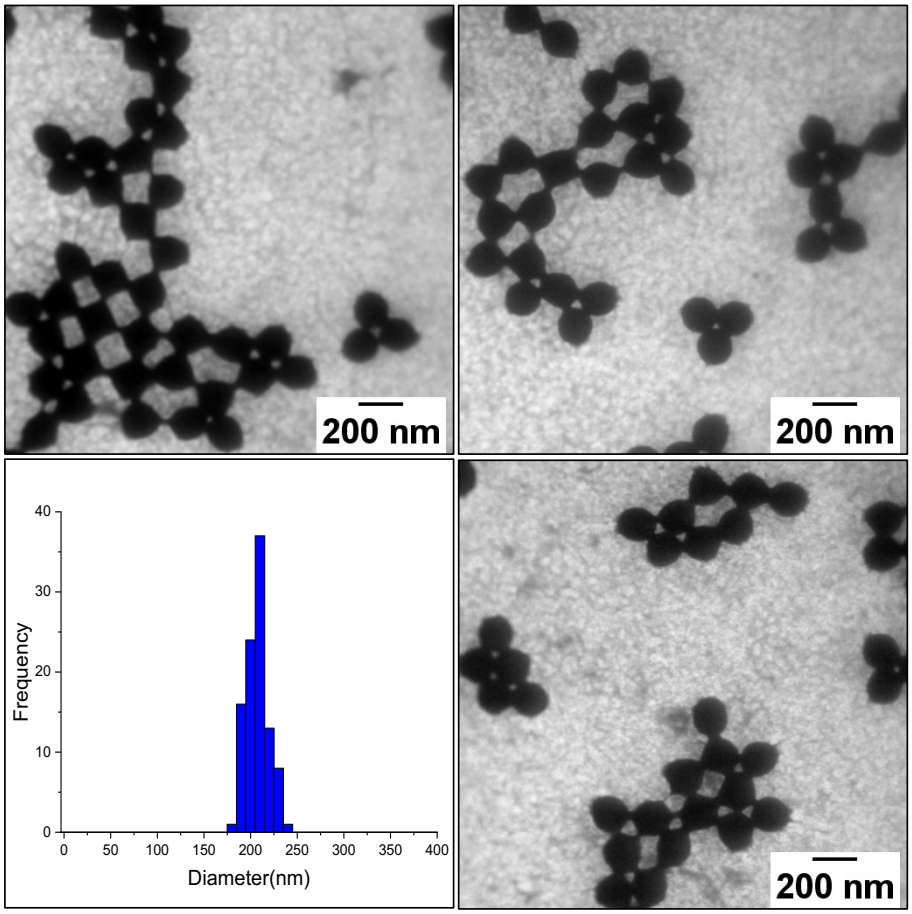



**Fig. S15.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-1GlyMA10) using R=1‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

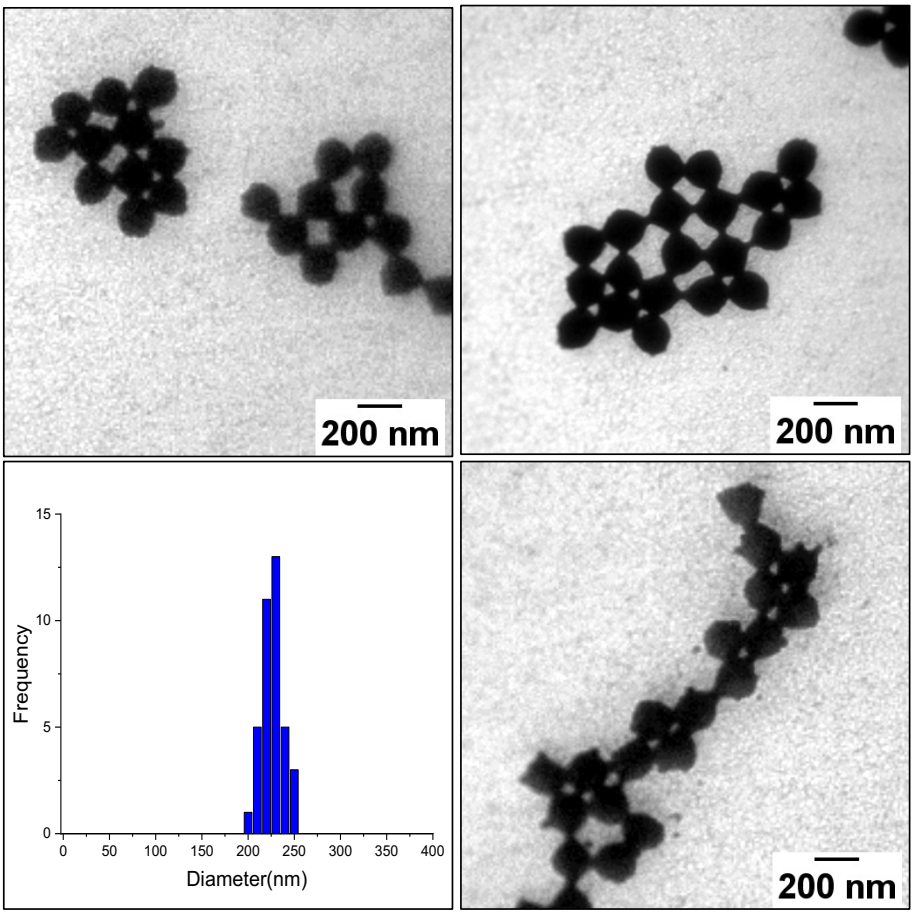



**Fig. S16.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-2.5GlyMA10) using R=2.5‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

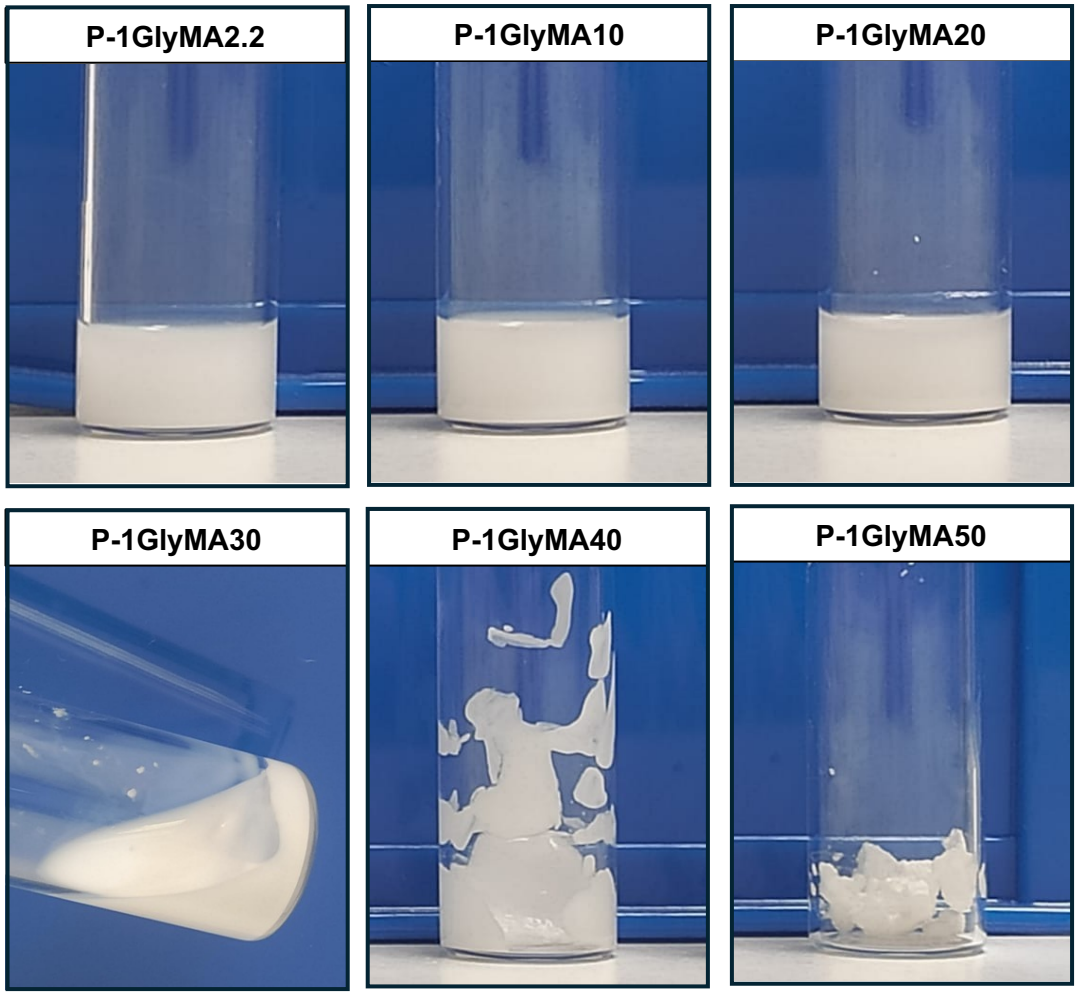



**Fig. S17.** Photographs of surfactant-free latex prepared *via* photo-SFEP of GlyMA under 405 nm irradiation using R=1‰ at different solids content.

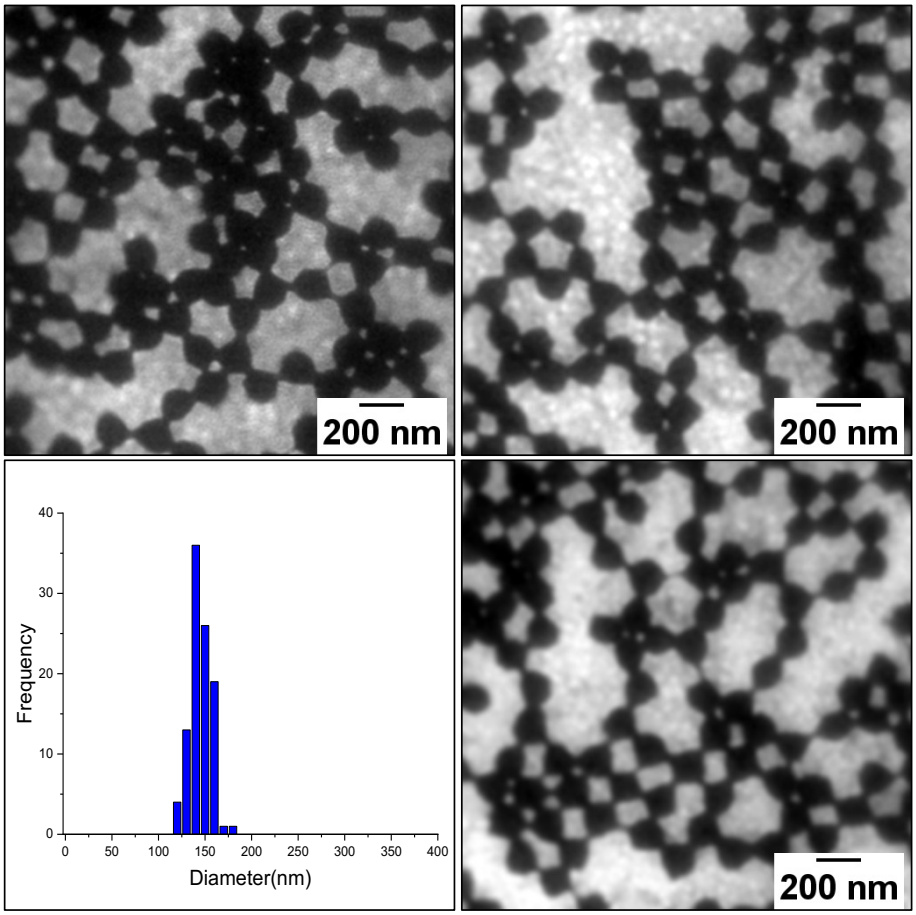



**Fig. S18.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-1GlyMA2.2) using R=1‰ and SC=2.2% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

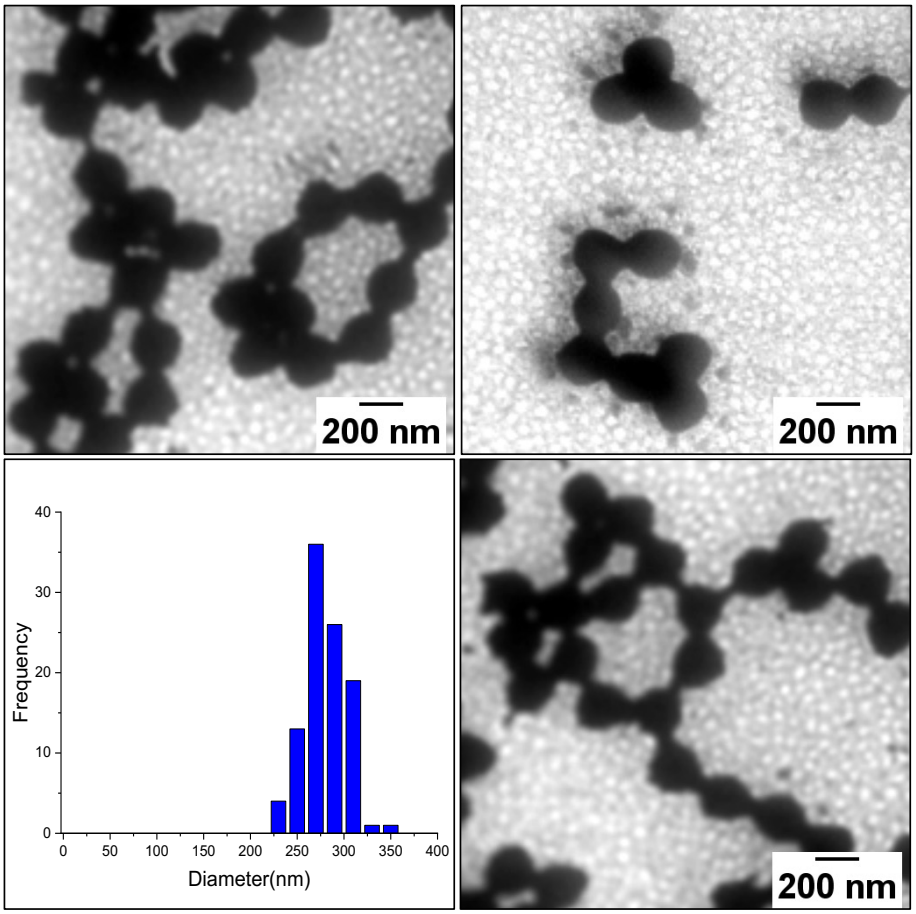



**Fig. S19.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-1GlyMA20) using R=1‰ and SC=20% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

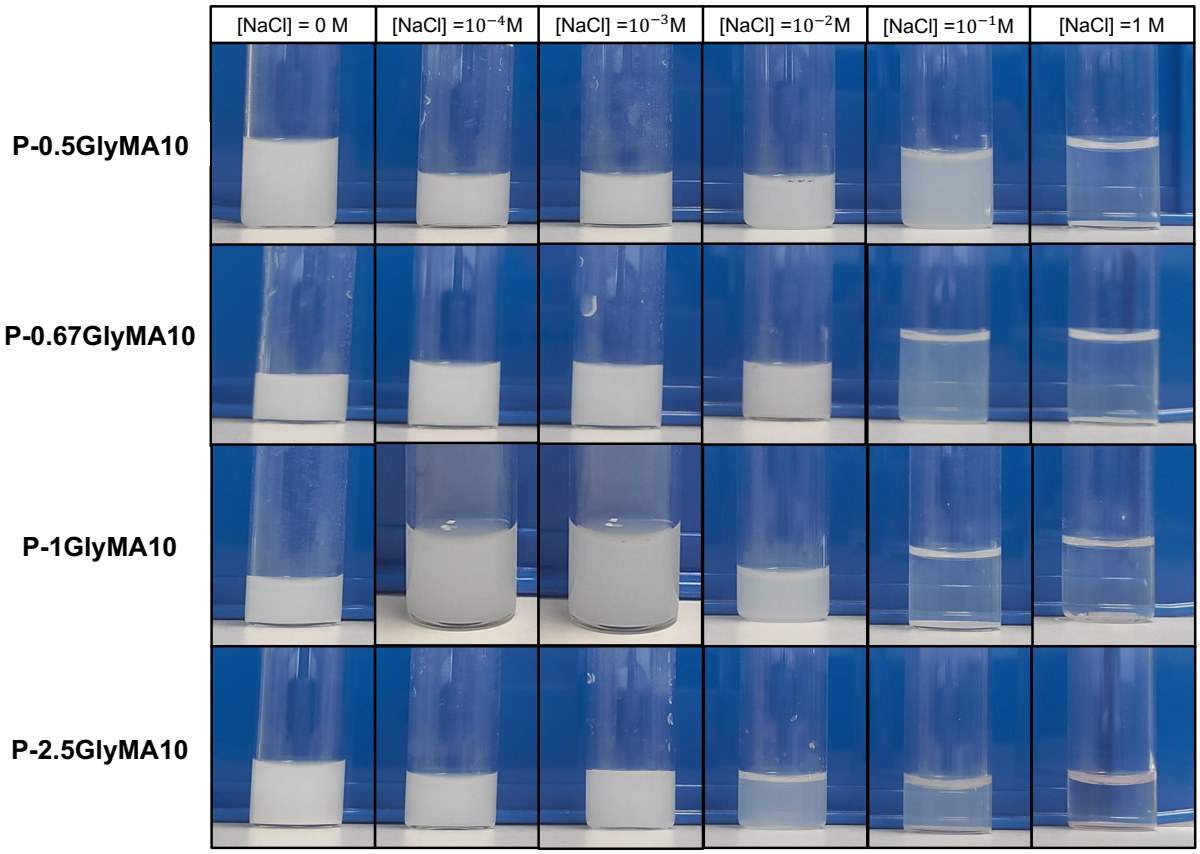



**Fig. S20.** Colloidal stability in ionic environment of surfactant-free latex prepared at SC=10%, *via* photo-SFEP of GlyMA under 405 nm irradiation using different TPO-Na/GlyMA ratio and different solids content, and diluted to 0.1% w/w using aqueous brine solutions with NaCl concentrations ranging from $10^{-4}$ to 1 mol/L.

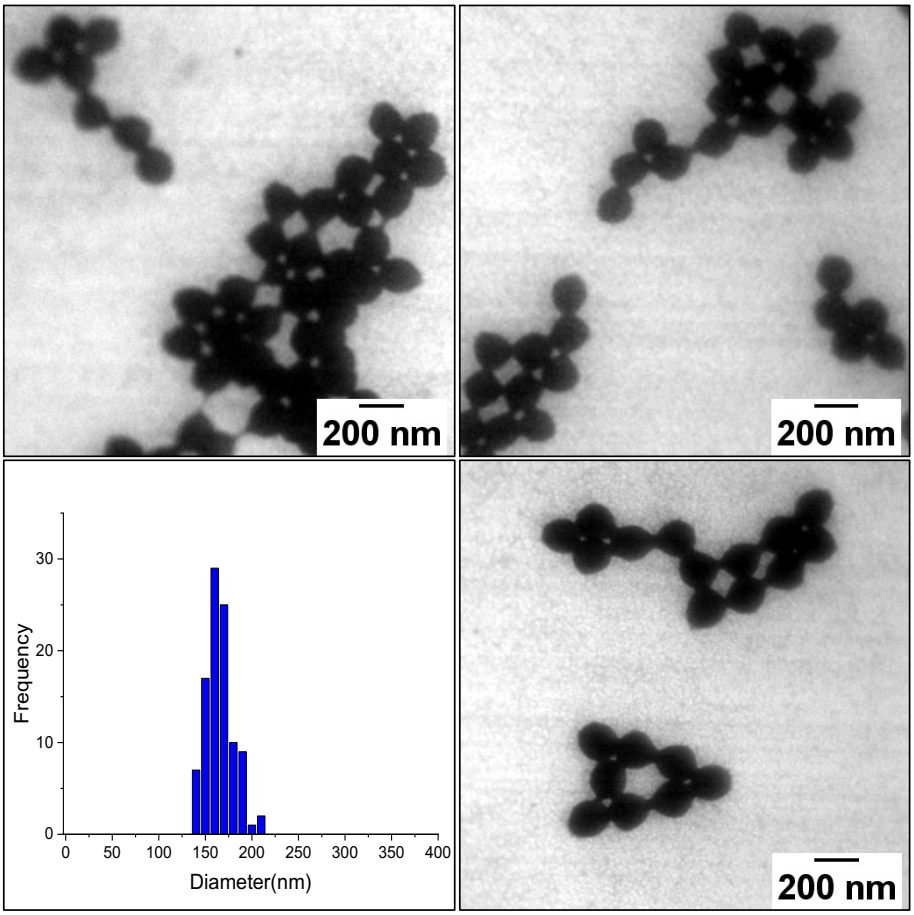



**Fig. S21.** Colloidal stability in ionic environment. TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-1GlyMA10) using R=1‰ and SC=10% w/w in water and diluted to 0.1% w/w using saline solution ($10^{-2}$ mol/L). The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

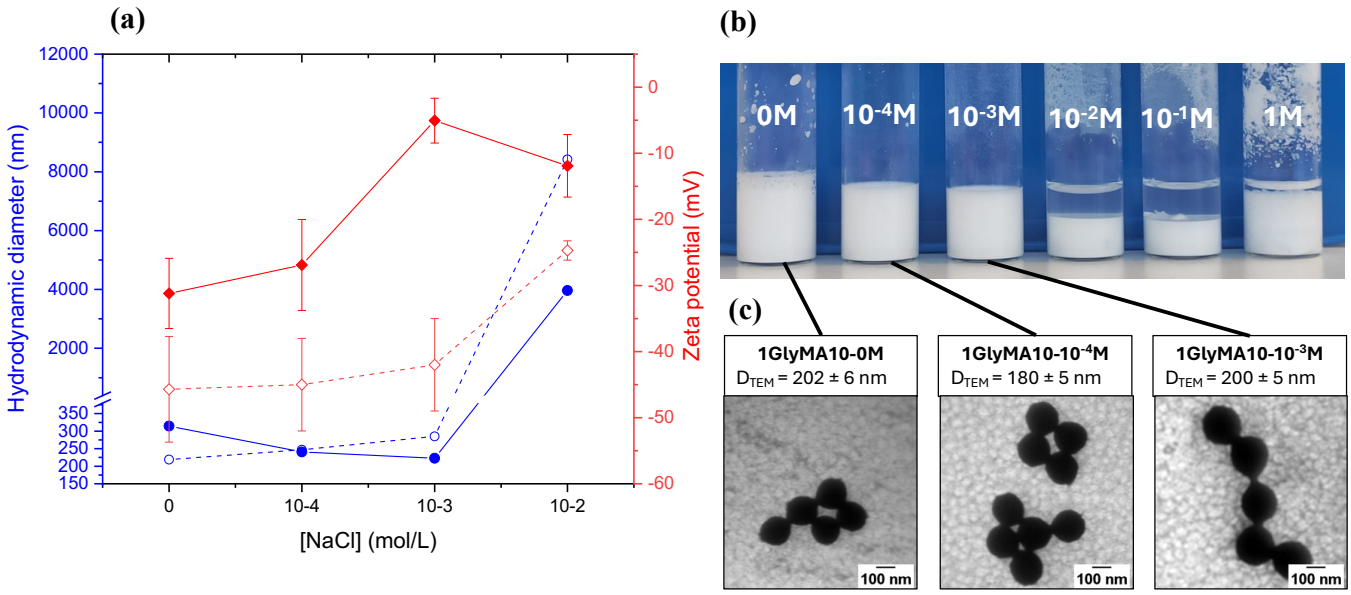



**Fig. S22.** Photo-SFEP of GlyMA in different NaCl concentration under 405 nm irradiation at SC=10% w/w and R=1‰ at RT. (a) Hydrodynamic diameters (circle) and zeta potentials (diamond) of nanoparticles immediately after formulation (open symbols) and after three months (solid symbols). (b) TEM images of nanoparticles immediately after formulation, and (c) photographs of latex dispersions after three months. $D_{TEM}$ values represent the average diameter of at least 50 nanoparticles, measured using ImageJ software.

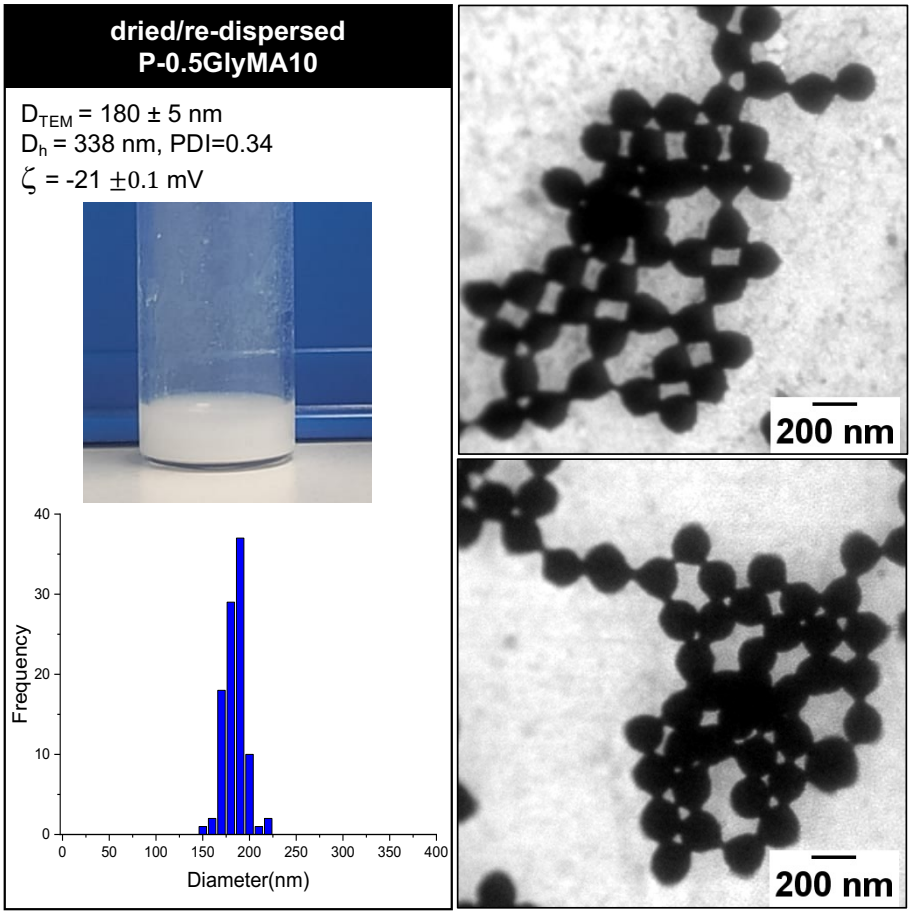



**Fig. S23.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-0.5GlyMA10) using R=0.5‰ and SC=10% w/w in water. The nanoparticles were lyophilized and subsequently re-dispersed in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

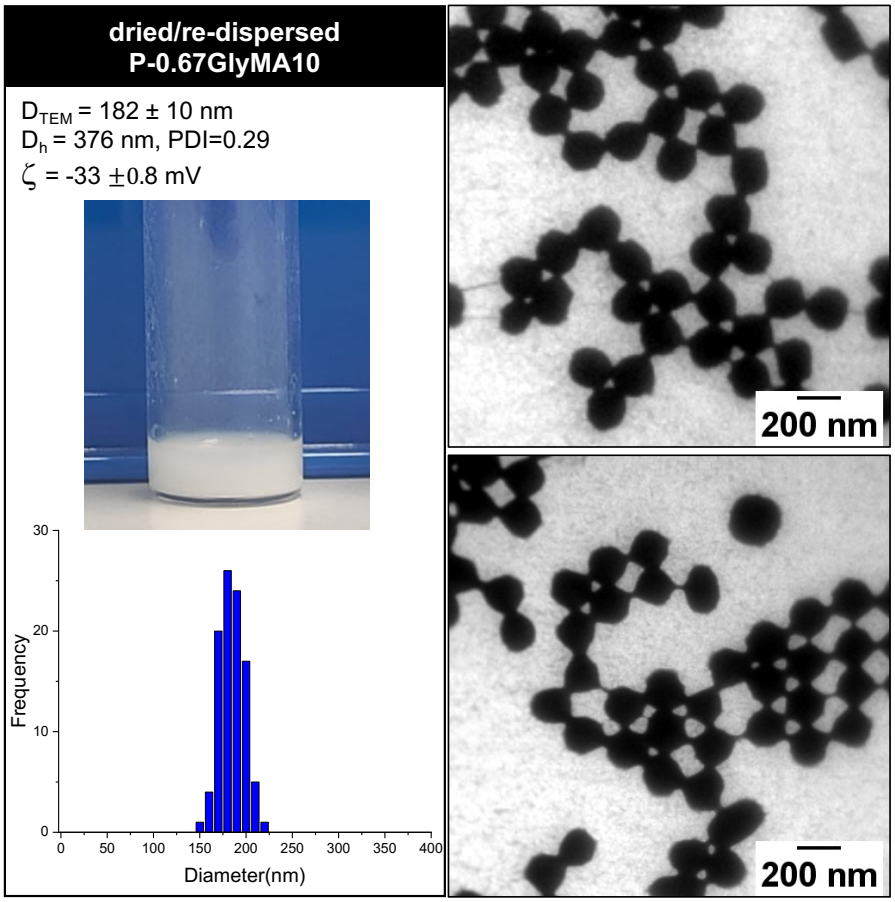



**Fig. S24.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-0.67GlyMA10) using R=0.67‰ and SC=10% w/w in water. The nanoparticles were lyophilized and subsequently re-dispersed in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

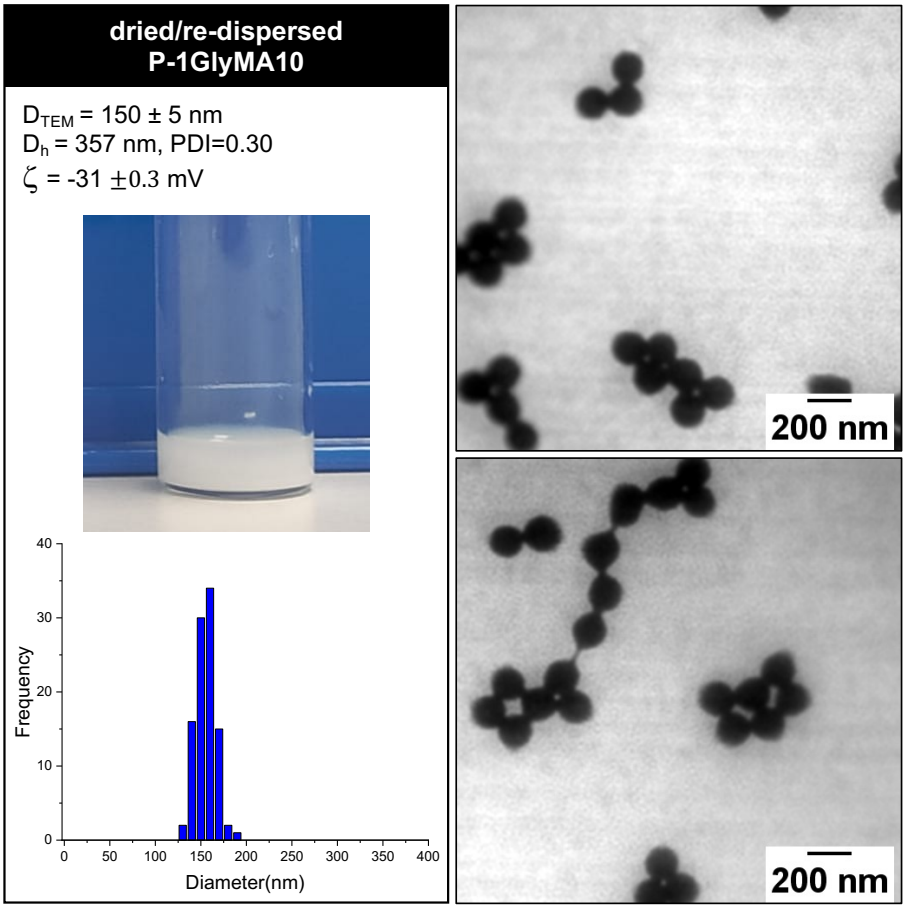



**Fig. S25.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-1GlyMA10) using R=1‰ and SC=10% w/w in water. The nanoparticles were lyophilized and subsequently re-dispersed in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

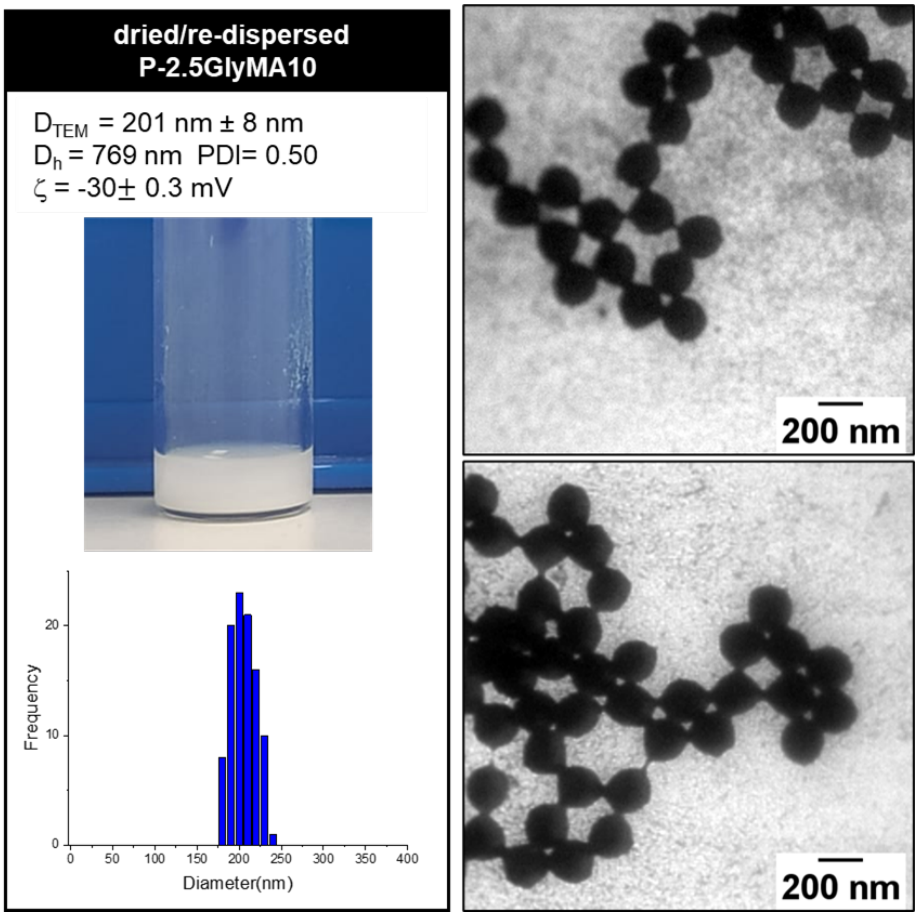



**Fig. S26.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under 405 nm at room temperature (P-2.5GlyMA10) using R=2.5‰ and SC=10% w/w in water. The nanoparticles were lyophilized and subsequently re-dispersed in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

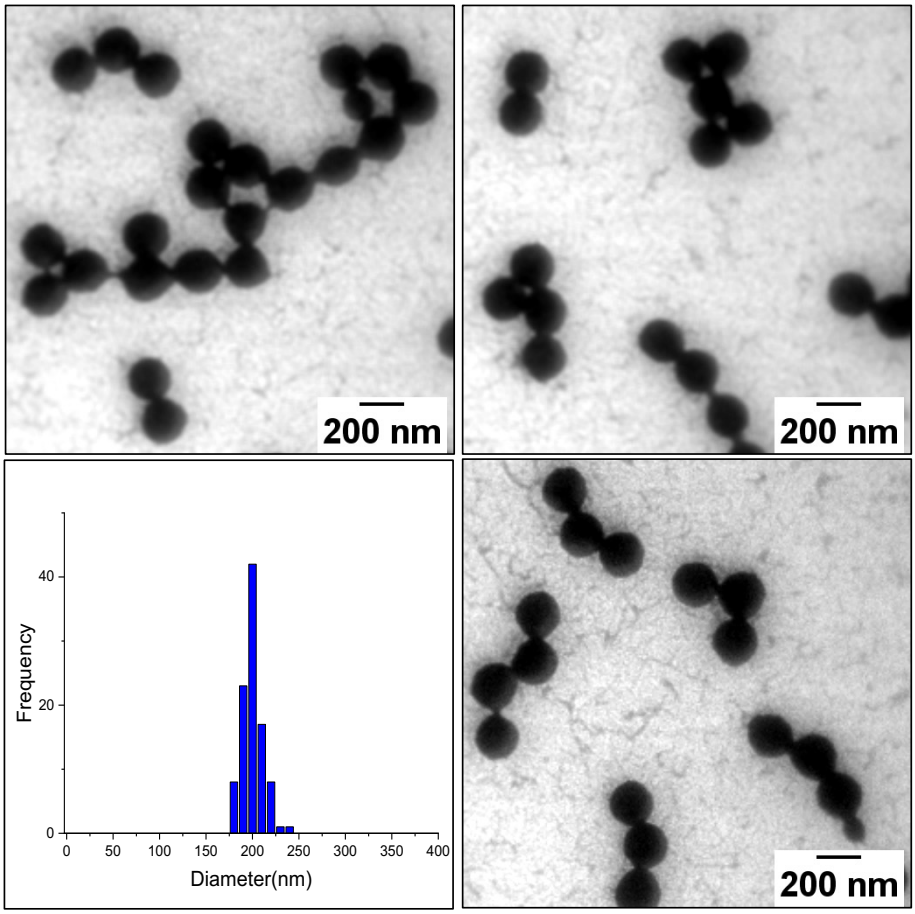



**Fig. S27.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA under sunlight (SL-1GlyMA10) using R=1‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

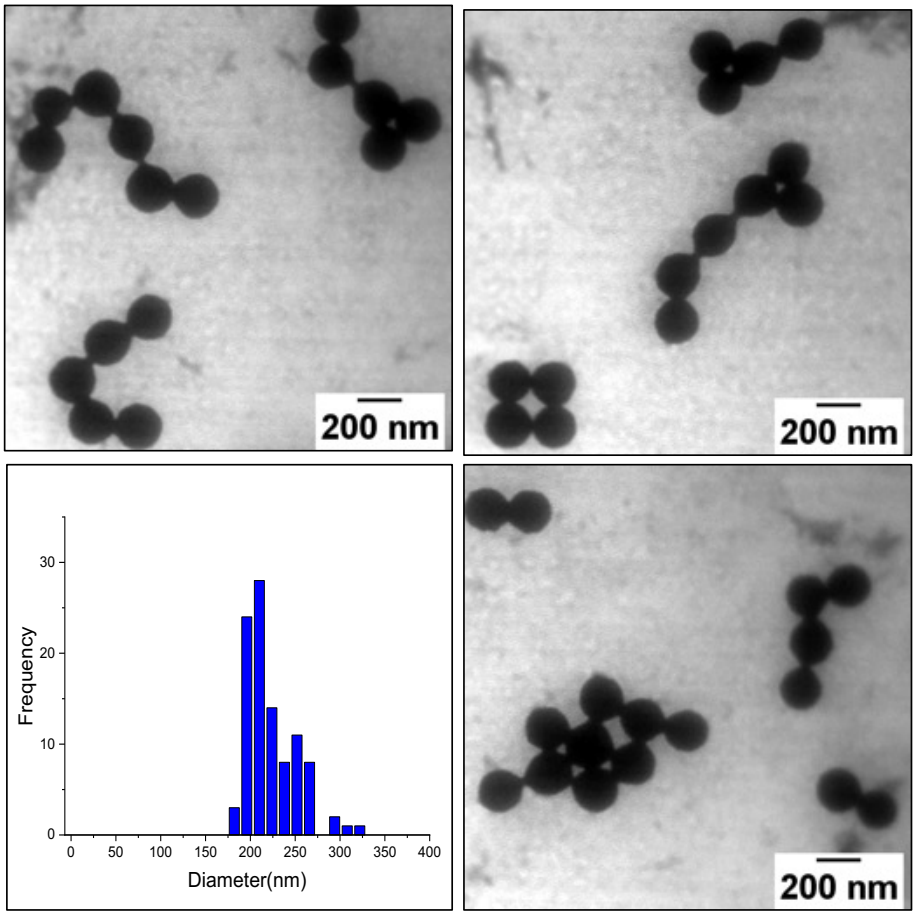



**Fig. S28.** TEM images of surfactant-free latex prepared *via* SFEP of GlyMA at large scalte (1L) under 405 nm using R=1‰ and SC=20% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

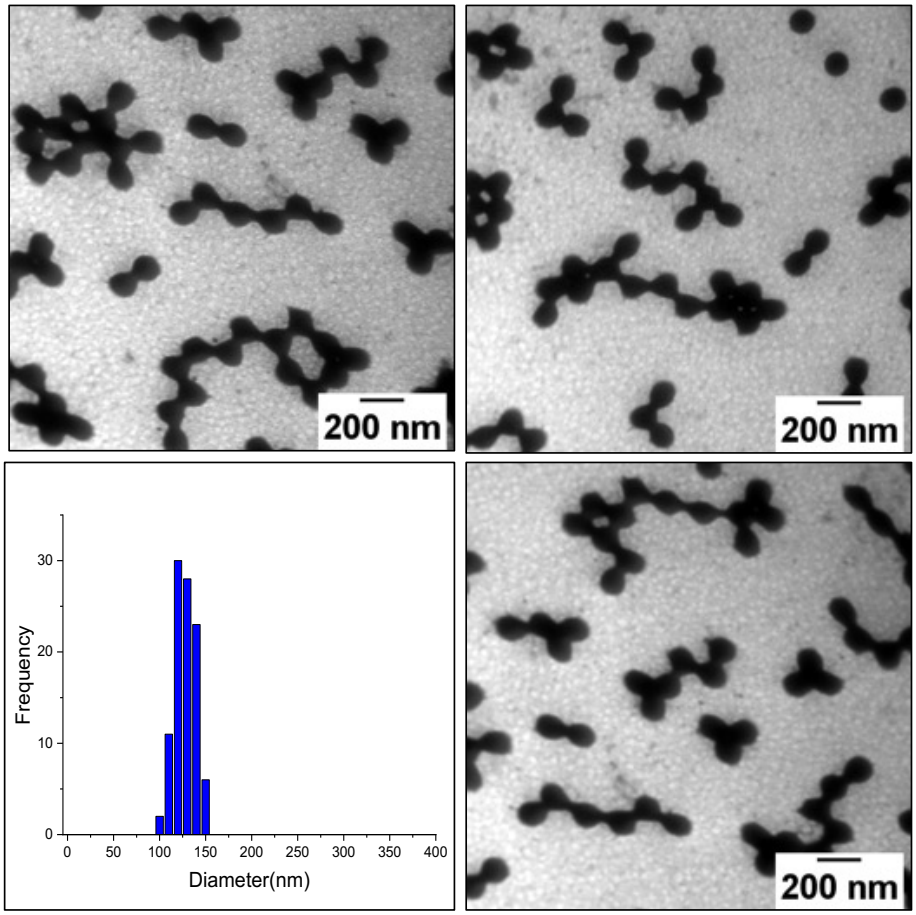



**Fig. S29.** TEM images of surfactant-free latex prepared *via* SFEP of VAc under 405 nm (P-1VAc10) using R=1‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

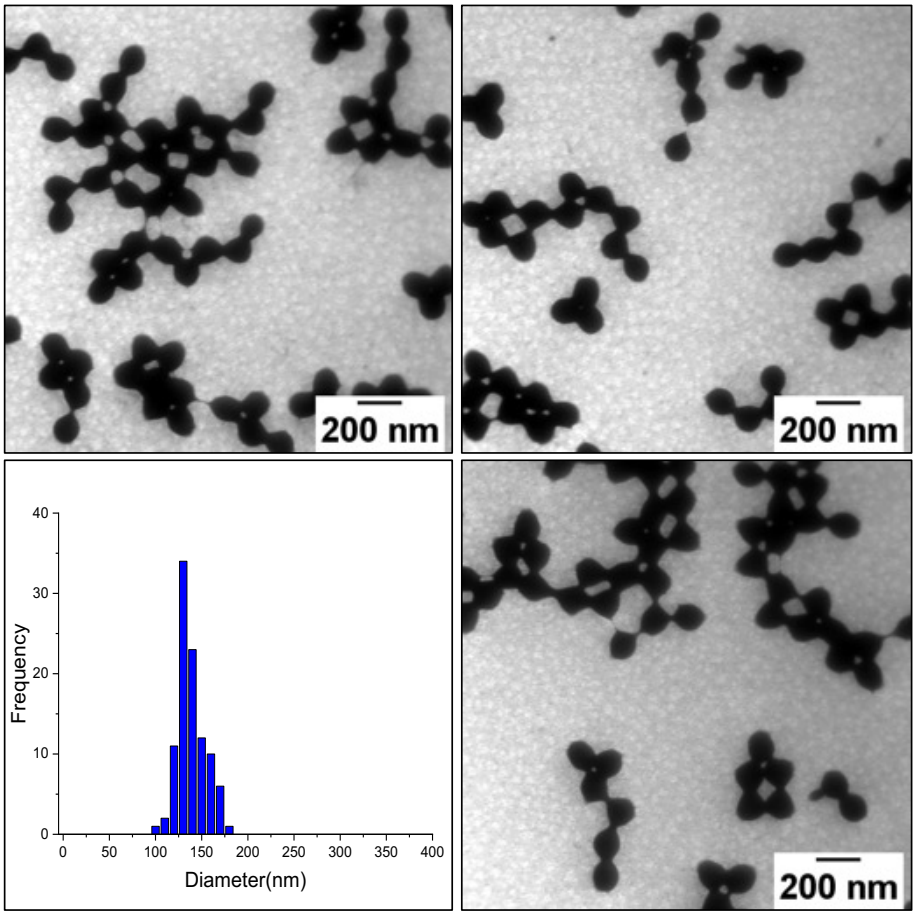



**Fig. S30.** TEM images of surfactant-free latex prepared *via* SFEP of MMA under 405 nm (P-1MMA10) using R=1‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.

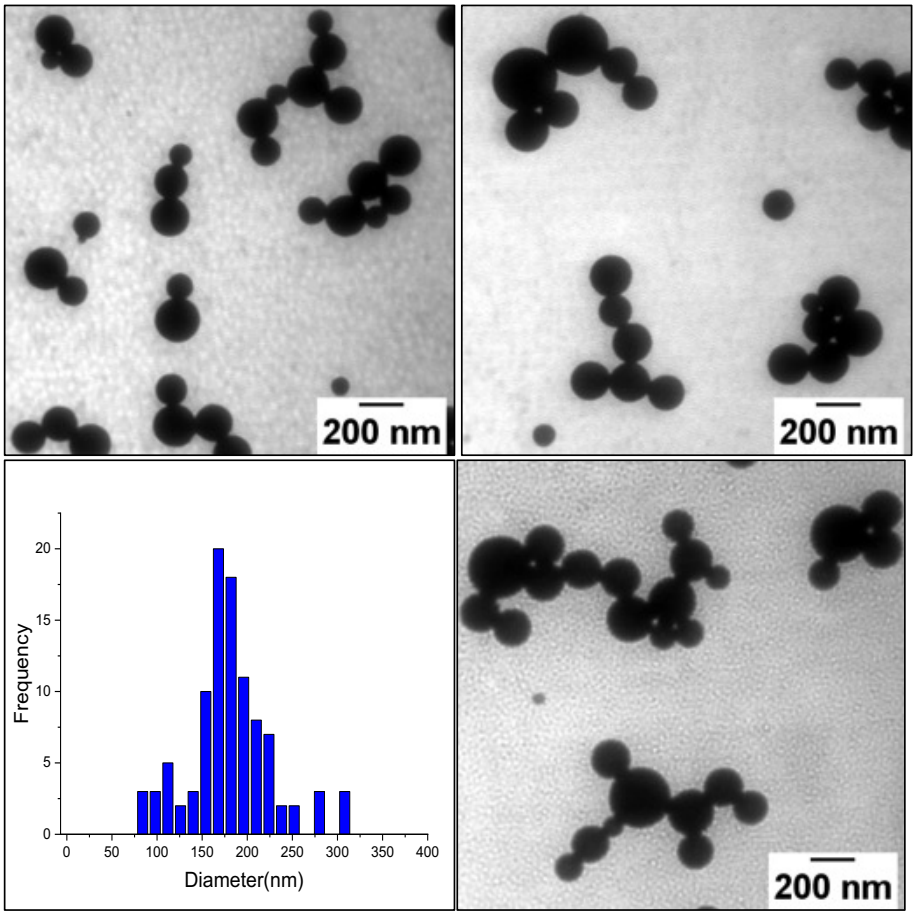



**Fig. S31.** TEM images of surfactant-free latex prepared *via* SFEP of styrene under 405 nm (P-1S10) using R=1‰ and SC=10% w/w in water. The histogram is the statistical analysis of the diameter measured for more than 50 nanoparticles using ImageJ software.