

Supporting Information

Miniemulsion Polymerization using Carboxylated Graphene Quantum Dots as Surfactants: Effects of Monomer and Initiator Type

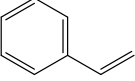
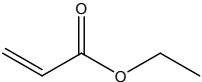
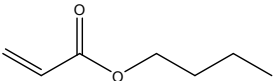
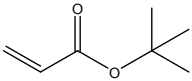
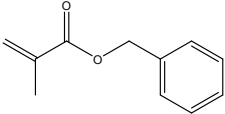
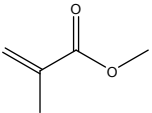
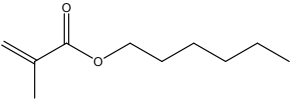
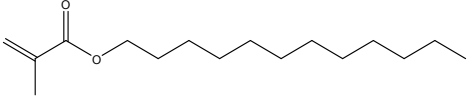
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Table S1. Water solubility and density of monomers employed for miniemulsion polymerization.

Monomer	Chemical structure	Solubility in water	Density at 25 °C¹ (g/mL)
St		300 mg/L at 25°C ¹	0.906
EA		20 g/L at 20°C	0.918
<i>n</i> BA		1.4 g/L at 20°C ²	0.894
<i>t</i> BA		c.a. 2 g/L	0.875
BzMA		190 mg/L at 20°C ³	1.04
MMA		15.3 g/L at 20°C	0.936
HMA		39.97 mg/L at 25°C (est.) ⁴	0.863
LMA		3 mg/L ⁵	0.868

Information obtained from supplier

Table S2. Conversion, PDI and zeta potential of the cGQDs/polymer nanocomposites after 24 h AIBN-initiated and VA-044-initiated miniemulsion polymerization using 7 wt.% cGQDs as sole surfactant.

Monomer	Conversion (%)		PDI		Zeta potential (mV)	
	AIBN	VA-044	AIBN	VA-044	AIBN	VA-044
St	62.0	88.1	0.10 ± 0.02	0.31 ± 0.07	-38.9 ± 0.2	51.1 ± 0.3
EA	16.3	58.9	0.04 ± 0.03	0.15 ± 0.04	-42.1 ± 1.1	59.3 ± 0.7
BA	10.4	81.8	0.43 ± 0.02	0.38 ± 0.04	-46.8 ± 1.1	67.3 ± 2.0
tBA	20.3	62.5	0.89 ± 0.18	0.10 ± 0.09	-48.6 ± 1.5	54.8 ± 0.4
BzMA	27.9	60.7	0.26 ± 0.04	0.87 ± 0.03	-46.3 ± 0.8	61.8 ± 0.4
MMA	53.2	69.2	0.79 ± 0.18	0.69 ± 0.12	-26.6 ± 0.4	55.3 ± 2.8
HMA	13.2	21.8	0.08 ± 0.03	0.85 ± 0.01	-44.5 ± 1.1	56.2 ± 0.7
LMA	43.4	9.7	0.26 ± 0.01	0.78 ± 0.19	-44.9 ± 0.8	8.11 ± 1.0

Table S3. DLS average particle size in nanometres (nm) in terms of z-average, intensity, volume, and number after 24 h miniemulsion polymerization initiated by AIBN and VA-044.

Monomer	Z-Average		Intensity		Number		Volume	
	AIBN	VA-044	AIBN	VA-044	AIBN	VA-044	AIBN	VA-044
St	212	657	233	540	173	513	236	571
EA	131	432	138	462	112	419	130	491
BA	454	901	349	775	326	662	363	888
tBA	1798	698	3508	728	365	697	3703	770
BzMA	241	1705	345	548	144	548	382	555
MMA	6046	1394	523	539	508	533	515	548
HMA	193	1347	208	562	168	555	213	570
LMA	164	879	152	2276	120	213	145	2584

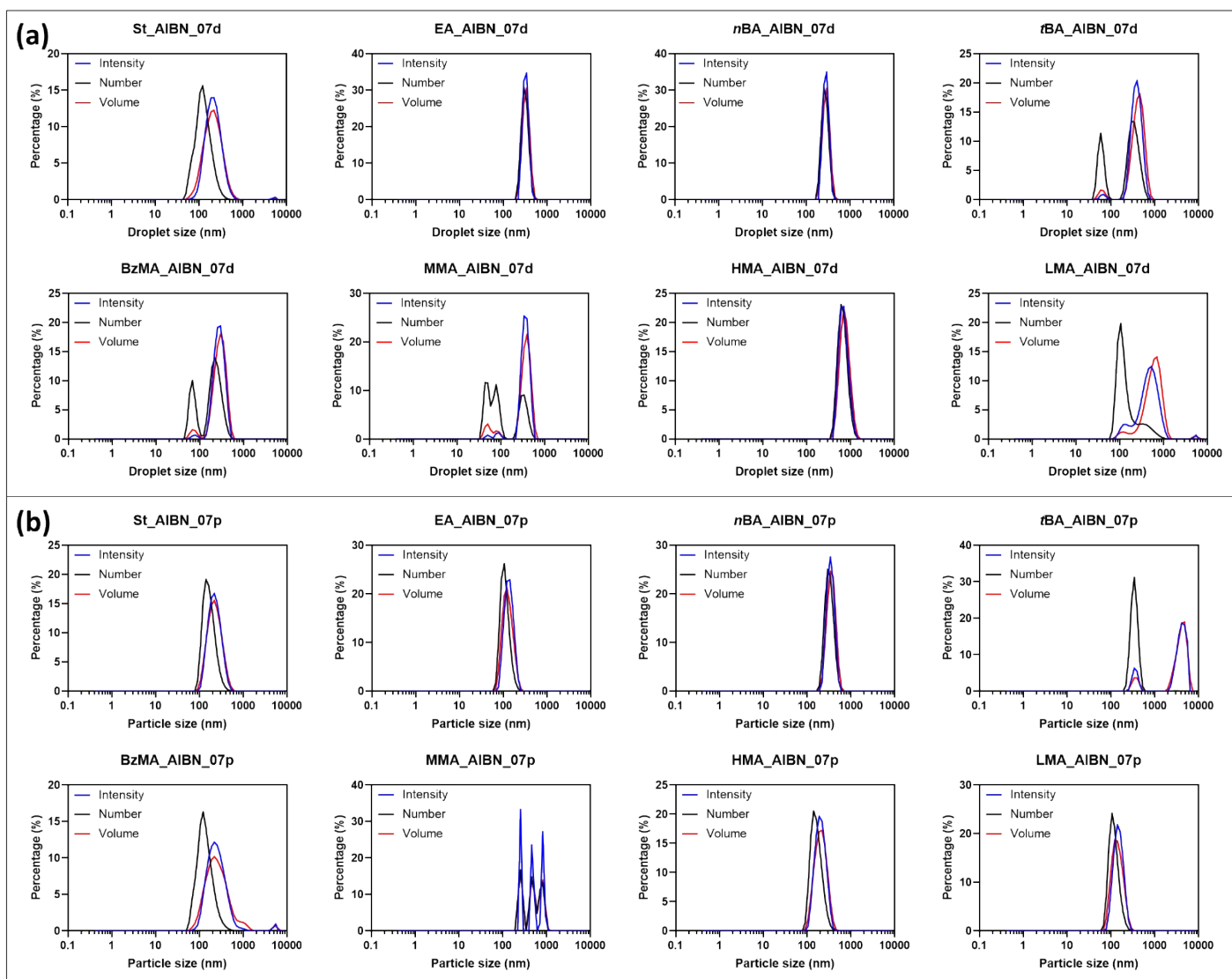


Fig. S1. DLS-generated (a) droplet size distribution after 10 min ultrasonication and (b) particle size distribution of miniemulsions after 24 h AIBN-initiated polymerization using 7 wt.% cGQDs relative to monomer as sole surfactant.

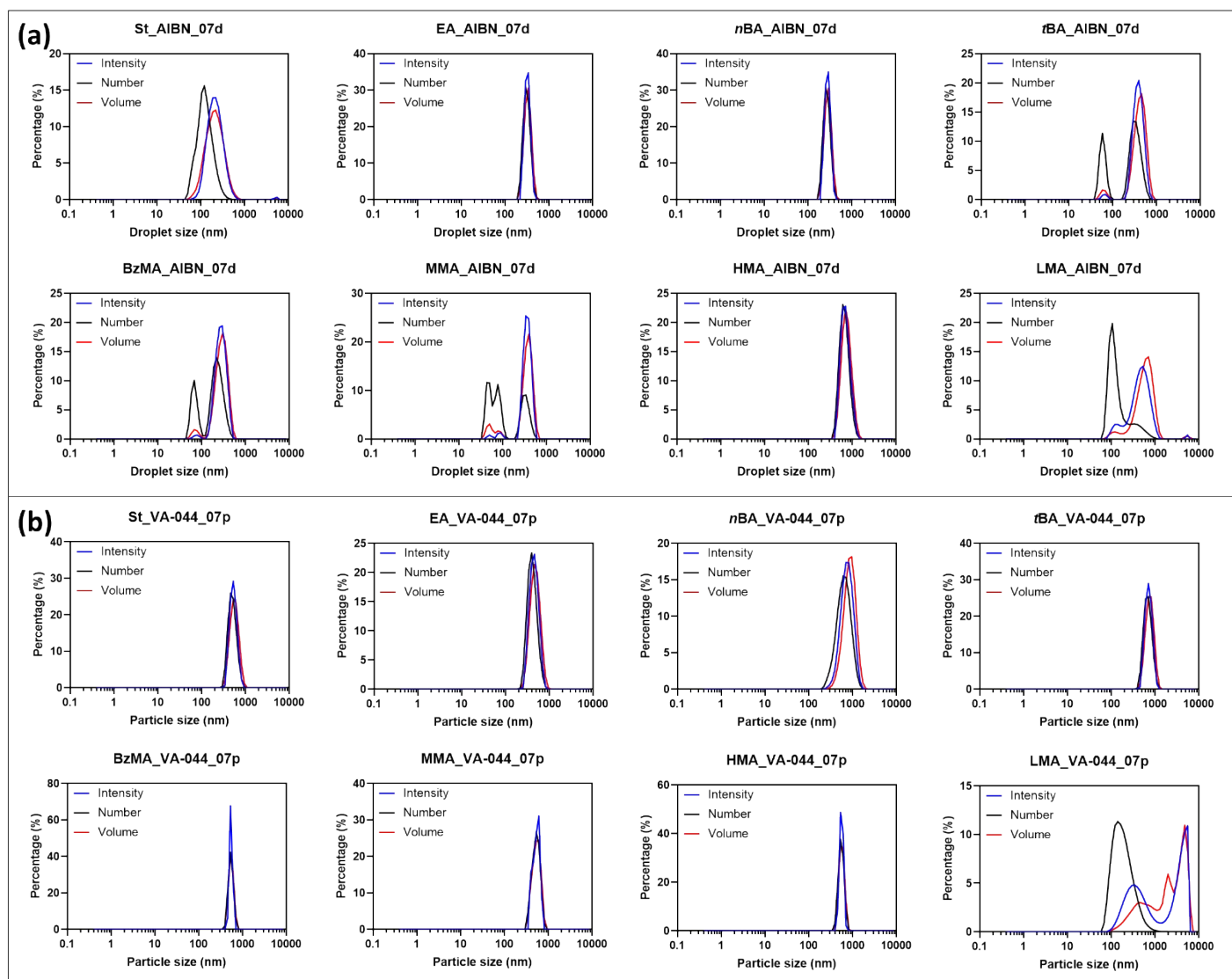


Fig. S2. DLS-generated (a) droplet size distribution after 10 min ultrasonication and (b) particle size distribution of miniemulsions after 24 h VA-044-initiated polymerization using 7 wt.% cGQDs relative to the monomer as sole surfactant.

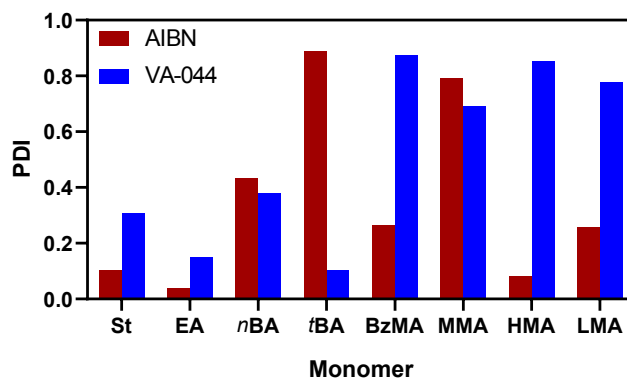


Fig. S3. Polydispersity index (PDI) after 24 h miniemulsion polymerization initiated by AIBN (red) and VA-044 (blue).

The cumulative concentration of radicals (*i.e.* total number of radicals generated from initiator decomposition as a function of time) generated from AIBN and VA-044 over 24 h of polymerization was calculated as follows:

$$[R]_{\text{gen}} = 2fI_0(1 - e^{-k_d t})$$

where: $[R]_{\text{gen}}$ is the concentration of generated radicals (M)

f is the initiator efficiency (an assumed value of 0.6 is used for both initiators)

I_0 is the initial concentration of initiator (0.25 M relative to organic phase)

k_d is the decomposition rate of initiator (s^{-1})

For AIBN, $k_d = 4.47 \times 10^{15} \times e^{\frac{-131.7}{RT}}$ and for VA-044, $k_d = 4.37 \times 10^{12} \times e^{\frac{-106.7}{RT}}$. The values of activation energies and pre-exponential factors are obtained from Moad.⁶ A cumulative radical concentration versus time plot was constructed below.

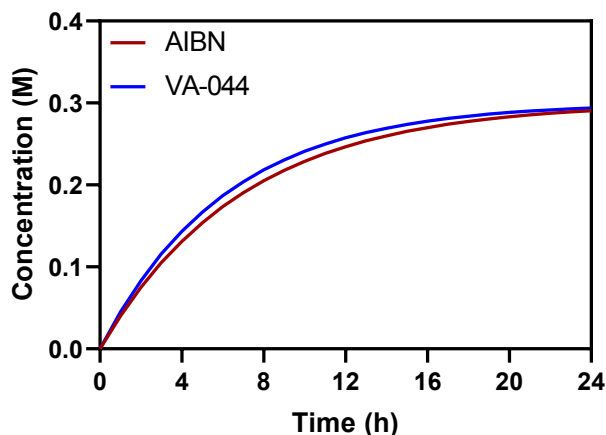


Fig. S4. Cumulative concentration of radicals generated from AIBN (blue, 70 °C) and VA-044 (red, 55 °C) over 24 h of polymerization. Note that these concentrations do not reflect actual radical concentrations in the system (which would be much lower) given that radical consumption is not accounted for – this is only to demonstrate that radical generation rates are similar.

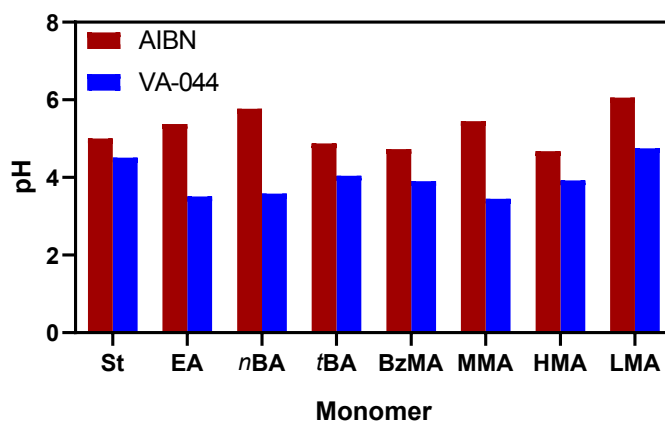


Fig. S5. pH values of each polymer after 24 h miniemulsion polymerization initiated by AIBN (red) and VA-044 (blue), measured using a pH meter.

References

1. Samuel, H.; Yalkowsky, H.; Jain, P., Handbook of aqueous solubility data. CRC Press Boca Raton: 2010.
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