A FAST EMULSION POLYMERIZATION IN AN OPEN-TO-AIR ENVIRONMENT

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Fenton Chemistry: The Fenton reaction is a chemical process that involves the production of hydroxyl radicals (HO•) by activating (reducing) hydrogen peroxide (H_2O_2) with ferrous (Fe^{2+}) ions. This complex reaction proceeds as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^{-} \quad (k = 63\text{-}76\ M^{-1}s^{-1}) \qquad \text{..... (1)}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad (k = 0.001\text{-}0.01\ M^{-1}s^{-1}) \qquad \text{..... (2)}$$

In situations where there is an excess of both H_2O_2 and Fe^{2+}, the hydroxyl radicals (HO•) generated in this process exhibit non-specific reactivity, leading to various competing reactions as described in Equations (3)-(5). These additional reactions are generally undesirable in other organic oxidation processes and are considered inhibitory pathways in the present study.

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^{-} \quad (k = 3.2 \times 10^{8}\ M^{-1}s^{-1}) \qquad \text{..... (3)}$$

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (k = 3.3 \times 10^{7}\ M^{-1}s^{-1}) \qquad \text{..... (4)}$$

$$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2 \quad (k = 6 \times 10^{9}\ M^{-1}s^{-1}) \qquad \text{..... (5)}$$

It's important to note that the rate constants mentioned here are obtained from the existing literature and are crucial parameters in understanding the kinetics of these reactions.

***β*-D-glucose oxidation process: H_2O_2 production**

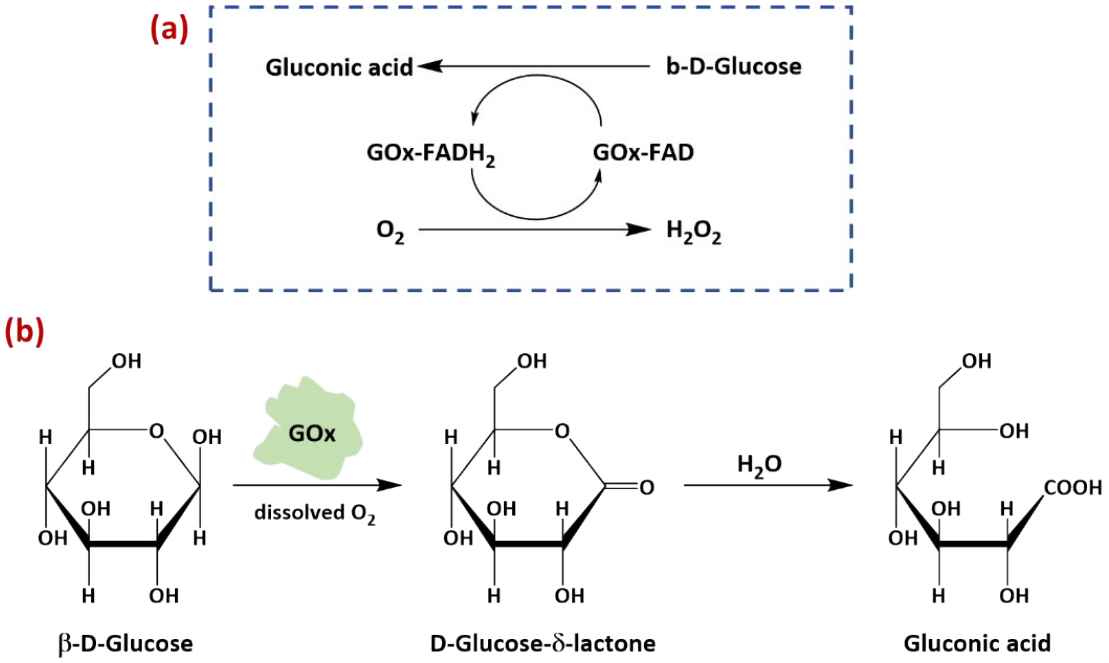


Figure S1: Enzymatic assisted removal of oxygen. Representation of GOx/D-glucose system: (a) schematic representation of H_2O_2 generation, and (b) mechanism of β-D-glucose oxidation to produce gluconic acid in aqueous medium in the presence of molecular oxygen.

Table S1: Monomer Conversion (wt. %) concerning time for BMA homopolymerization. Reaction conditions utilized: Temperature = R.T., time = varied; reagent concentrations: BMA = 5% v/v, SDS = 1 wt. %, GOx/Fe(II) = 2 µM/1 mM, D-glucose = 0.55 mM.

Time	Conversion[ψ] (wt. %)	$M_{n,GPC}$[Ŧ] (g/mol)	Đ[Ŧ]
5 min	65	104,000	1.77
10 min	67	105,000	1.82
15 min	68	104,000	1.85
30 min	70	105,000	1.81
1 hour	75	105,000	1.70
2 hours	84	104,000	1.83
3 hours	93	105,000	1.78
4 hours	100	105,000	1.77

ψ Conversion (wt. %) was calculated gravimetrically, as discussed in the experimental section.
Ŧ $M_{n,GPC}$ and Đ represent the Number average molecular weight and dispersity of the polymers obtained via GPC, respectively.

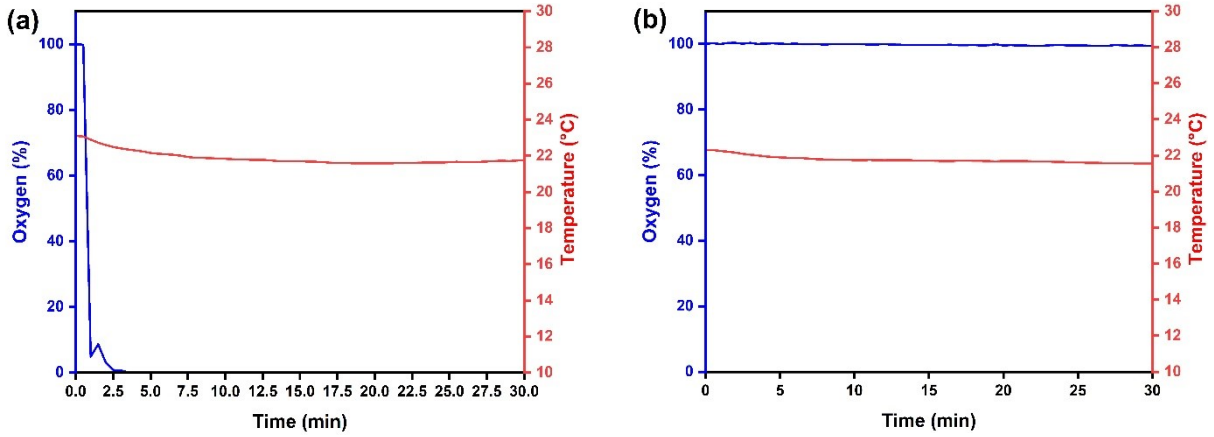
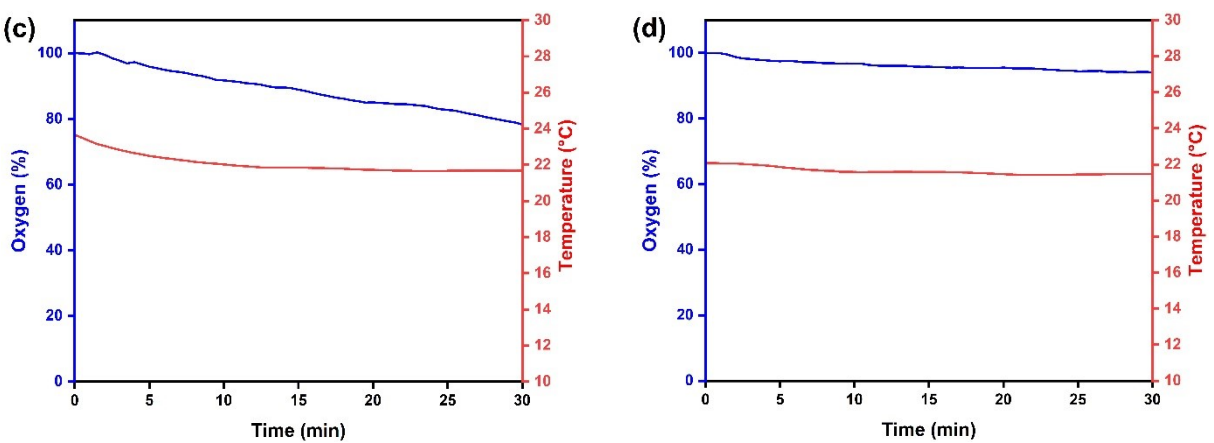


Figure S2: Monitoring the dissolved oxygen concentration of water-based solution containing (a) GOx and D-glucose, (b) only water, (c) D-glucose, and (d) GOx. Reaction conditions utilized: [GOx] = 2 µM, D-glucose = 0.1 g.



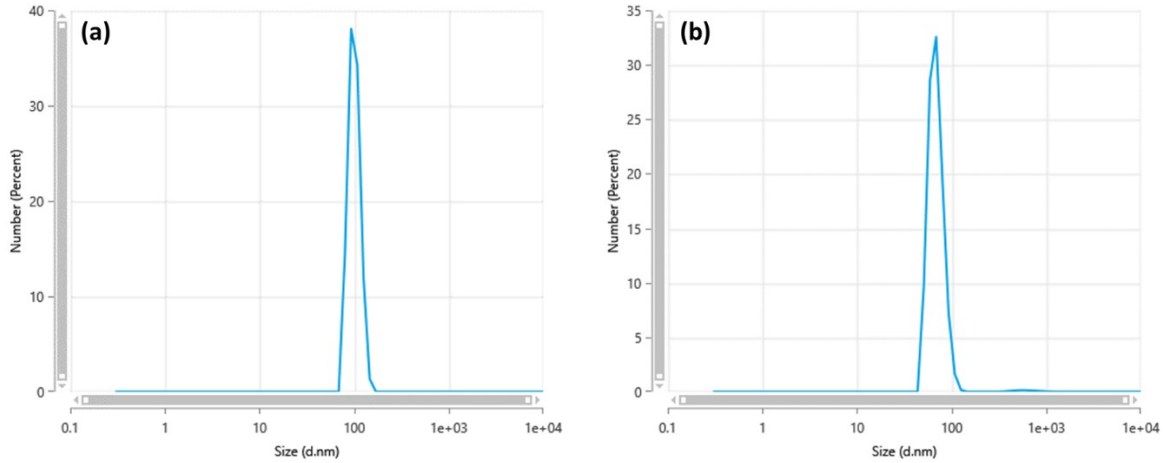


Figure S3: DLS Z-avg size of particles pre-polymerization for (a) Entry 10 and (b) Entry 12 from Table 1. The values were found to be 138.34 nm for 1 wt.% SDS (Entry 10) and 80.25 nm for 2.5 wt.% SDS (Entry 12).

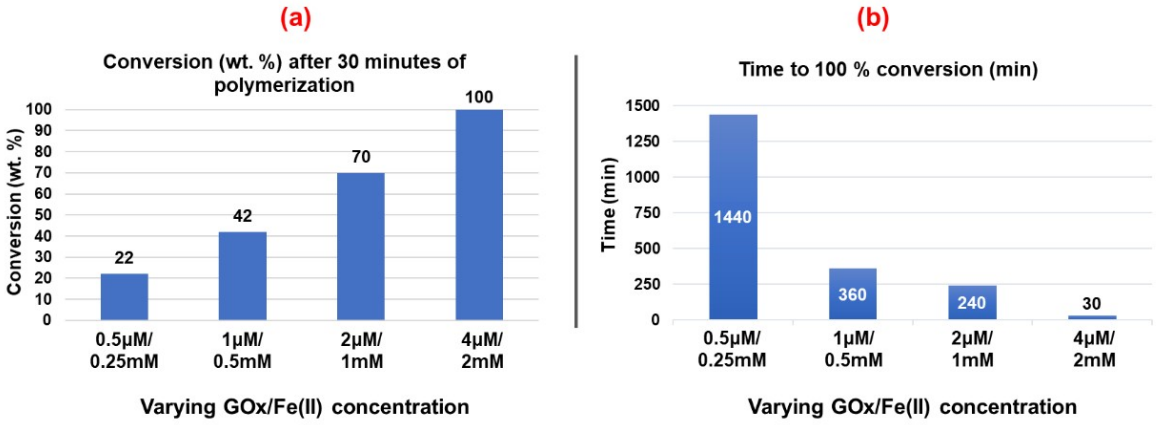


Figure S4: (a) Monomer conversion (wt.%) after 30 min of polymerization for each initiating catalyst system; (b) time (min) required for a full conversion of monomer under varying catalyst concentrations. Conditions utilized for these polymerizations: BMA = 5 % v/v, SDS = 1 wt. %, GOx/Fe(II) = varied, D-glucose = 0.55 mM.

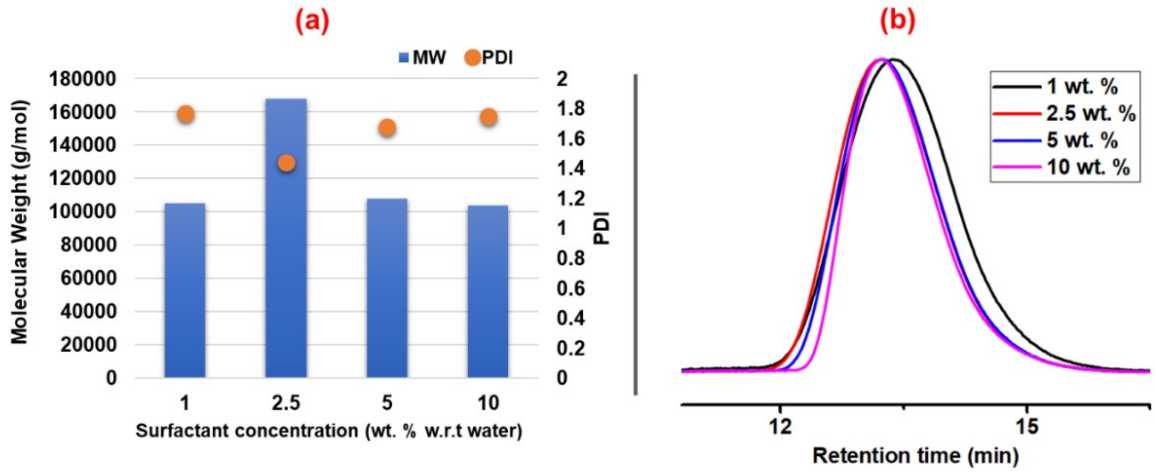


Figure S5: Effect of change in SDS concentration on (a) molecular weight and dispersity; (b) GPC traces of the polymers produced (PBMA). Conditions utilized for these polymerizations: BMA = 5 % v/v, SDS = varied, GOx/Fe(II) = 2μM/1mM, D-glucose = 0.55 mM.

Table S2: Effect of SDS concentration on molecular weight and dispersity of the polymers obtained. Conditions utilized for these polymerizations: BMA= 5 % v/v, GOx/Fe(II) = 2 μM/ 1mM, D-glucose= 0.55 mM, SDS= varied.[a]

SDS Concentration (wt. %)	Conversion[b] (wt. %) (after 5 min)	M_n[c] (g/mol)	Đ[c]
0.5	--	--	--
1	65	105,000	1.77
2.5	> 99	168,000	1.44
5	> 99	108,000	1.68
10	> 99	104,000	1.75

[a]Reaction conditions: Temperature = R.T., stirring speed = 300 rpm. [b]Conversion (wt. %) was calculated gravimetrically, as discussed in the experimental section. [c]M_n and Đ were obtained from the GPC analysis.

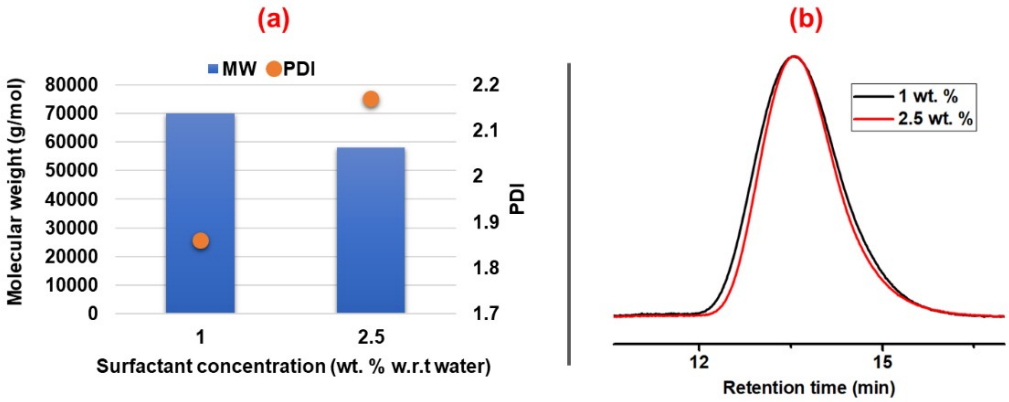


Figure S6: Effect of change in SDS concentration on (a) molecular weight and dispersity; (b) GPC traces of the polymers produced (PBMA). Conditions utilized for these polymerizations: BMA = 5 % v/v, SDS= varied, GOx/Fe(II) = 4 µM/2 mM, D-glucose= 0.55 mM.

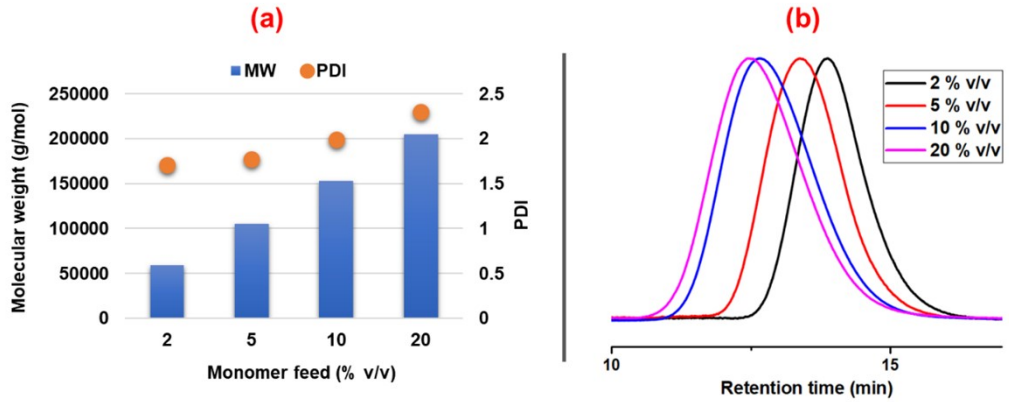


Figure S7: Effect of change in monomer concentration (% v/v w.r.t. water) on (a) molecular weight and dispersity; (b) GPC traces of the polymers produced (PBMA). Conditions utilized for these polymerizations: BMA= varied, SDS= **1 wt.%**, GOx/Fe(II) = 2 µM/1 mM, D-glucose= 0.55 mM.

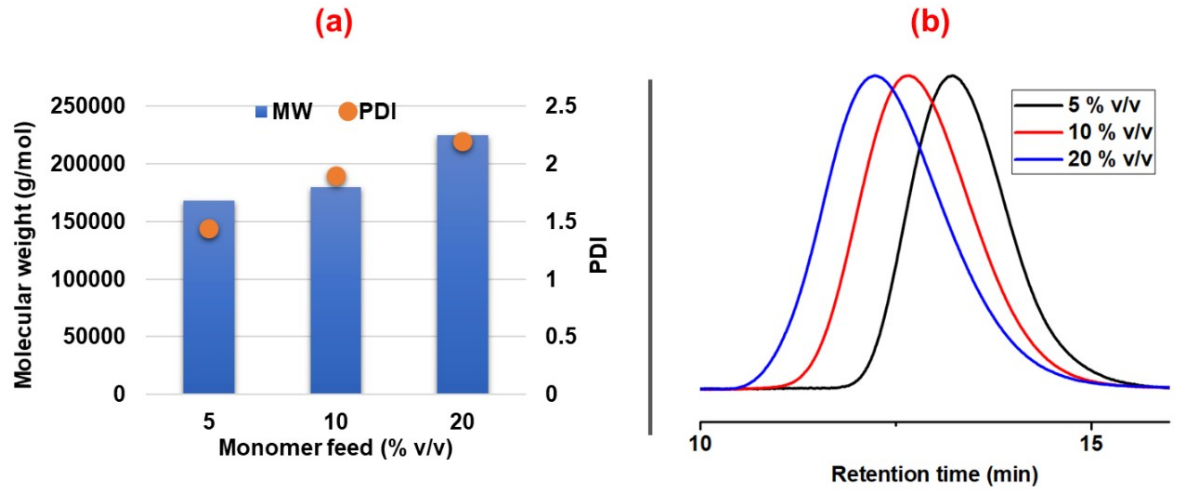


Figure S8: Effect of change in monomer concentration (% v/v w.r.t. water) on (a) molecular weight and dispersity; (b) GPC traces of the polymers produced (PBMA). Conditions utilized for these polymerizations: BMA= varied, SDS= **2.5 wt.%**, GOx/Fe(II) = **2 µM/1 mM**, D-glucose= 0.55 mM.

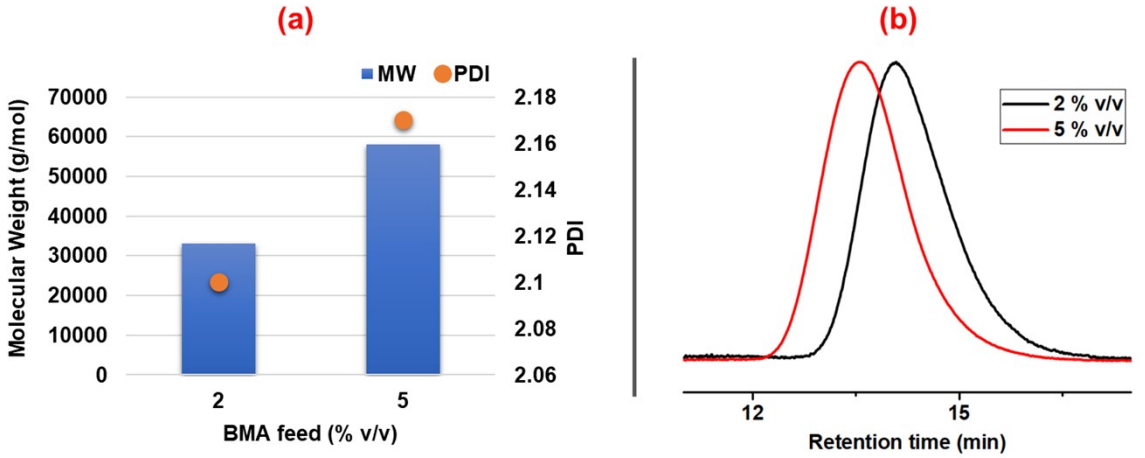


Figure S9: Effect of change in monomer concentration (% v/v w.r.t. water) on (a) molecular weight and dispersity; (b) GPC traces of the polymers produced (PBMA). Conditions utilized for these polymerizations: BMA= varied, SDS= **2.5 wt.%**, GOx/Fe(II) = **4 µM/2 mM**, D-glucose= 0.55 mM.

Table S3: DLS measurement data of the latexes collected after polymerization using the semi bio-Fenton emulsion method.

Entries[a]	Monomer	$[BMA]_0$ (v/v)	SDS wt%	Z-avg[b] (nm)	PdI	M_n (g/mol)	N_c[c] (Chains/particle)
1	BMA	5	1	22.11	0.172	105,000	19
2	BMA	5	1	23.36	0.312	156,500	16
3	BMA	5	1	21.87	0.379	120,000	17
4	BMA	5	1	19.98	0.182	70,000	20
5	BMA	5	2.5	17.24	0.283	168,000	7
6	BMA	5	5	14.65	0.267	108,000	6
7	BMA	5	10	13.81	0.258	104,000	5
8	BMA	2	1	15.88	0.332	59,000	13
9	BMA	10	1	25.05	0.259	153,000	17
10	BMA	20	1	34.40	0.213	202,000	29
11	BMA	10	2.5	20.13	0.219	180,000	8
12	BMA	20	2.5	32.30	0.311	225,000	23
13	BMA	2	2.5	16.34	0.340	33,000	21
14	BMA	5	2.5	20.05	0.500	58,000	21
15	BMA	20	2.5	32.05	0.650	185,000	25
16	MMA	5	2.5	16.95	0.397	130,000	7
17	VAc	5	2.5	19.75	0.378	135,000	15

[a] GOx, Fe(II), and D-glucose amounts for all these polymerization reactions have been fixed at 2 µM, 1 mM, and 0.55 mM, respectively.

[b] The Z-average diameter was determined using a dynamic light scattering (DLS) instrument, calculated as the average of three measurements, and it denotes the particle diameter.

[c] N_c was calculated based on the weight average molecular weight (M_w) of the polymer and the Z-average size of the latex particle.[1] During this calculation, density of PBMA, PMMA and PVAc was assumed to be 1050, 1020, 1190 kg/m^3, respectively.

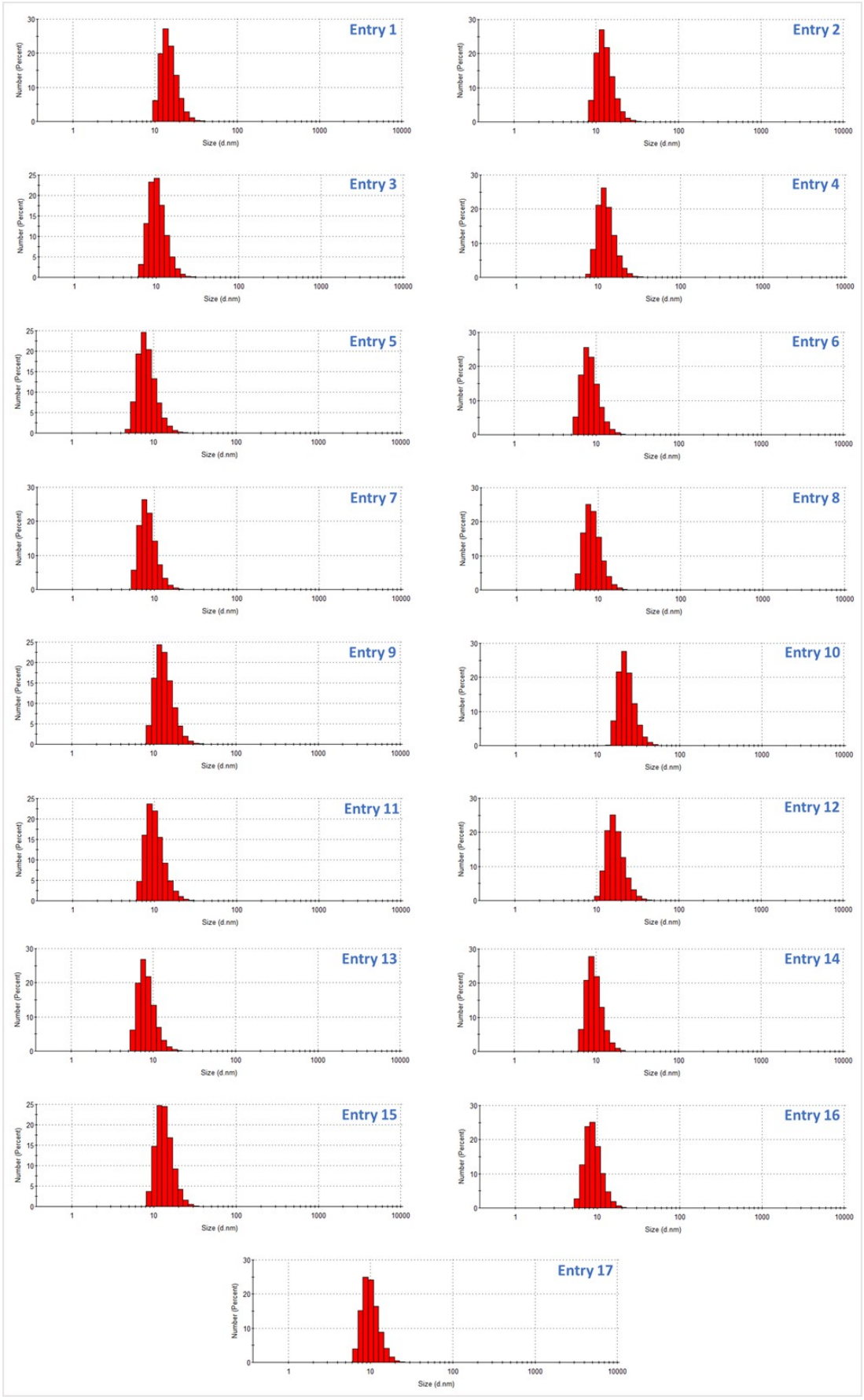


Figure S10: DLS data of the various latexes after polymerization.

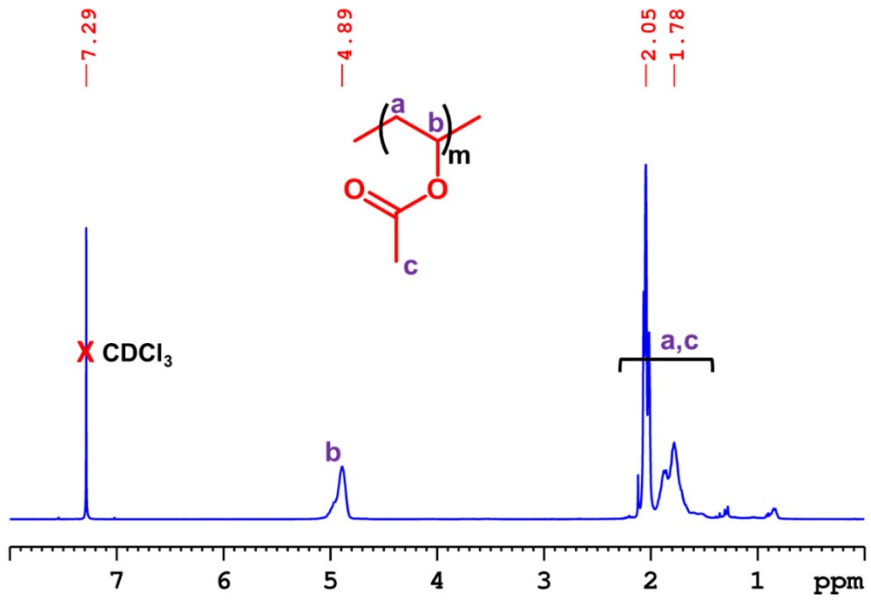


Figure S11: ^{1}H NMR of polyvinyl acetate (PVAc) in $CDCl_3$ synthesized using semi bio-Fenton emulsion polymerization. Successful preparation of the polymer is verified using this spectrum.

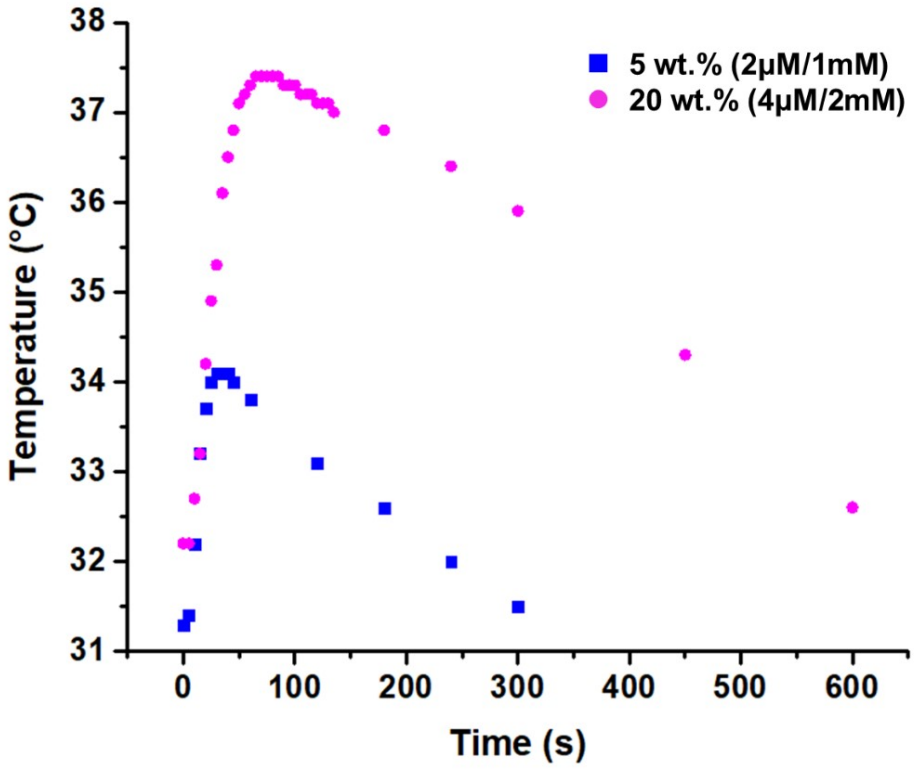


Figure S12: Change of temperature (°C) of the reaction mixture with time in seconds. Conditions utilized for the polymerizations: BMA = 5% v/v, SDS = 2.5 wt.%, GOx/Fe(II) = 2 μM/1 mM, D-glucose = 0.55 mM; and BMA = 20% v/v, SDS = 2.5 wt.%, GOx/Fe(II) = 4 μM/2 mM, D-glucose = 0.55 mM.

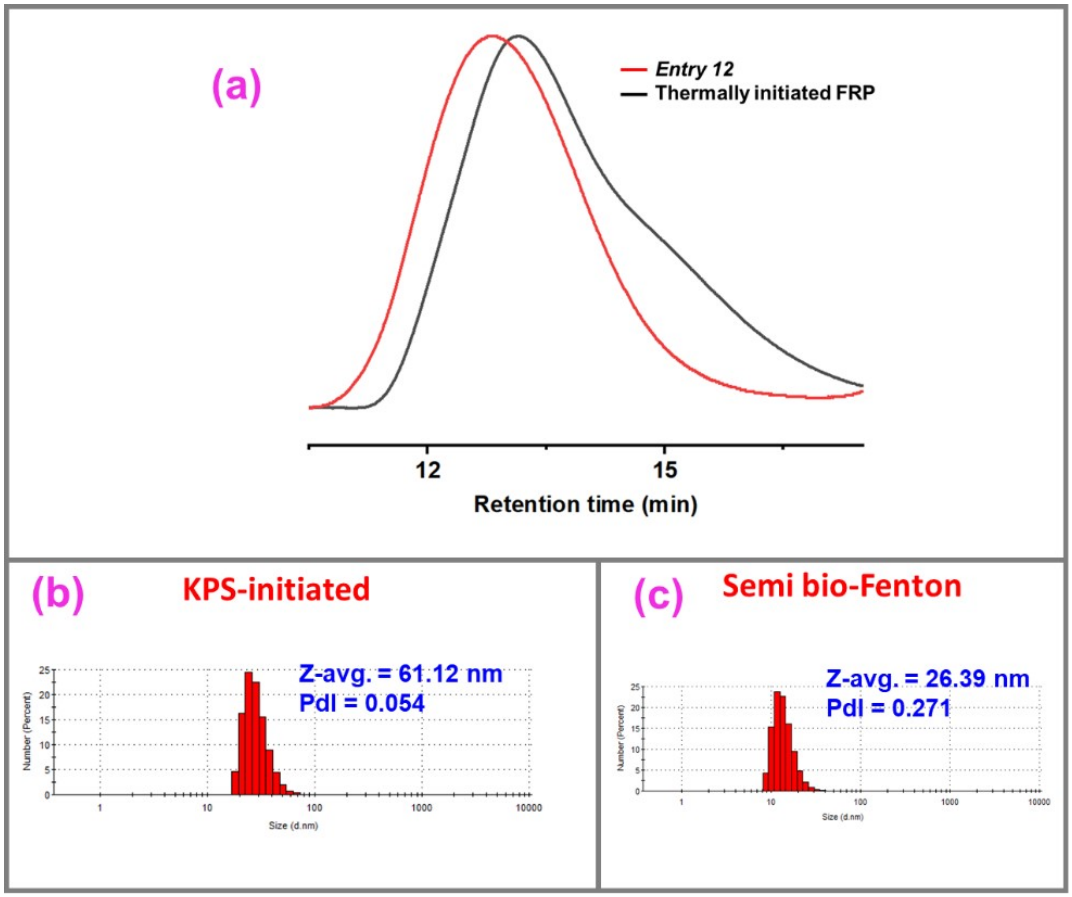


Figure S13: (a) GPC traces of ***Entry 12*** and a thermally initiated emulsion polymerization under identical conditions. Reaction conditions utilized for the thermally-initiated polymerization: BMA = 20% v/v of water, SDS = 2.5 wt.%, Potassium persulfate (KPS) = 1 wt.% of monomer; and for the semi bio-Fenton initiated emulsion polymerization: BMA = 20% v/v, SDS = 2.5 wt.%, GOx/Fe(II) = 2 µM/1 mM, D-glucose = 0.55 mM. Under identical conditions, the Đ recorded for ***Entry 12*** and the KPS-initiated (thermal) polymerization were 2.20 and 2.53, respectively. DLS data of (b) KPS-initiated emulsion polymerization and (c) semi bio-Fenton initiated emulsion polymerization.

Table S4: Reaction conditions used and the resulting data obtained after purging the reaction mixture with Argon with respect to ***Entry 1***, **Table 1**.

Variations[a]	Reaction time	M_n (g/mol)	Đ	Yield (wt.%)
5 min Argon purging	4 h	131,000	1.98	91
10 min Argon purging	4 h	87,820	2.21	90
30 min Argon purging	4 h	162,600	1.94	95
1 h Argon purging	4 h	100,700	1.97	86
2 h Argon purging	4 h	118,500	1.88	68

[a] GOx, Fe(II), and D-glucose amounts for all these polymerization reactions have been fixed at 0.5 µM, 0.25 mM, and 0.55 mM, respectively.

References:

[1] U. Kalita, V. F. Jafari, M. Ashokkumar, N. K. Singha, G. G. Qiao, *Commun. Chem.* **2024**, *7*, 113.