

High Chain-End Fidelity in Sono-RAFT Polymerization

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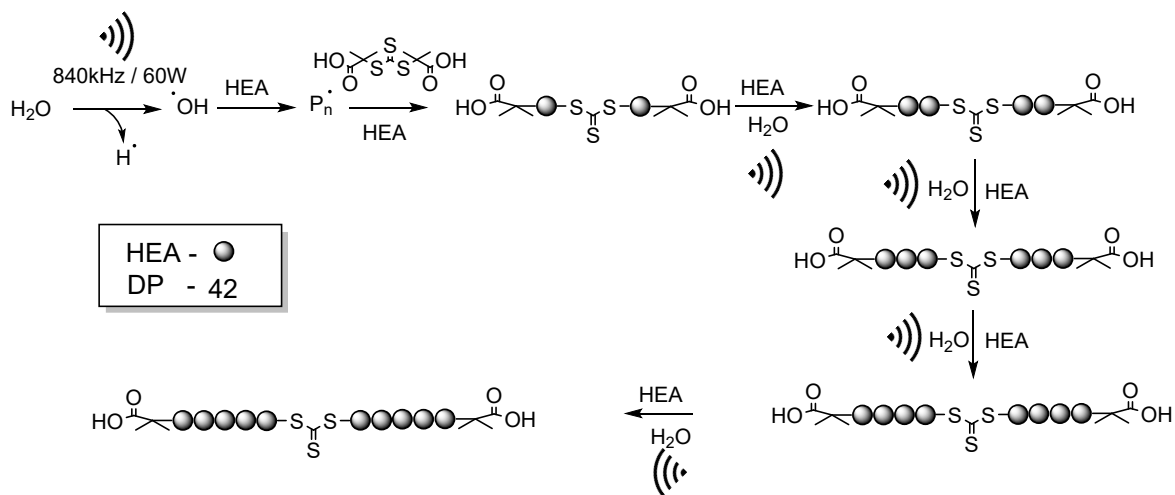
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Supporting Information

Synthesis of poly(HEA) via Sono-RAFT

HEA (0.17 g, 1.5 mmol) and TTC (5 mg, 0.02 mmol) were dissolved in distilled water (1.85 mL). The monomer concentration was fixed at 0.75 M as reported in our previous publications.¹ The solution was prepared in a 14-mL glass vessel fitted with a rubber stopper and degassed with ultra-high purity argon gas (>99 % pure). After degassing the solution for 30 min, the vial was immersed in a sonication bath of 150 mL of water in a double-walled glass cell ultrasonic vessel (with a cooling jacket to maintain ambient temperature). The base of the glass cell was placed on an ultrasonic transducer with a diameter of 5.4 cm. The frequency of the plate (840 kHz, 60 W) was configured in the amplifier and the amplifier was switched on, which marks the initiation step of the polymerization.



Scheme S1. Chain extension of poly(HEA) via sono-RAFT

Chain extension of acrylates. Chain extension experiments with HEA have been carried out in an aqueous system at ambient temperature. The initial block was polymerized for 3 h and the monomer conversion was observed to be more than 98%, as observed from ^1H NMR analysis. Interestingly, the monomer conversion reaches almost 94% within 1 h of sonication, following which the rate of polymerization almost reaches a plateau. ^1H NMR revealed that the monomer conversion was 98% after 3 h of sonication. For the synthesis of the subsequent blocks, HEA (0.17 g, 1.5 mmol) and distilled water (1.85 mL) were further added to the preceding block and degassed. The reaction conditions for the subsequent blocks were the same as for the initial block. This is a one-pot chain extension experiment where the first block was used as such without further purification for chain extension experiments. Encouragingly, there is excellent agreement between the theoretical and experimental molecular weights. The GPC chromatogram (**Figure S1**) for the chain extension experiments indicates a clear shift in the peak from right to left without any tailing nor residue, indicating that the polymer chains have a high degree of livingness and can form narrow disperse block copolymers with excellent control of molecular weight in a very short time compared to that of other external stimuli mediated RAFT polymerization.

Table S1. Summary of chain extension experiments via sono-RAFT

number of blocks	$M_{n,\text{th}}$ (g mol^{-1}) ^a	$M_{n,\text{gpc}}$ (g mol^{-1}) ^b	\mathcal{D}	conv. (%) ^c
1	9800	9400	1.01	>98
3	19600	19300	1.01	>98
5	29400	29300	1.03	>98
7	39200	39200	1.06	>98

Reaction conditions: HEA/TTC = 84/1, $[\text{HEA}]_0 = 0.75 \text{ M}$, $f = 840 \text{ kHz}$, $P = 60 \text{ W}$, $t = 180 \text{ min}$. ^aDefined as: $M_{n,\text{th}} = (\text{conv.} \times \text{DP}_n) \times \text{MW}_{\text{mon}} + \text{MW}_{\text{TTC}}$, where $\text{DP}_n = [\text{HEA}]_0/[\text{TTC}]_0$. ^bCalculated via GPC-MALS using ASTRA software. ^cDetermined via ^1H NMR spectroscopy.

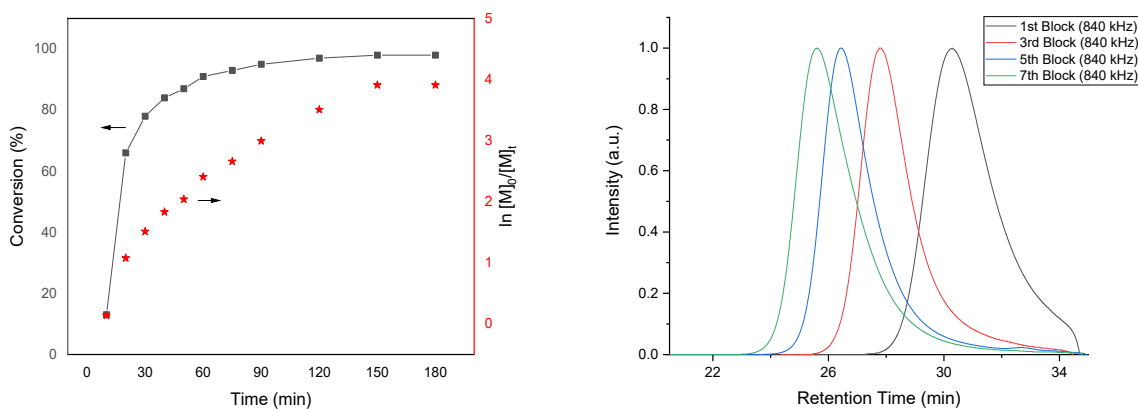


Figure S1. (A) Reaction kinetics of poly(HEA) (98 equiv. per TTC, $[HEA]_0 = 0.75$ M) under continuous ultrasonic irradiation ($f = 840$ kHz, power = 60 W) (B) GPC traces of successive chain extensions of poly(HEA) in water at room temperature (3h per block)

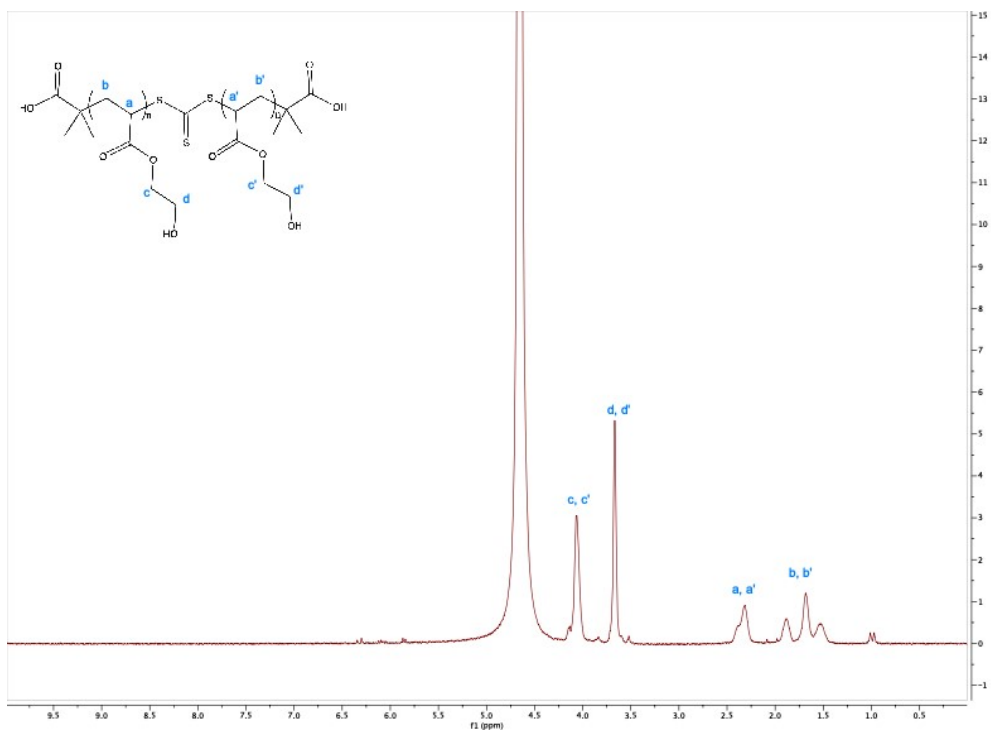


Figure S2. 1H NMR spectrum (solvent: D_2O) of poly(HEA). Reaction condition: HEA/TTC = 84/1, $f = 840$ kHz, $P = 60$ W, $[HEA]_0 = 0.75$ M, $t = 180$ min

Table S2 Summary of pentablock copolymer synthesized via sono-RAFT

number of blocks	monomer	DP _n	M _{n,theo} (g mol ⁻¹) ^a	M _{n,gpc} (g mol ⁻¹) ^a	Đ	conv. (%) ^b	time (h)
1	NAM	20	3000	2580*	-*	>97	4
3	DMA	28	6100	5200	1.02	>98	4
5	HEA	24	9100	8600	1.06	>98	3

*Molecular weight for 1st block was measured using MALDI-TOF, hence dispersity value is not available

Reaction conditions: [M]₀ = 0.75 M, *f* = 840 kHz, P = 60 W.

^aCalculated via GPC-MALS using ASTRA software. ^bDetermined via ¹H NMR spectroscopy.

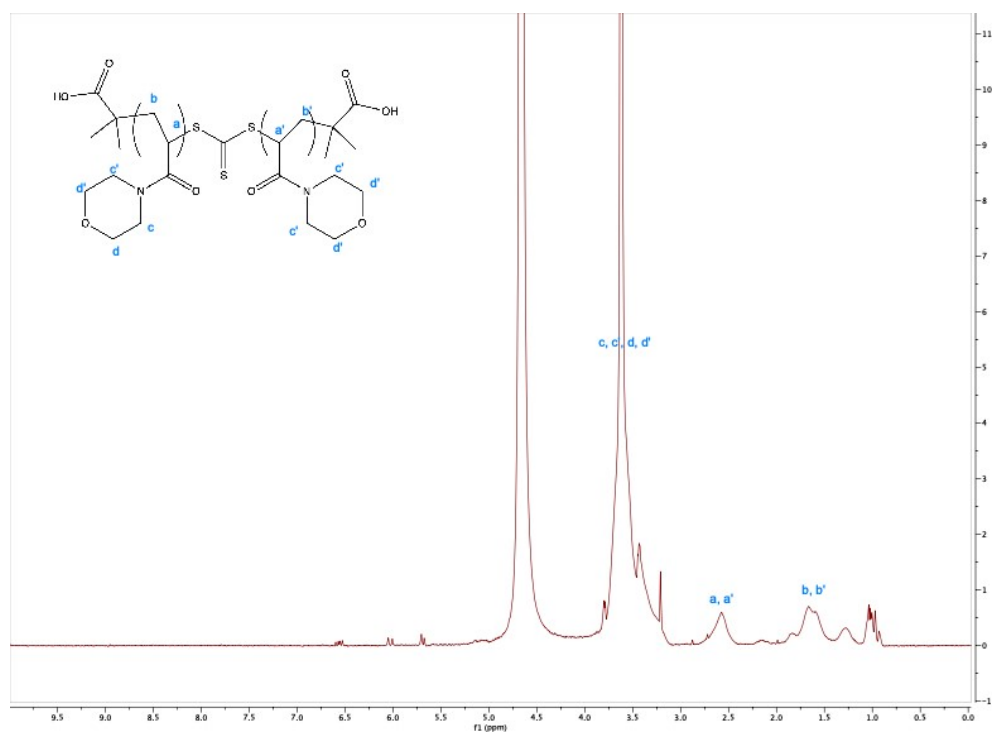


Figure S3. ¹H NMR spectrum (solvent: D₂O) of poly(NAM). Reaction condition: NAM/TTC = 20/1, *f* = 840 kHz, P = 60 W, [NAM]₀ = 0.75M, t = 240 min

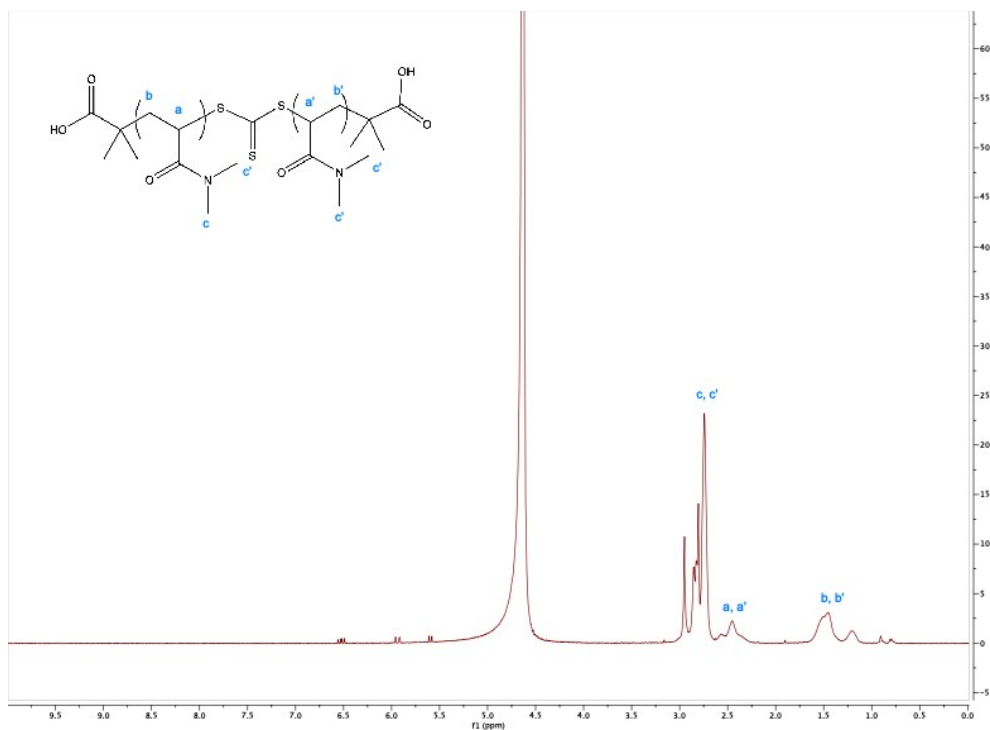


Figure S4. ^1H NMR spectrum (solvent: D_2O) of poly(DMA). Reaction condition: DMA/TTC = 98/1, f = 840 kHz, P = 60 W, $[\text{DMA}]_0$ = 0.75M, t = 240 min

Characterization

To perform the ^1H NMR spectra, deuterium oxide was used as a reference, and the spectra were obtained using a Varian Unity 400 MHz spectrometer operating at 400 MHz at ambient temperature in deuterium oxide (D_2O). The molecular weight and dispersity of the synthesized polymers were determined using aqueous gel permeation chromatography (GPC) at 25°C using Milli-Q water with 0.1 vol% TFA at a flow rate of 1 mL min^{-1} with multi-angle light scattering (MALS) and inline differential refractive index (DRI) detectors. The GPC unit had three Waters Ultra hydrogel columns in series ((i) 250 Å porosity, $6\ \mu\text{m}$ bead size; (ii) $10\ \mu\text{m}$ bead size). A Shimadzu RID-10A interferometric refractometer and Wyatt 3-angle MiniDawn light scattering detector were connected in series. For all polymers, dn/dc values were determined via a method of

100% mass recovery. Molecular weight and dispersity values were calculated using the Wyatt ASTRA software package from MALS data using the Debye model. At 25 °C, the dn/dc of RAFT-mediated PHEA and PDMA in water was measured and found to be 0.134 and 0.190 mL/g, respectively. Using equation S1, the dn/dc value for each multiblock block was calculated. The change in dn/dc for each multiblock is assumed to be the weighted linear combination of the change in the constitutive monomers dn/dc values²:

$$(\text{dn/dc})_{\text{block}} = w_X (\text{dn/dc})_X + (1-w_X) (\text{dn/dc})_Y \quad (\text{S1})$$

Where, $(\text{dn/dc})_{X/Y}$ represents the refractive index of monomer X/Y and w_X is the weight fraction of monomer X.

Matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) mass spectroscopy was carried out on a Bruker Autoflex III Mass Spectrometer operating in positive linear mode. The matrix (trans-2-[3-(4-tert-butyl)-2-methyl-2-propenylidene] malononitrile) (DCTB), the cationisation agent potassium trifluoroacetate (KTFA), and the analyte were dissolved in MeOH at a concentration of 10 mg mL⁻¹ and mixed in a volume ratio of 10:1:1. 0.5 L of this solution was spotted onto a ground steel target plate and the FlexAnalysis (Bruker) was used to analyze the data.

Quantification of Hydroxyl Radical (H₂O₂ assay)

The H₂O₂ assay to determine the concentration of hydroxyl radicals produced was carried out as reported by Hochanadel.³ 5 mL of distilled water was sonicated in an ultrasonic cell filled with 150 mL distilled water. 1 mL of sonicated sample for specific recorded intervals (5, 10, 15- and 20-min intervals) was added to 1 mL of reagent A (0.4 M KI, 0.1 M NaOH, and 0.02 mM (NH₄)₆Mo₇O₂₄) and reagent B (0.1 M C₈H₅KO₄) and thoroughly mixed for 1 min. UV/Vis

spectroscopy was performed for each sample with an absorbance range 200-800 nm. The absorbance at 351 nm was recorded.

Acoustic cavitation in water produces hydrogen (H \cdot) and hydroxyl radicals (HO \cdot). Hydroxyl radicals are unstable; hence it forms hydrogen peroxide (H₂O₂) which is estimated using “Weissler” method. The reaction scheme is shown in **Equation S2**.



Iodide ion react with hydrogen peroxide forming I₃⁻ whose concentration can be estimated using UV-Visible spectroscopy at 353 nm. Using the absorbance from UV-Visible spectroscopy, the concentration of I₃⁻ is calculated using **Equation S3**

$$\text{The concentration of I}_3^- \text{ (M)} = \frac{\text{Absorbance}}{\text{Molar extinction coefficient} * \text{pathlength of cuvette}} * \text{dilution factor}\tag{S3}$$

Where molar extinction coefficient for I₃⁻ is 26400 M⁻¹cm⁻¹, pathlength of cuvette is 1 cm. The concentration of I₃⁻ is equivalent to the concentration of the hydrogen peroxide formed. As explained in our previous publications⁴, The shearing forces produced by the implosion of the bubble and the radicals formed by sonolysis of the solvent are the two primary effects that can be used for sonochemical reactions. The mechanical forces are relatively higher for low frequencies (20 kHz to 200 kHz) and they decrease with increase in frequency. Additionally, the radical concentration is lower at 20 kHz and 1 MHz but peaks around 400 kHz to 500 kHz. To synthesize polymers with good chain-end fidelity, the shear force must be low while maintaining high radical

concentration. Despite 400 kHz to 500 kHz exhibiting higher radical concentration, we chose 840 kHz as they exhibited lower mechanical effects. **Figure S5** shows the formation of hydrogen peroxide at 840 kHz over a range of applied power (W). Although with respect to the intensity of applied power, the concentration of hydrogen peroxide increases proportionally. The cavitation effect cannot increase indefinitely with increase in power due to various reasons such as breakdown in transducer material over prolonged cavitation and decoupling at higher amplitude. The graphical representation shows that, the concentration of I_3^- increases linearly with increase in applied power at 840kHz. However, after 70W, nebulization was observed. Hence 60W has been selected as the optimum power to initiate the RAFT polymerization.

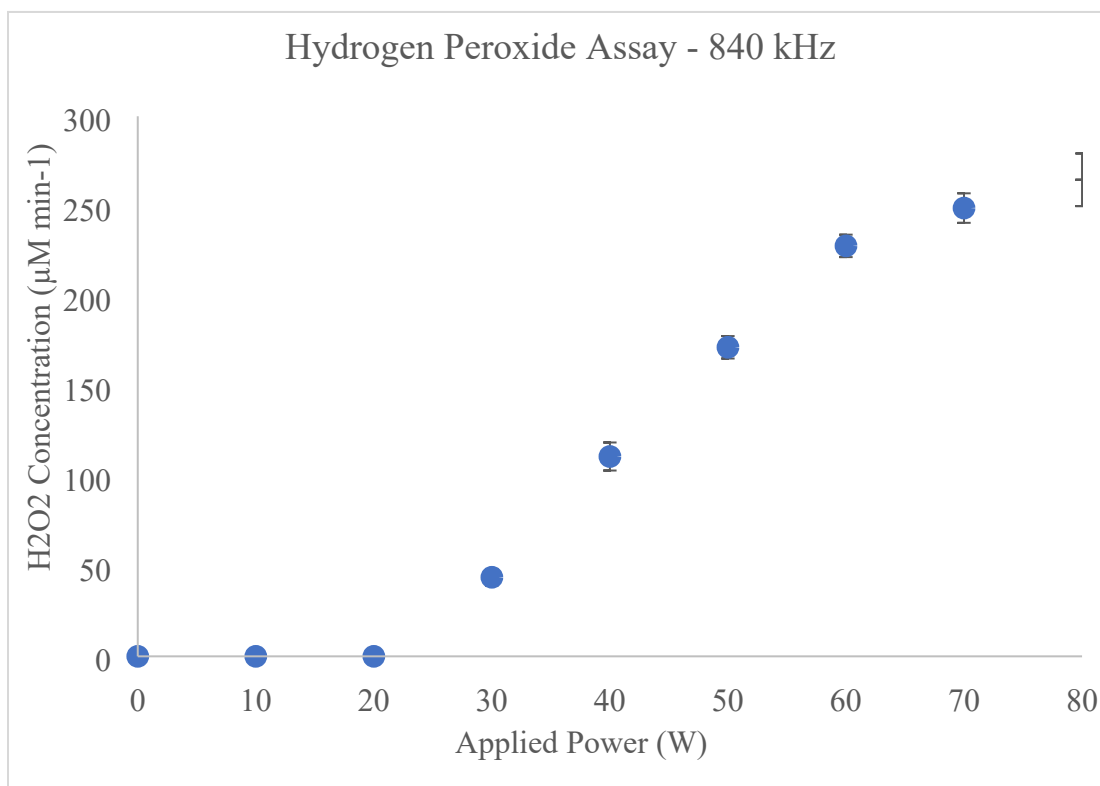


Figure S5. Plot for radical concentration for 840kHz transducer plate across various applied power

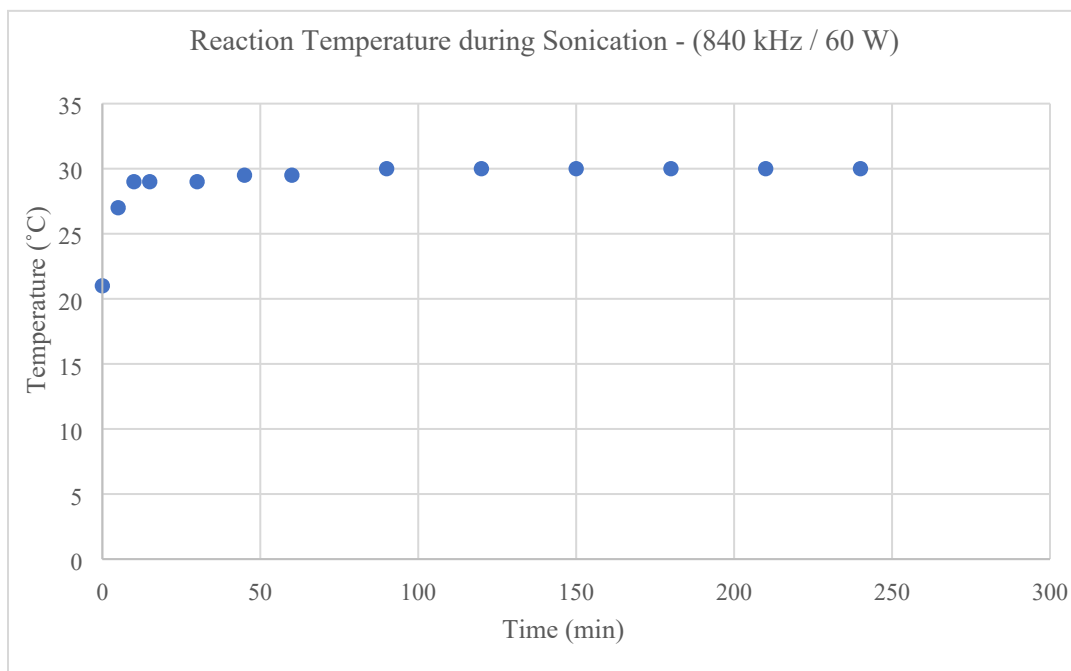


Figure S6. Plot for reaction temperature Vs time for 840kHz transducer plate at 60 W applied power

Reference

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