Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information For:

Diaryliodonium Salts Facilitate Metal-Free Mechanoredox Free Radical Polymerizations

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1. General Considerations

Materials

All chemicals were obtained from commercial sources and used as received unless otherwise stated. *Tert*-butyl acrylate (*t*BA), butyl acrylate (BA), ethyl acrylate (EA), methyl acrylate (MA), and methyl methacrylate (MMA) were purchased from Tokyo Chemical Industry (TCI). Styrene was purchased from Acros. All monomers were purified by passing through basic alumina immediately before use. Diphenyl iodonium hexafluorophosphate (DPIHP) and 4-bromobenzenediazonium tetrafluoroborate (BBDT) were obtained from TCI. Cubic $BaTiO_3$ nanoparticles (<100 nm size) and ZnO nanoparticles (18 nm) were purchased from Sigma-Aldrich and US Research Nanomaterials, respectively. Anhydrous TiO_2 powder was obtained from Fisher Chemical. All ultrasound reactions were carried out in 4 mL vials (ChemGlass #CG-4904-05) unless otherwise stated. Large scale (5 g) polymerization reactions were carried out in 10 mL round bottom flasks. Unless otherwise noted, reaction solvents, dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), toluene, dioxane, and anisole, were sourced from commercially available sources and used without further purification.

Acrylate monomers used in glovebox experiments were dried over molecular sieves, filtered through basic alumina, and degassed via freeze-pump-thaw. Anhydrous dimethylformamide (DMF) used in glovebox experiments was obtained from a JC Meyer solvent purification system[1].

All air-sensitive free radical polymerization (FRP) reactions were performed under inert atmosphere (nitrogen) using standard Schlenk technique or, when indicated, in an Innovative Technology PureLab HE glovebox.

Ultrasonication (US) experiments were performed in a Branson Ultrasonic Cleaner (model 1510R-MT, 70 W, 40 kHz) equipped with an immersed coil of copper tubing connected to a ThermoScientific recirculating chiller for temperature control (see Figure S1 for a photograph of the experimental setup). Ball-milling (BM) experiments were performed using a Retsch Mixer Mill (MM 400) ball mill instrument in 1.5 mL stainless steel screw-top jars (Verder Scientific #014620230) with a single 5 mm Ø stainless steel grinding ball (Verder Scientific #224550003).

Characterization

All ^1H nuclear magnetic resonance (^1H NMR) spectra were obtained on a Bruker AVANCE-300, Bruker AVANCE-301, or Bruker AVANCE-500 NMR spectrometer at 25 °C. ^1H NMR spectra samples were prepared in chloroform-*d* ($CDCl_3$) and referenced to Me_4Si (TMS chemical shift, δ, at 0.00 ppm). All ^1H NMR spectra were analyzed using Bruker TopSpin or MestreNova processing software. Chemical shifts are represented in parts per million (ppm). Integration values of the sidechains from monomers (and their corresponding polymers) were used as internal standards and compared to the decreasing integration values of the olefinic (ca. 5.5 – 6.5 ppm) protons of each monomer to calculate monomer conversion. See Figure S3 for a graphical example.

Gel permeation chromatography (GPC) data were obtained on an Agilent 1260 HPLC equipped with a Wyatt 8-angle DAWN NEON light-scattering detector, ViscoStar NEON viscometer, and Optilab NEON refractive index detector. GPC samples were analyzed at a flow rate of 1 mL/min in chloroform stabilized with 0.5%-1.0% ethanol through two Agilent PLgel MIXED-C columns at 35 °C. GPC samples were prepared at ca. 10 mg/mL in chloroform and were filtered through 0.2 µm PTFE filters before analysis. The following dn/dc values were used; they were measured by the 100% mass recovery method using Wyatt Astra 7.3 software:

poly(*t*BA): 0.024; **poly(BA)**: 0.033; **poly(EA)**: 0.029; **poly(MA)**: 0.039; **poly(MMA)**: 0.053

2. Synthetic and Experimental Procedures

Synthesis of 4-methoxybenzenediazoium tetrafluoroborate (MBDT):

Following the literature procedure from Kubota and Ito[2], 4-methoxyaniline (1.2 g, 10 mmol) was added to tetrafluoroboric acid (50%, 5.0 mmol, 3.5 mL) and water (4.0 mL) and stirred at 0 °C. Sodium nitrite (700 mg, 10 mmol) was dissolved into water (1.5 mL) and added into the aniline mixture (portionwise in 0.25 mL aliquots). The reaction mixture stirred for 30 minutes at 0 °C. The mixture was then filtered and the resulting solid was dissolved in acetone. Diethyl ether was added to precipitate the target diazonium salt. The precipitate was filtered, washed with ether, and dried under vacuum to afford MBDT as a white solid (1.5 g, 68%). The purity of the compound was confirmed by ^{1}H NMR spectroscopy and was in agreement with the literature.

^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ(ppm) 8.65 (d, J = 10 Hz, 2H), 7.42 (d, J = 10 Hz, 2H), 4.04 (s, 3H).

Representative experimental procedure for US-mechanoredox FRP:

In a typical polymerization experiment, DPIHP (0.017 g, 0.039 mmol, 1 equiv) and dimethylformamide (0.50 g) were loaded into a 4 mL glass vial and thoroughly mixed until all DPIHP was fully dissolved. Then, $BaTiO_3$ nanoparticles (0.072 g, 7 wt%) were added into that solution. Finally, *tert*-butyl acrylate (0.50 g, 3.9 mmol, 100 equiv) was added and the vial was capped with a rubber septum (Sigma #Z167258) and sealed with electrical tape. The reaction mixture was then degassed by sparging with N_2 for 40 minutes. After the completion of sparging, vials were then immersed into the ultrasonic bath (20 °C, 70 W, 40 kHz) via clamps and sonicated for 20 h (see Figure S1 for setup). Afterwards, samples were diluted with chloroform and passed through a column of neutral alumina for ^{1}H NMR and GPC sample preparation.

Representative kinetics experiment procedure for US-mechanoredox FRP ($BaTiO_3$/DMF):

In a typical kinetics experiment, DPIHP (0.017 g, 0.039 mmol, 1 equiv) and dimethylformamide (0.50 g) were loaded into a 4 mL glass vial and thoroughly mixed until all DPIHP was fully dissolved. Then, $BaTiO_3$ nanoparticles (0.072 g, 7 wt%) were added into that solution. Finally, *tert*-butyl acrylate (0.50 g, 3.9 mmol, 100 equiv) was added and the vial was capped with a rubber septum (Sigma #Z167258) and sealed with electrical tape. Reaction mixtures were prepared for each time point of the kinetics experiment. The reaction mixtures were then degassed by sparging with N_2 for 40 minutes and then immersed into the ultrasonic bath (20 °C, 70 W, 40 kHz) via clamps and sonicated for the target period of time (see Figure S1 for setup). Afterwards, samples were diluted with $CHCl_3$ and passed through a column of neutral alumina. Afterwards, samples were diluted with chloroform and passed through a column of neutral alumina for ^{1}H NMR and GPC sample preparation.

Representative kinetics experiment procedure for US-mechanoredox FRP (ZnO/DMAc):

In a typical kinetics experiment, DPIHP (0.017 g, 0.039 mmol, 1 equiv) and dimethylacetamide (0.50 g) were loaded into a 4 mL glass vial and thoroughly mixed until all DPIHP was fully dissolved. Then, $BaTiO_3$ nanoparticles (0.072 g, 7 wt%) were added into that solution. Finally, *tert*-butyl acrylate (0.50 g, 3.9 mmol, 100 equiv) was added and the vial was capped with a rubber septum (Sigma #Z167258) and sealed with electrical tape. Reaction mixtures were prepared for each time point of the kinetics experiment. The reaction mixtures were then degassed by sparging with N_2 for 40 minutes and then immersed into the ultrasonic bath (20 °C, 70 W, 40 kHz) via clamps and sonicated for the target period of time (see Figure S1 for setup). Afterwards, samples were diluted with $CHCl_3$ and passed through a column of neutral alumina. Afterwards, samples were diluted with chloroform and passed through a column of neutral alumina for ^1H NMR and GPC sample preparation.

Representative experiment procedure for DPIHP addition kinetic study:

In a typical kinetics experiment, butyl acrylate (0.50 g, 3.9 mmol) and dimethylformamide (0.50 g) were loaded into a 4 mL glass vial and thoroughly mixed. Then, $BaTiO_3$ nanoparticles (0.072 g, 7 wt%) were added into that solution and the vial was capped with a rubber septum (Sigma #Z167258) and sealed with electrical tape. In a separate vial, DPIHP (0.017 g, 0.039 mmol) was dissolved in dimethylformamide (0.10 g). Reaction mixtures were then degassed by sparging with N_2 for 40 minutes and the vial containing butyl acrylate was immersed into the ultrasonic bath (20 °C, 70 W, 40 kHz) via clamps and sonicated for 8 h. Afterwards, the previously prepared DPIHP solution was added into the reaction vial using a syringe/needle; the reaction mixture was then sonicated for an additional 12 h. Afterwards, samples were diluted with $CHCl_3$ and passed through a column of neutral alumina. Afterwards, samples were diluted with chloroform and passed through a column of neutral alumina for ^1H NMR and GPC sample preparation.

Representative procedure for monitoring poly(meth)acrylate degradation by US:

A poly(*t*BA) or poly(MMA) sample was synthesized by the standard US-mechanoredox FRP procedure described above and was isolated by precipitation in cold methanol/water (50%/50%). Following removal of solvent under vacuum, a white polymer was obtained. The polymer was dissolved in dimethylformamide (final concentration = 2.1 M) in a 4 mL glass vial. The vial was capped with a rubber septum (Sigma #Z167258) and sealed with electrical tape. The mixture was degassed by sparging with N_2 for 40 minutes. Finally, the sparged mixture was placed in an ultrasonic bath (20 °C, 70 W, 40 kHz). A GPC sample was taken after 24 h (Figure S7).

Representative procedure for BM-mechanoredox FRP of *t*BA:

To a 1.5 mL stainless steel milling jar charged with a 5 mm stainless steel milling ball was added DPIHP (0.017 g, 0.04 mmol), dimethylformamide (0.12 mL, 0.030% v/w = volume of DMF relative to total mass of all other reaction components) for liquid assisted grinding (LAG), *tert*-butyl acrylate (0.26 g, 2 mmol), and $BaTiO_3$ (0.14 g, 0.60 mmol). The jar was sealed under air, secured in the ball mill, and shaken at 30 Hz for the desired amount of time. Then, a small aliquot was extracted from the ball mill jar with a spatula and dissolved in an appropriate solvent for ^1H NMR and GPC characterization.

Representative procedure for "air-free" BM-mechanoredox FRP of *t*BA:

"Air-free" ball milling experiments were set up in an identical fashion to those described above except the milling jars were charged with all reagents and sealed in the glovebox before securing in the ball mill. Note that all liquid reagents (DMF and acrylate monomer) were degassed via the freeze-pump-thaw method prior to transferring into the glovebox.

Representative procedure for monitoring poly(meth)acrylate degradation by ball-milling:

To a 1.5 mL stainless steel milling jar charged with a 5 mm stainless steel milling ball was added previously synthesized poly(*t*BA) or poly(MMA) (61 mg) and dimethylformamide (0.018 mL, 0.030% v/w = volume of DMF relative to total mass of all other reaction components). The jar was sealed under air, secured in the ball mill, and shaken at 30 Hz for 3 h. Then, a small aliquot was extracted from the ball mill jar with a spatula and dissolved in chloroform for GPC characterization.

3. Supplementary Figures

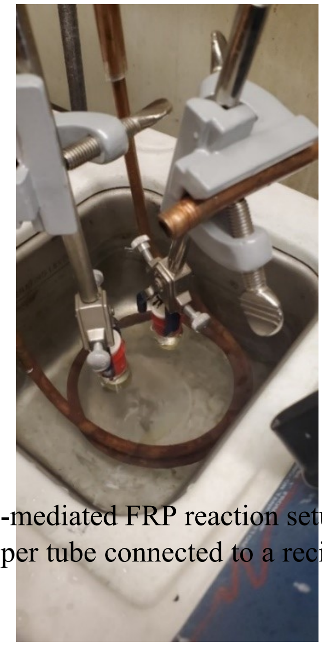

Figure S1: Photograph of a typical US-mediated FRP reaction setup. Reaction vials are immersed into the water bath via clamps and a coiled copper tube connected to a recirculating chiller is used for temperature control of the bath.

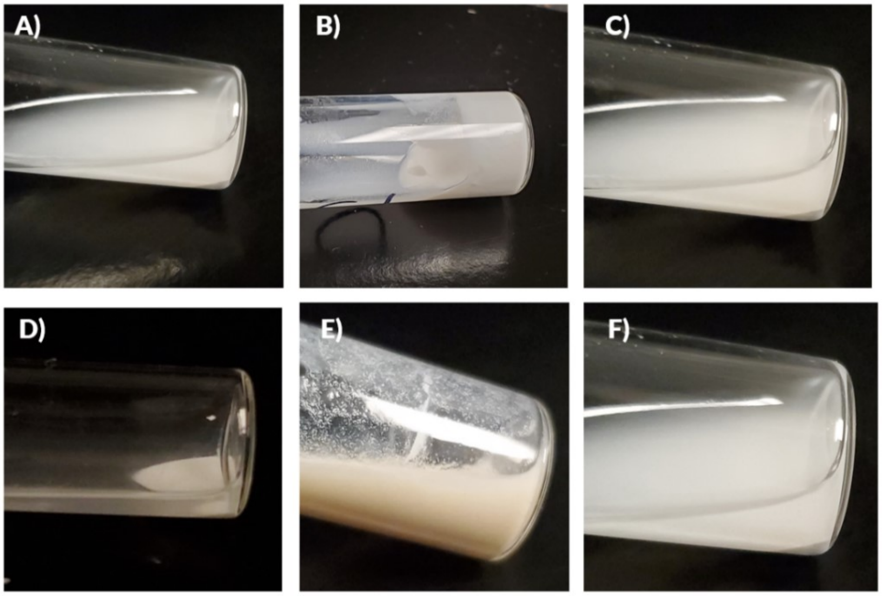

Figure S2: Photographs of US-mediated FRP reaction mixtures: A) at time = 0 h, $BaTiO_3$ (before sonication); B) at time = 20 h, $BaTiO_3$ (after sonication); C) at time = 20 h, $BaTiO_3$ (without sonication); D) at time = 0 h, ZnO (before sonication); E) at time = 20 h, ZnO (after sonication); F) at time = 20 h, TiO_2 (after sonication).

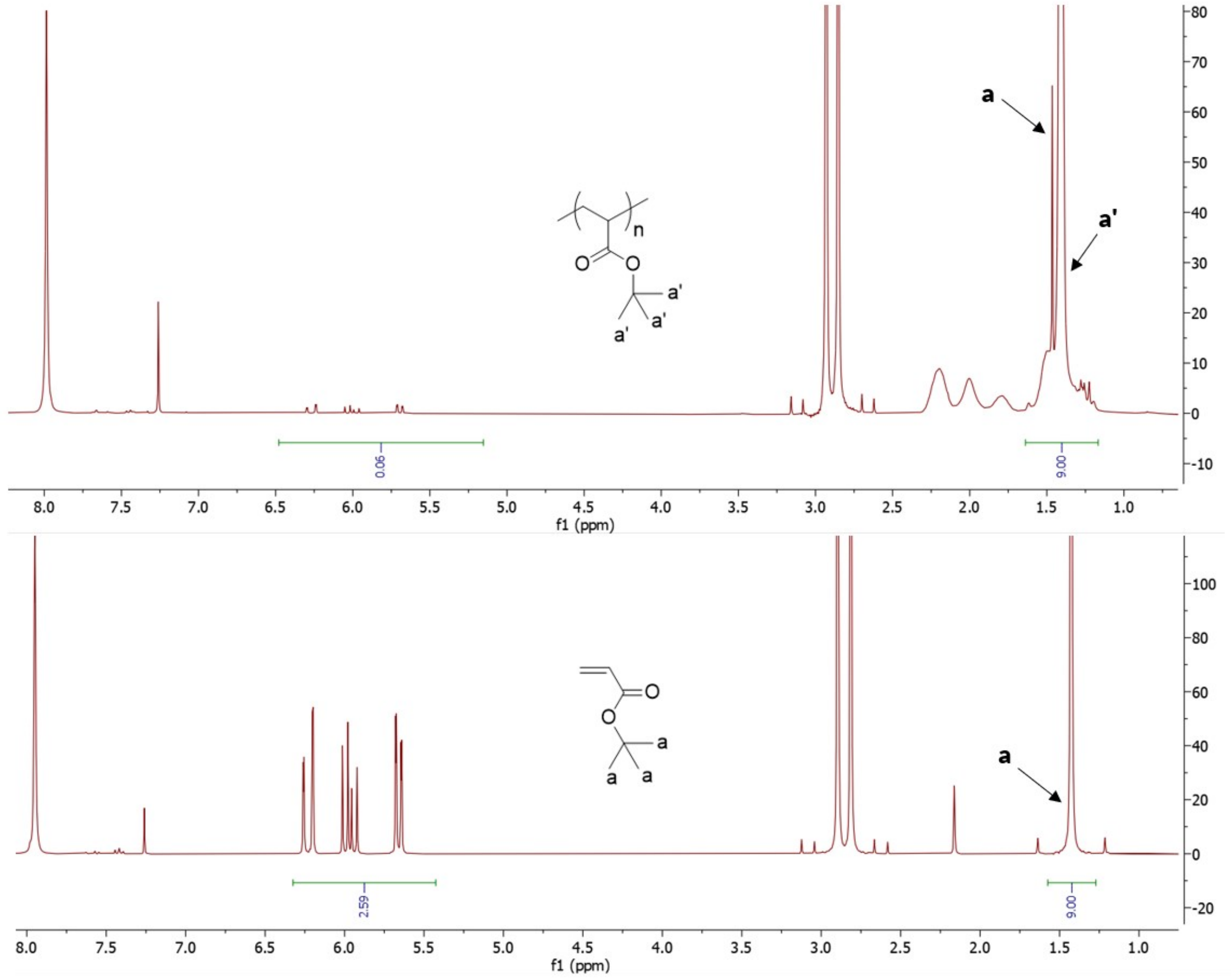

Figure S3: Representative crude ^{1}H NMR spectra of *t*BA US-mechanoredox FRP at time = 0 h (bottom) and time = 20 h (top). Reaction conditions: $[tBA]_0:[DPIHP]_0 = 100:1$. $[tBA] = 7.3$ M in DMF. Ultrasonic bath (40 kHz, 70W, 20 °C). >90% monomer conversion is measured by the disappearance of olefinic protons (ca. 5.5 – 6.5 ppm) relative to methyl internal standard peaks (a and a') on the *tert*-butyl groups present in the monomer and polymer.

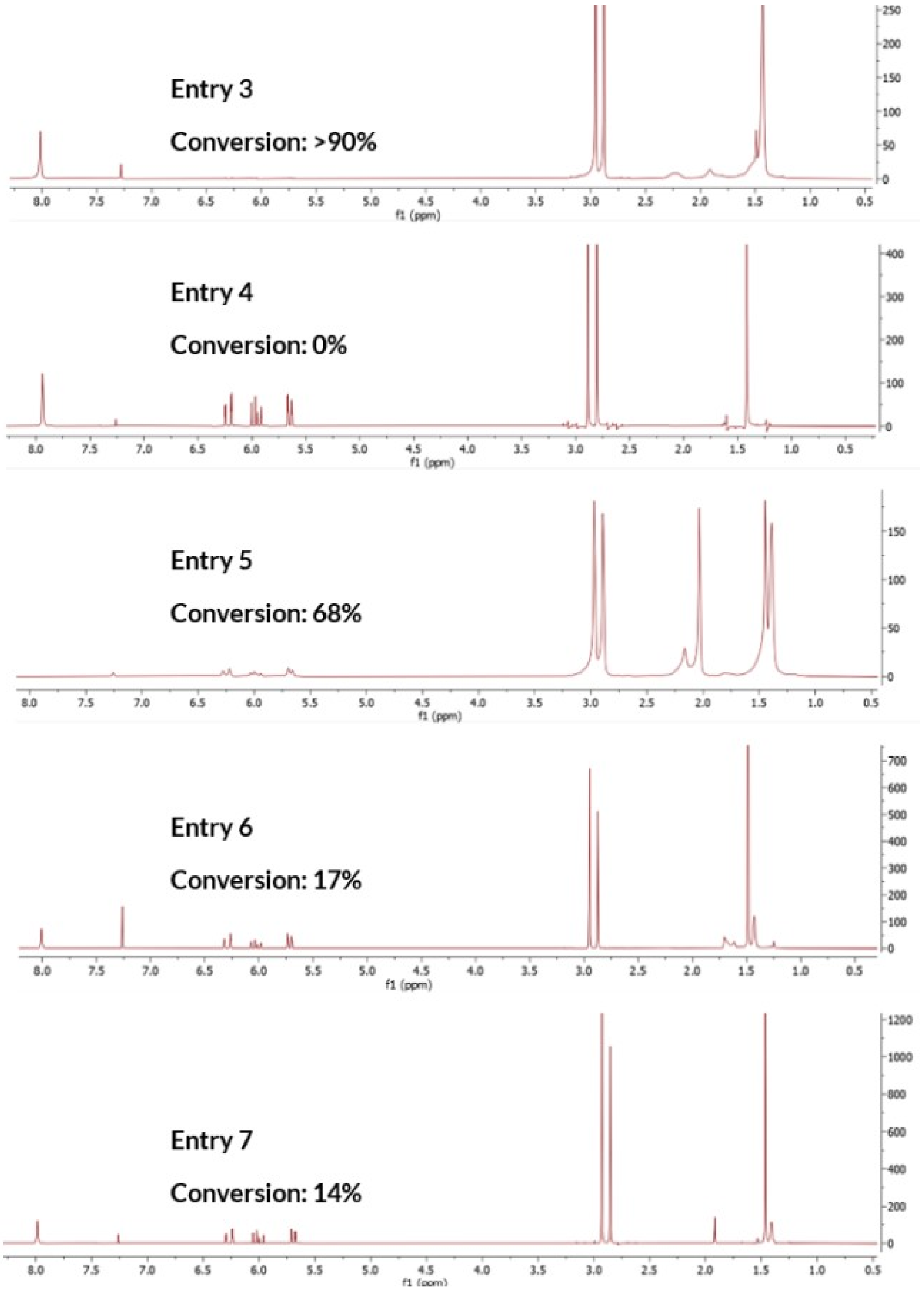

Figure S4: Representative crude ^{1}H NMR spectra of reaction mixtures from Table 1 in the main text.

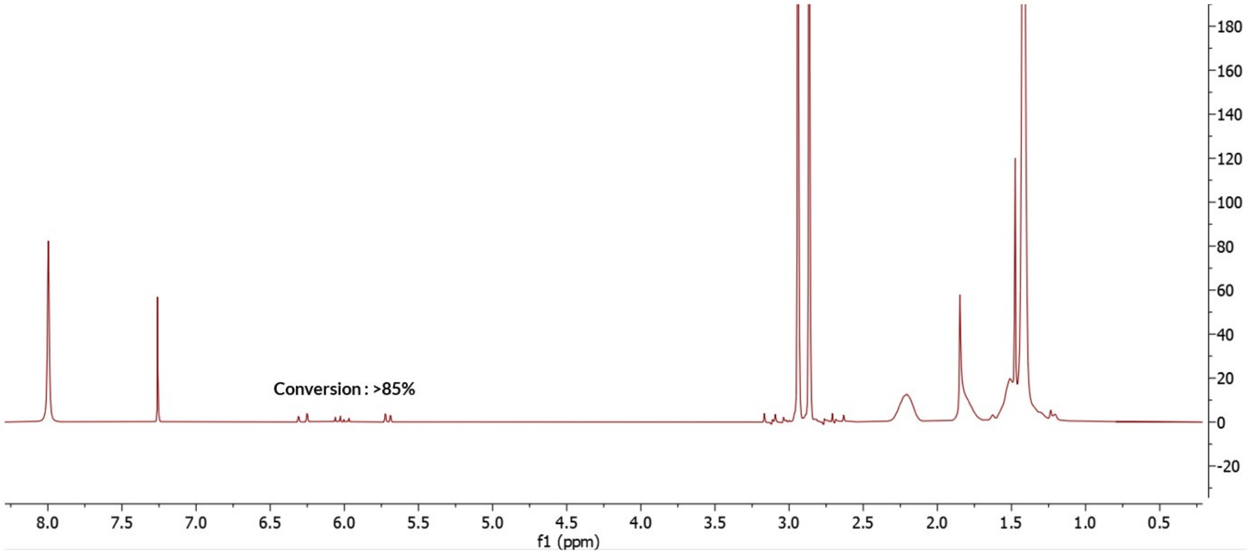

Figure S5: Representative crude ^{1}H NMR spectrum of poly(*t*BA) synthesized on 5 g scale in 10 mL round bottom flask using US-mechanoredox FRP. Reaction conditions $[t\text{BA}]_0$:$[\text{DPIHP}]_0$ = 100:1. [*t*BA] = 7.3 M in DMF. Ultrasonic bath (40 kHz, 70 W, 20 °C). Reaction time: 20 h. >85% monomer conversion is measured by ^{1}H NMR spectroscopy; M_n (GPC-MALS): 180 kDa.

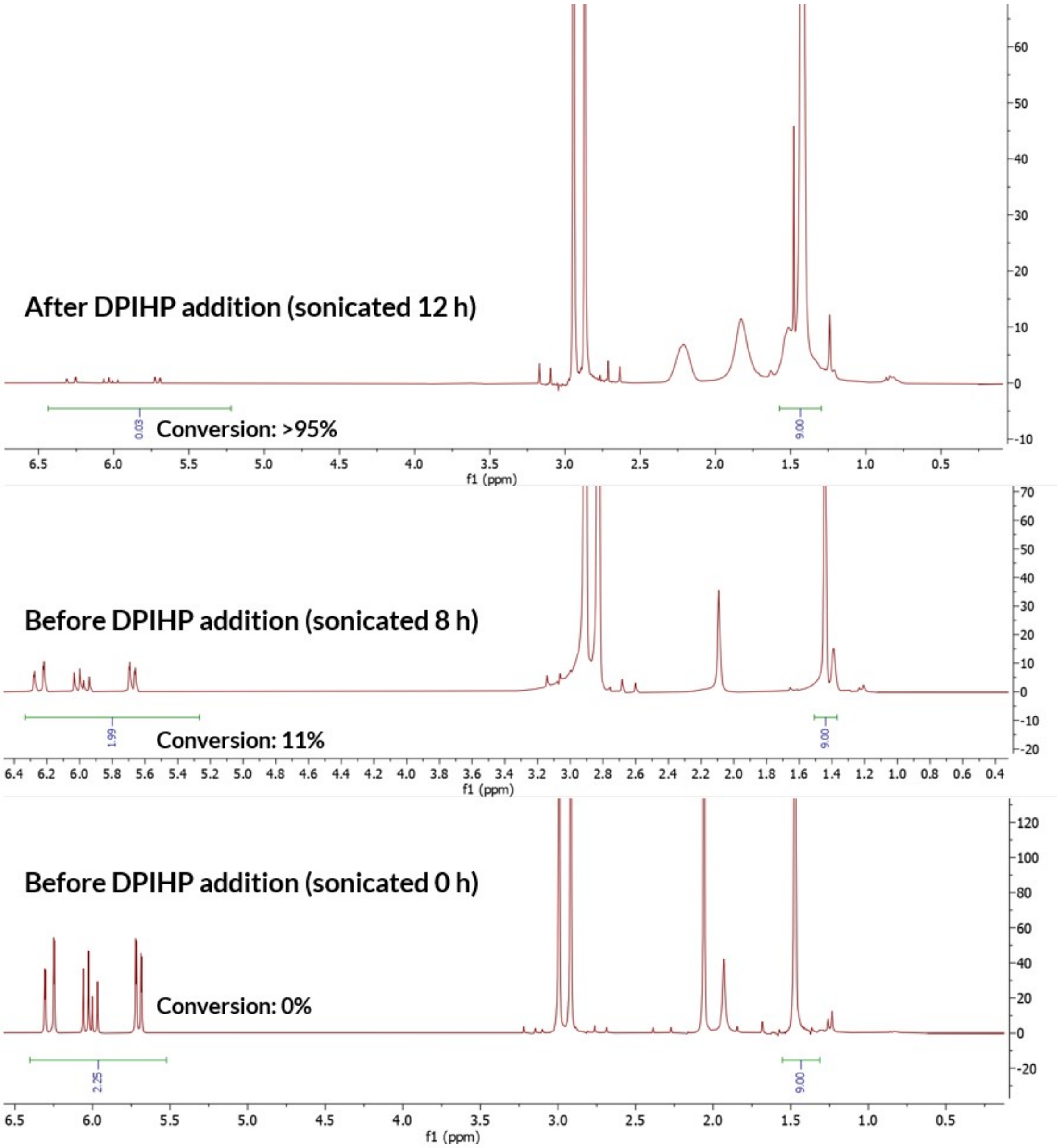

Figure S6: Crude ^{1}H NMR spectra of *t*BA US-mechanoredox FRP reaction mixtures **before DPIHP addition** (*t*BA, $BaTiO_3$, DMF; 8 h total reaction time) and **after DPIHP addition** (*t*BA, $BaTiO_3$, DPIHP, DMF; additional 12 h reaction time → 20 h total reaction time). Experimental conditions are given on Page S3.

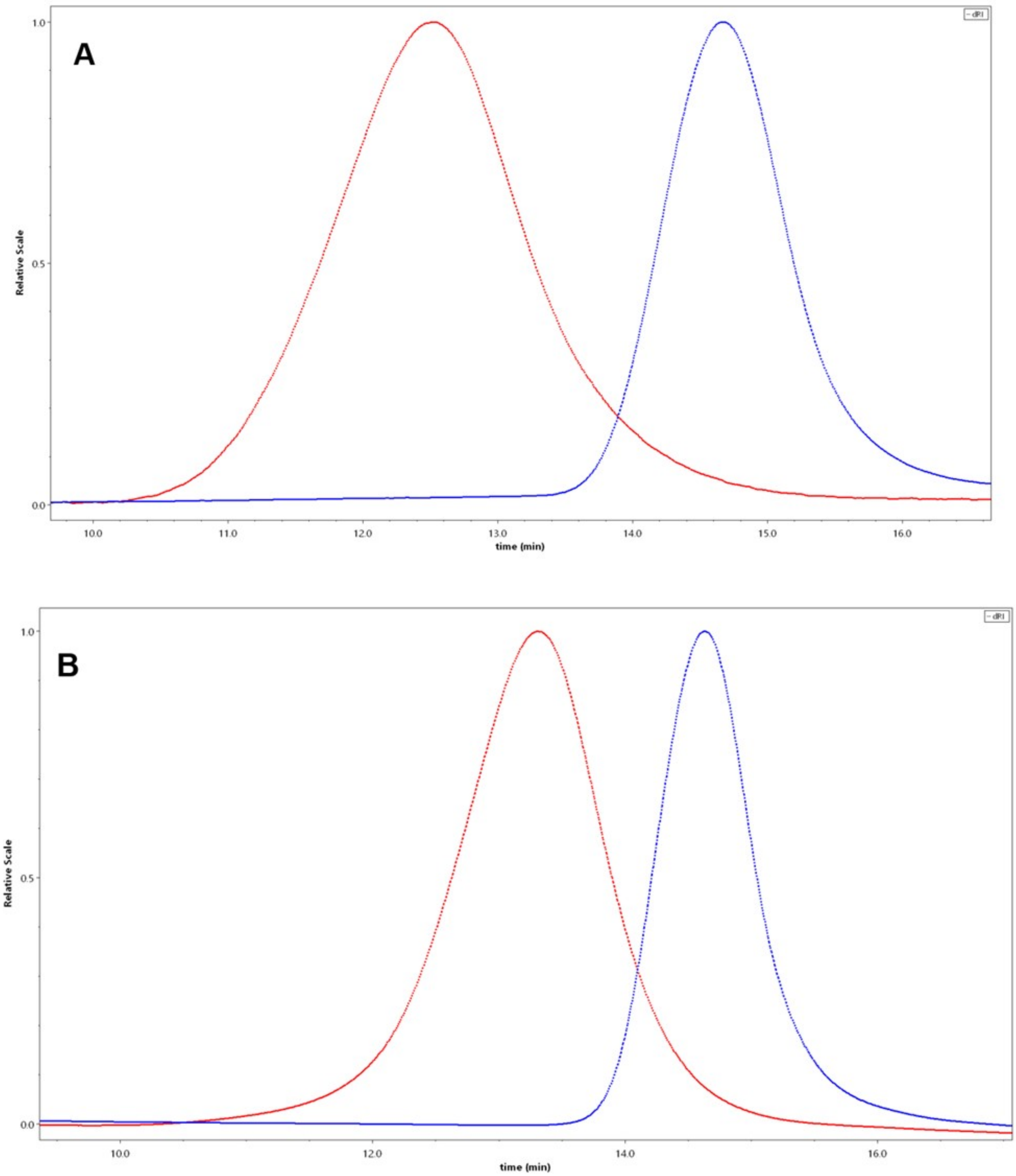

Figure S7: GPC-RI traces of **(A)** poly(*t*BA) before (M_n – 170 kDa, Đ – 1.7, red) and after (M_n – 21 kDa, Đ – 1.3, blue) and **(B)** poly(MMA) before (M_n – 110 kDa, Đ – 1.6, red) and after (M_n – 20 kDa, Đ – 1.1, blue) sonication in DMF (2.1 M) for 24 h. US-mediated polymer chain scission is observed for both types of polymers as assessed by change in retention time and measurement of absolute molar masses by GPC-MALS.

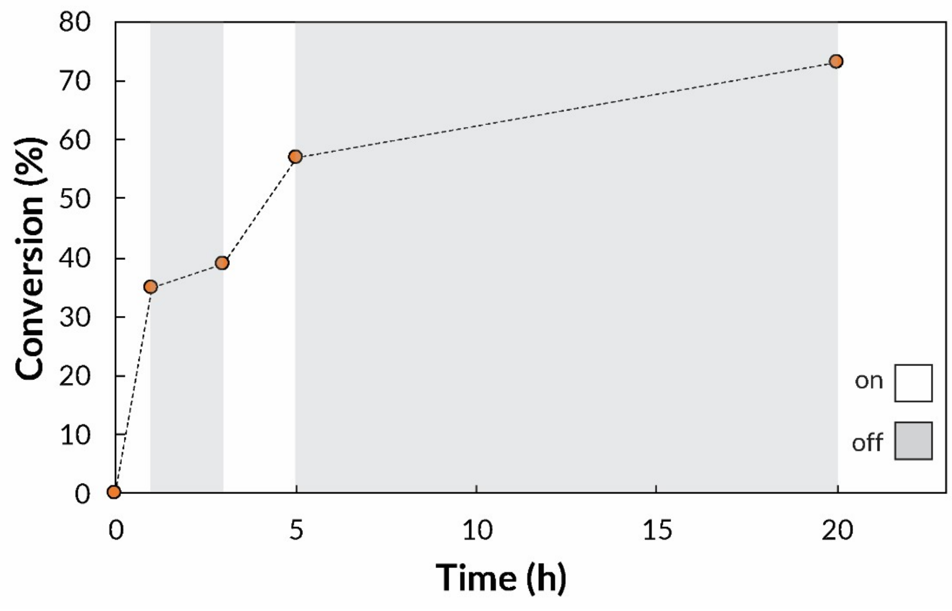

Figure S8: On/Off US-mechanoredox FRP of *t*BA. Reaction conditions: [*t*BA]$_0$:[DPIHP]$_0$ = 100:1. [*t*BA] = 7.3 M in DMF, Ultrasonic bath (40 kHz, 70 W, 20 °C).

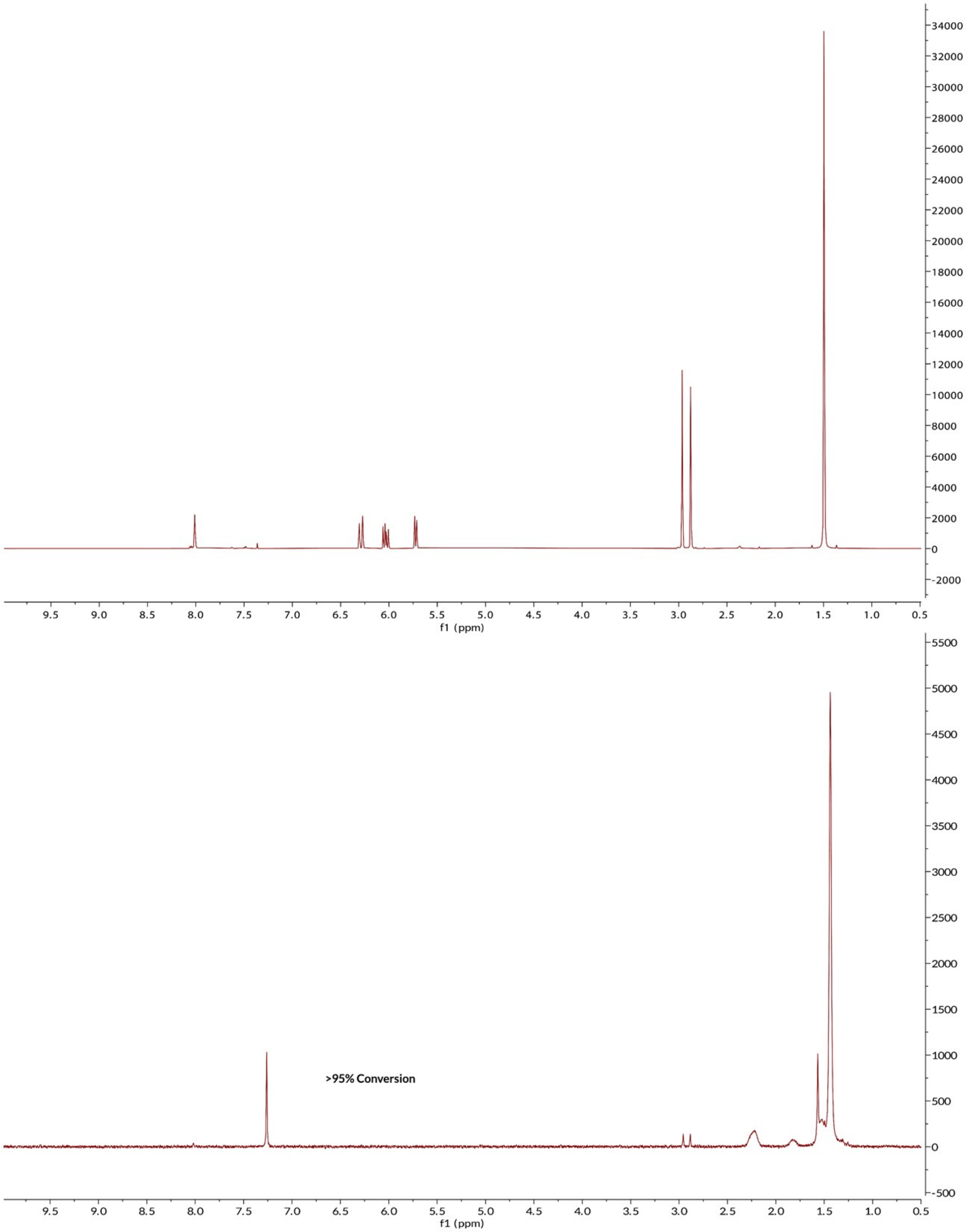

Figure S9: Representative ^{1}H NMR spectum of poly(*t*BA) synthesized using BM-mechanoredox FRP from which >95% monomer conversion was determined (bottom). Representative ^{1}H NMR spectrum of reaction mixture prior to ball milling is shown on top. Polymer sample was synthesized using conditions from entry 1 of Table S6: *t*BA = 0.026 g, 2.0 mmol; DPIHP = 0.017 g, 0.040 mmol; $BaTiO_3$ = 0.14 g, 0.60 mmol; DMF (LAG) = 0.12 mL; 0.030% v/w. Milled for 180 minutes at 30 Hz.

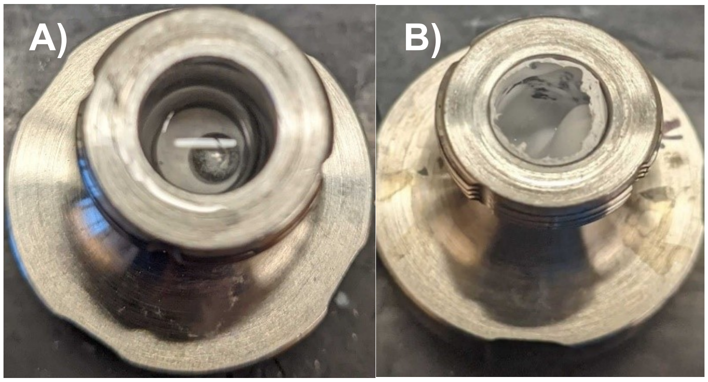

Figure S10: Photographs of a typical BM-mediated FRP reaction before and after ball milling. Photograph **(A)** is before milling and Photograph **(B)** is after milling with >95% monomer conversion.

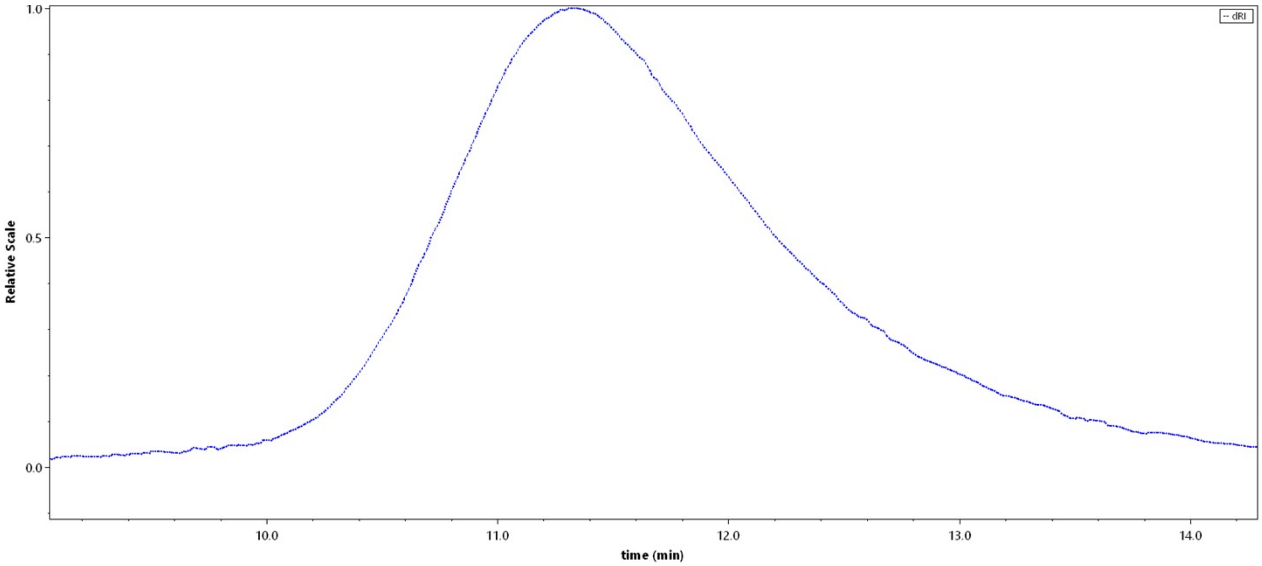

Figure S11: Representative of GPC-RI trace of poly(*t*BA). M_n (GPC-MALS): 475 kDa. Synthesized by ball-milling for 3 h with conditions as follows: *t*BA = 0.26 g, 2.0 mmol; DPIHP = 0.017 g, 0.040 mmol; $BaTiO_3$ = 0.14 g, 0.60 mmol; DMF (LAG) = 0.12 mL; 0.030% v/w.

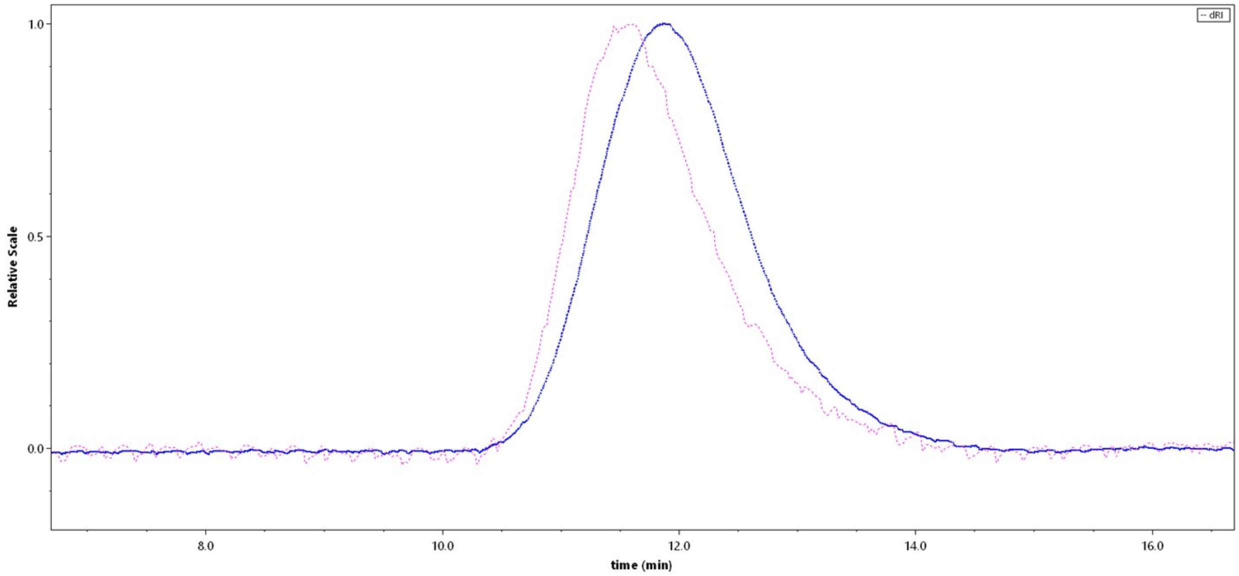

Figure S12: GPC-RI traces of poly(*t*BA) before (M_n – 290 kDa, Đ – 1.4, pink) and after (M_n – 260 kDa, Đ – 1.4, blue) ball milling in DMF (61 mg of polymer in 0.018 mL solvent) for 3 h as determined by GPC-MALS.

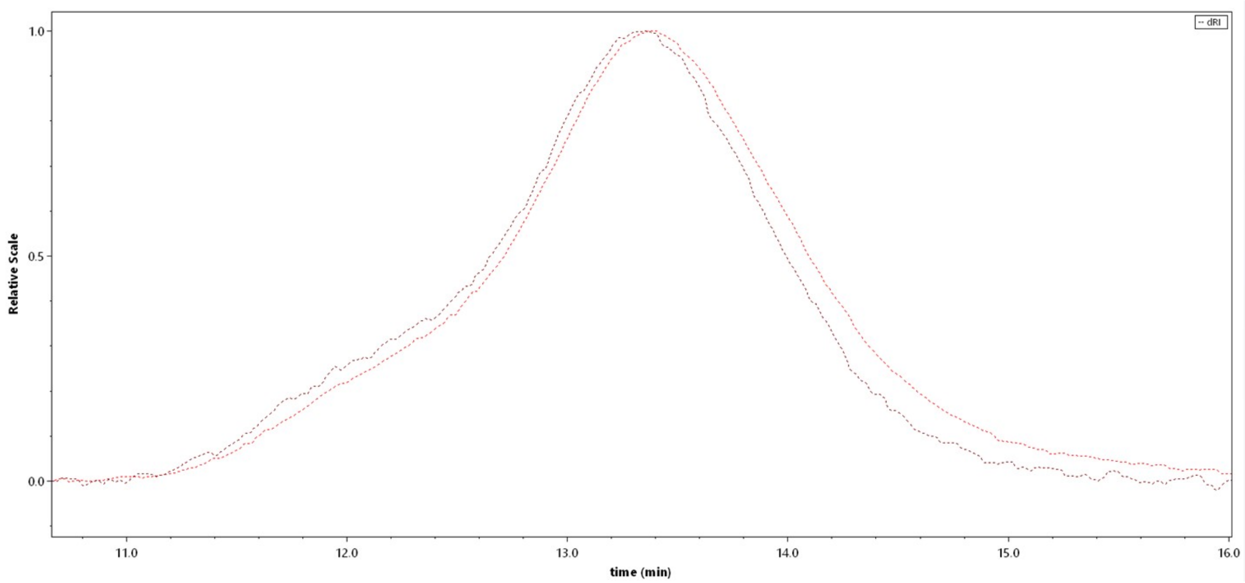

Figure S13: GPC-RI traces of poly(MMA) before (M_n – 95 kDa, Đ – 1.7, brown) and after (M_n – 75 kDa, Đ – 1.8, red) ball milling in DMF (61 mg of polymer in 0.018 mL solvent) for 3 h as determined by GPC-MALS.

4. Supplementary Tables

Table S1: Results for US-mechanoredox FRP using aryl diazonium initiators

Entry	Nanoparticle	Ultrasound ?	Monomer	Solvent	Initiator	Conversion (%)[c]
1[a]	ZnO	Yes	*t*BA	DMAc	BBDT	95%
2[a]	ZnO	No	*t*BA	DMAc	BBDT	70%
3[a]	ZnO	Yes	BA	DMF	BBDT	90%
4[a]	ZnO	No	BA	DMF	BBDT	55%
5[a]	ZnO	Yes	*t*BA	DMAc	MBDT	63%
6[a]	ZnO	No	*t*BA	DMAc	MBDT	32%
7[b]	ZnO	Yes	EA	DMAc	MBDT	62%
8[b]	ZnO	No	EA	DMAc	MBDT	27%
9[a]	$BaTiO_3$	No	*t*BA	DMAc	BBDT	90%

Reaction conditions: $[\text{monomer}]_0:[\text{DPIHP}]_0 = 100:1$. [a] [monomer] = 7.3 M, [DPIHP] = 0.073 M. [b] [monomer] = 9.3 M, [DPIHP] = 0.093 M. [c] conversion was determined by ^{1}H NMR spectroscopy. PNP loading: 7 wt%. Ultrasonic bath (40 kHz, 70 W, 20 °C). Reaction time: 20 h.

Table S2: Results for US-promoted ("solvent initiated") FRP in different organic solvents

Entry[a]	Solvent	Conversion (%) [b]
1	DMAc	13
2	DMF	12
3	DMSO	15
4	Dioxane	14
5	Toluene	0
6	Anisole	0

Reaction conditions: [a] [*t*BA] = 7.3 M; [b] Conversion was determined by ^{1}H NMR spectroscopy. Ultrasonic bath (40 kHz, 70 W, 20 °C). Reaction time: 20 h.

Table S3: Results for US-mechanoredox *t*BA FRP in different solvents

Entry[a]	Solvent	Nanoparticle	Conversion[b] (%)
1	DMF	$BaTiO_3$	92
2	DMF	ZnO	62
3	DMAc	$BaTiO_3$	82
4	DMAc	ZnO	68
5	DMSO	$BaTiO_3$	62
6	DMSO	ZnO	52
7	Dioxane	$BaTiO_3$	82
8	Dioxane	ZnO	32
9	Toluene	$BaTiO_3$	<5
10	Toluene	ZnO	<5
11	Anisole	$BaTiO_3$	<5
12	Anisole	ZnO	<5

Reaction conditions: $[\text{monomer}]_0$:$[\text{DPIHP}]_0$ = 100:1. [a][*t*BA] = 7.3 M, [DPIHP] = 0.073 M; PNP loading: 7 wt%. [b] Conversion was determined by ^{1}H NMR spectroscopy. Ultrasonic bath (40 kHz, 70W, 20 °C). Reaction time: 20 h.

Table S4: US-mechanoredox FRP controls: conversion of *t*BA in the absence of US as a function of solvent

Entry[a]	Solvent	Nanoparticle	Conversion[b] (%)
1	DMF	$BaTiO_3$	<5
2	DMF	ZnO	<5
3	DMAc	$BaTiO_3$	<5
4	DMAc	ZnO	<5
5	DMSO	$BaTiO_3$	<5
6	DMSO	ZnO	<5
7	Dioxane	$BaTiO_3$	<5
8	Dioxane	ZnO	<5
9	Toluene	$BaTiO_3$	<5
10	Toluene	ZnO	<5
11	Anisole	$BaTiO_3$	<5
12	Anisole	ZnO	<5

Reaction conditions: $[\text{monomer}]_0$:$[\text{DPIHP}]_0$ = 100:1. [a] [*t*BA] = 7.3 M, [DPIHP] = 0.073 M; PNP loading: 7 wt%. [b] Conversion was determined by ^{1}H NMR spectroscopy. Reaction time: 20 h, 23 °C.

Table S5: US-mechanoredox FRP controls: conversion of (meth)acrylate in the absence of US

Entry	Monomer	Nanoparticle	Solvent	Conversion[d] (%)
1[a]	*t*BA	$BaTiO_3$	DMF	<5
2[a]	*t*BA	ZnO	DMAc	<5
3[a]	BA	$BaTiO_3$	DMF	<5
4[a]	BA	ZnO	DMAc	<5
5[b]	EA	$BaTiO_3$	DMF	<5
6[b]	EA	ZnO	DMAc	<5
7[c]	MA	$BaTiO_3$	DMF	<5
8[c]	MA	ZnO	DMAc	<5
9[b]	MMA	$BaTiO_3$	DMF	<5
10[b]	MMA	ZnO	DMAc	<5

Reaction conditions: $[\text{monomer}]_0$:$[\text{DPIHP}]_0$ = 100:1. [a] [monomer] = 7.3 M, [DPIHP] = 0.073 M; [b] [monomer] = 9.3 M, [DPIHP] = 0.093 M; [c] [monomer] = 10.9 M, [DPIHP] = 0.109 M. [d] Conversion was determined by ^{1}H NMR spectroscopy. PNP loading: 7 wt%. Reaction time: 20 h, 20 °C.

Table S6: Control experiment results for ball-milling and PNP mediated polymerization of acrylate monomers.

Entry	Deviation from Standard Conditions	Conversion[a] (%)
1	None	>95
2	Without DMF	<5
3	Without $BaTiO_3$	<5
4	Without DPIHP	14

5	Without $BaTiO_3$ and DMF	7
6	Without ball	<5

Reaction conditions: Standard Conditions: *t*BA = 0.26 g, 2.0 mmol; DPIHP = 0.14 g, 0.040 mmol; $BaTiO_3$ = 0.14 g, 0.60 mmol; DMF (for LAG) = 0.12 mL, 0.030% v/w. [a] Conversion was determined by ^{1}H NMR spectroscopy. Ball mill (1.5 mL stainless steel jar, 5 mm stainless steel grinding ball, 30 Hz). Reaction time: 3 h.

Table S7: BM-mechanoredox controls: ball-milling *t*BA with different nanoparticles

Entry	**Nanoparticle**	**Conversion[a] (%)**
1	ZnO	<5
2	TiO_2	<5
3	None	<5

Reaction conditions: *t*BA = 0.26 g, 2.0 mmol; DPIHP = 0.14 g, 0.040 mmol; PNP = 0.60 mmol; DMF (for LAG) = 0.12 mL, 0.030% v/w. [a] Conversion was determined by ^{1}H NMR spectroscopy. Ball mill (1.5 mL stainless steel jar, 5 mm stainless steel grinding ball, 30 Hz). Reaction time: 3 h.

Table S8: BM-mechanoredox controls: ball-milling *t*BA under nitrogen at different time points

Entry[a]	**Time**	**Conversion (%)**	**M_n (kDa)**	**Đ**
1	10	14	525	1.3
2	90	69	561	1.3
3	120	86	520	1.3

Reaction conditions: *t*BA = 0.26 g, 2.0 mmol; DPIHP = 0.14 g, 0.040 mmol; $BaTiO_3$ = 0.14 g, 0.60 mmol; DMF (for LAG) = 0.12 mL, 0.030% v/w. [a] Conversion was determined by ^{1}H NMR spectroscopy. Ball mill (1.5 mL stainless steel jar, 5 mm stainless steel grinding ball, 30 Hz). Reaction time: 3 h.

5. References

1 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518–1520.

2 K. Kubota, Y. Pang, A. Miura and H. Ito, *Science*, 2019, **366**, 1500–1504.