Piezoelectrically Mediated Reversible Addition-Fragmentation Chain Transfer Polymerization

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Materials

N-butyl acrylate (BA), tert-butyl acrylate (tBA), methyl acrylate (MA), methyl methacrylate (MMA), and polyethylene glycol methacrylate (PEGMA, $M_n = 500$) were obtained from Sinopharm Chemical Reagents and purified by passing it through a column of basic alumina. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), et al., and other chemicals are purchased from TCI and used as received. ZnO nanoparticles with a particle size of 10 ~ 30 nm were purchased from J&K Scientific LTD.

Deuterated solvents were obtained from Deutero GmbH. Sodium sulfate anhydrous (99%), n-hexane (97%), methanol (99.7%), diethyl ether anhydrous (99.7%), dichloromethane (99.5%), ethyl acetate (99.5%), acetone, and dimethyl sulfoxide (DMSO, 99.9%) were purchased from commercial supplier named Sinopharm Chemical Reagent Co., Ltd. All reagents were used directly as received without further purification unless otherwise stated.

Measurements

Nuclear magnetic resonance (NMR) spectra of the samples were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz) by using CDCl$_3$ as the solvent and tetramethylsilane as the internal standard at room temperature.

Gel permeation chromatography (GPC) data were obtained using a TOSOH HLC-8320 SEC equipped with a TSK gel Multipore HZ-N (3) 4.6 × 150 mm column at 40 °C. THF served as the eluent with a flow rate of 0.35 mL min$^{-1}$. SEC samples were injected using the TOSOH HLC-8320 SEC plus autosampler. The molecular weights were calibrated with PMMA or PS standards.

$^1$H DOSY experiments were performed on an Agilent Direct-Drive II 600 MHz spectrometer (USA) equipped with four broad-band rf channels and a 5mm 1H19F/15N-31P triple-resonance pulse field gradient (PFG) probe tuned to the recording frequency of 599.829 MHz. All
experiments were run without spinning to avoid convection. The DOSY bipolar pulse pair stimulated echo with convection compensation (Dbppste_cc) sequence was utilized with 1s relaxation delay, 9.6 kHz spectral window, 32 transients, and 10.3 μs 90° pulse width. Diffusion time was 40 ms and gradient duration was 2 ms. The number of gradient steps was set to be 15 and the diffusion encoding pulse strength (gzwvl1) value was linearly increased from 1130 to 28260. DOSY spectra were processed by MestReNova12 software.

MALDI-TOF mass spectrum (MS) was acquired on an UltrafleXtreme III MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with an Nd: YAG smart beam-II laser with 355-nm wavelength and 200 Hz firing rate. The compound trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%), served as the matrix, was dissolved in CHCl₃ at a concentration of 20 mg/mL. The cationizing agent sodium trifluoroacetate was dissolved in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). The instrument was calibrated before each measurement with external PMMA at the molecular weight under consideration. All samples were dissolved in THF at a concentration of 10 mg/mL. The sample solutions were then deposited onto the MTP 384 target plate. After sample preparation and solvent evaporation, the target plate was inserted into the MALDI-TOF mass spectrometer. For high resolution mass analysis, the instrument was operated in reflector mode.

X-ray photoelectron spectroscopy (XPS) was measured with the Thermo Fisher Scientific ESCALAB 250 Xi, Al KR source (MA, USA).

The structures of the samples were characterized by X-ray diffraction (XRD) employing an X-ray diffractometer (D8 Advance, Bruker Inc., 40 kV, 40 mA, a nickel-filtered Cu Kα radiation).

Ultraviolet visible (UV-vis) spectra were recorded on a Shimadzu UV-2600 spectrophotometer (Kyoto, Japan).

Rheological studies of the hydrogels were performed on a strain-controlled Advanced Rheology Expanded Systems HAAKE RS6000 (Thermo Scientific, Germany). The hydrogels rheological properties were studied by measuring geometry with P20/Ti-02150209. Zero gap calibrations at 25 °C were ensured prior to each test. Linear viscoelastic regions (LVR) of nanocomposites were confirmed by conducting the strain sweep tests at a frequency of 1 Hz and 0.1–100% strain.
Experimental procedure for synthesis of chain transfer agent precursor bis-(ethanesulfanylthiocarbonyl) disulfide (CTA)

CTA were prepared according to the method previously reported with slight modification [1]. Briefly, a flame dried round bottom flask was charged with sodium hydride (60% suspension in mineral oil, 20.8 mmol, 832 mg, 1.04 equiv) followed by diethyl ether (Et₂O, 15 mL, 1.39 M) under N₂. The flask was cooled to 0 °C with an ice bath. Ethanethiol (20.0 mmol, 1.5 mL, 1.0 equiv) was added slowly under N₂. The suspension was stirred at 0 °C for 30 min, then stirred for another 3 h at room temperature (RT) under N₂. Then carbon disulfide (20.8 mmol, 1.26 mL, 1.04 equiv) was then added slowly at 0 °C. The reaction mixture was allowed to warm to RT and stirred for another 3 h under N₂. N-hexane (30 mL) was added to the reaction mixture and the solid was filtered and washed with additional n-hexane. The solid was redispersed in diethyl ether (30 mL) under ambient conditions, cooled to 0 °C, followed by the addition of iodine (11 mmol, 2.8 g, 0.55 equiv) over 5 min with vigorous stirring. The reaction was stirred overnight under ambient conditions. The resultant solid NaI was removed via filtration, then the filtrate was washed with water (20 mL), followed by saturated sodium thiosulfate (3 x 30 mL) solution at which point the washings became colorless. The organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated. The product was recrystallized in cold methanol twice and dried under a high vacuum to afford an orange oil which was analytically pure by ¹H NMR. (2.23 g, 81.24% yield).

¹H NMR (300 MHz, CDCl₃, ppm): δ 3.32 (q, J = 7.5 Hz, 4H), 1.36 (t, J = 7.5 Hz, 6H).

¹³C NMR (300 MHz, CDCl₃): δ 221.37, 32.62, 12.38.

Experimental procedure for mechano-radical polymerization

In a typical experiment, 0.11 mmol of CTA, 0.0772 mmol of tris(2-pyridylmethyl) amine (TPMA) were mixed in 1 mL DMSO and loaded into a Schlenk flask. Then 8 mmol of monomers (BA) and 0.22 mmol of ethyl α-bromoisobutyrate (EBiB) were added into the reaction mixture. Finally, ZnO nanoparticles (4.4 wt%) were added and thoroughly mixed with the solution. The reaction mixture was degassed by freeze-pump-thaw (3X) until no gas bubbles were detected and flushed with Ar. The reaction mixture was immersed in the ultrasound bath (33 °C, 40 kHz, 110 W) and sonicated for 8 h. Aliquots were collected at intervals and analyzed using ¹H-NMR and GPC for calculating the conversion and molecular weight.
Experimental procedure for synthesis of Poly(BA-b-MA)

In a typical experiment, Poly(BA) was synthesized as described above. After first polymerization, the resulting polymer was purified by centrifugation to remove the ZnO nanoparticle. The purified product was obtained after precipitation in cold methanol and dried under vacuum. In the chain extension, 25 µmol of Poly(BA) was dissolved in 1 mL DMF, followed by addition of 4.9 µmol AIBN, and 1mL MA into a 25 mL Schlenk flask. The reaction mixture was degassed by freeze-pump-thaw (3X) until no gas bubbles were detected and flushed with Ar. The reaction mixture was immersed in an oil bath kept at 90 °C and sonicated for 10 h. Finally, the purified product was obtained after precipitation DMF in cold methanol and dried under vacuum. The block copolymers were analyzed using ¹H DOSY experiments and GPC for the diffusion coefficient (Ɖ), and molecular weight (Mₙ).

Experimental procedure for TEMPO trapping

0.0772 mmol of TPMA, 0.22 mol TEMPO were mixed in 2 mL DMSO and loaded into a Schlenk flask. Then 0.22 mmol of EBiB were added into the reaction mixture. Finally, ZnO nanoparticles (4.4 wt%) were added and thoroughly mixed with the solution. The reaction mixture was degassed by freeze-pump-thaw (3X) until no gas bubbles were detected and flushed with Ar. The reaction mixture was immersed in the ultrasound bath (33 °C, 40 kHz, 110 W) and sonicated for 8 h. Aliquots were collected at intervals and analyzed using ¹H NMR.

Control experiment: The TEMPO was not added, and the other operations were the same as those described above.

Experimental procedure for gels curing reaction

US-ZnO sample: 0.11 mmol of CTA, 0.0772 mmol of TPMA, and 0.8 mmol divinyl adipate were mixed in 1 mL DMSO and loaded into a 10 mL ampoule. Then 8 mmol of BA and 0.22 mmol of EBiB were added into the reaction mixture. Finally, ZnO nanoparticles (10 wt%) were added and thoroughly mixed with the solution. The reaction mixture was degassed by freeze-pump-thaw (3X) until no gas bubbles were detected and flushed with Ar. The reaction mixture was immersed in the ultrasound bath (33 °C, 40 kHz, 110 W) and sonicated for 4 h.

Light-ZnO sample: 0.11 mmol of CTA, 0.0772 mmol of TPMA, 0.8 mmol divinyl adipate, and 0.22 mmol of benzoin dimethyl ether were mixed in 1 mL DMSO and loaded into a 10 mL ampoule. Then 8 mmol of BA and 0.22 mmol of EBiB were added into the reaction mixture. Finally, ZnO nanoparticles (10 wt%) were added and thoroughly mixed with the solution. The
reaction mixture was degassed by freeze-pump-thaw (3X) until no gas bubbles were detected and flushed with Ar. The reaction mixture was irradiated with a UV source (33 °C, 6.35 W/m²) and stirred (50 rpm) for 4 h.

**Light** sample: The operations were the same as those described above, except adding ZnO nanoparticles.

**Light & US-ZnO** sample: The reaction mixture was first irradiated with a UV source (33 °C, 6.35 W/m²) and stirred (50 rpm) for 1 h. Then, the reaction mixture was immersed in the ultrasound bath (33 °C, 40 kHz, 110 W) and sonicated for 3 h.

*Preparation for ¹H DOSY characterized samples*

Preparation of PBA sample: 0.11 mmol of CTA, 0.0772 mmol of TPMA were mixed in 1 mL DMSO and loaded into a Schlenk flask. Then 8 mmol of BA and 0.22 mmol of EBiB were added into the reaction mixture. Finally, ZnO nanoparticles (4.4 wt%) were added and thoroughly mixed with the solution. The reaction mixture was degassed by freeze-pump-thaw (3X) until no gas bubbles were detected and flushed with Ar. The reaction mixture was immersed in the ultrasound bath (33 °C, 40 kHz, 110 W) and sonicated for 6 h. The final reaction mixture was precipitated in cold methanol, collected and dried under vacuum until constant weight. The $M_n$ and $Đ$ measured by GPC were 19800 Da, and 1.25, respectively.

Preparation PMA sample: operations were the same as the PBA sample described above. The $M_n$ and $Đ$ measured by GPC were 21100 Da, and 1.31, respectively.

5 mg PBA and 5mg PMA were mixed in 0.5 mL CDCl₃ for ¹H DOSY measurement.

10 mg PBA-b-PMA was mixed in 0.5 mL CDCl₃ for ¹H DOSY measurement.

*Preparation for XPS, XRD, and UV-vis characterized samples*

Pure ZnO sample: used directly.

ZnO/TPMA before ultrasonication: 0.11 mmol of CTA, 0.0772 mmol of TPMA were mixed in 1 mL DMSO and loaded into a Schlenk flask. Then 8 mmol of BA and 0.22 mmol of EBiB were added into the reaction mixture. Next, ZnO nanoparticles (4.4 wt%) were added, and then the mixed solution was continuously stirred (50 rpm) overnight. Finally, the white ZnO/TPMA was collected by centrifugation, washed 3 times with THF, and then dried at 60 °C for 12 h in a vacuum drying oven.
ZnO/TPMA after ultrasonication sample: The reaction mixture was ultrasonic for 8 hours. Gray powder was collected by centrifugation, washed 3 times with THF, dried at 60 °C for 12 h in a vacuum drying oven.

**Calculate percentage of cure for each sample**

The prepared gels were immersed in THF and washed 3 times to remove the residual monomer and solvent. The sample was then dried at 60 °C for 12 h in a vacuum drying oven. The percentage of cure was calculated according to Eq. (1):

\[
\text{Percentage of cure (\%)} = \frac{\text{Mass cured resin}}{\text{Mass total resin}} \times 100\% \tag{1}
\]

where Mass \text{ cured resin} and Mass \text{ total resin} represent the weight of cured resin after drying and total weight of resin before curing.
Table S1. Results of piezo-RAFT of BA under various conditions.

| Entry | Condition | Conversion (%) | $M_n$ (Da) | $D$ |
|-------|-----------|----------------|------------|-----|
| 1     | No US     | 0              | N/A        | N/A |
| 2     | No ZnO    | 0              | N/A        | N/A |
| 3     | No EBiB   | 0              | N/A        | N/A |
| 4     | No TPMA   | 0              | N/A        | N/A |
| 5     | No CTA    | 25.3           | 72200      | 1.69|

*aReaction conditions: [BA]₀:[EBiB]₀:[CTA]₀:[TPMA]₀ = 75:2:1:0.7 with 4.4 wt% ZnO in 50% (v/v) DMSO; Ultrasonic bath (33 °C, 40 kHz, 110 W). React for 8 hours.

*bConversion determined by ¹H NMR.

*cDetermined by GPC in THF.

Table S2. Results for mechano-RAFT polymerization of various monomers.

| Entry | Monomer | Conversion (%) | $M_n$ (Da) | $D$ |
|-------|---------|----------------|------------|-----|
| 1     | BA      | 85.9%          | 25200      | 1.23|
| 2     | tBA     | 72.3%          | 28900      | 1.29|
| 3     | MA      | 68.5%          | 18500      | 1.32|
| 4     | MMA     | 85.1%          | 20100      | 1.25|
| 5     | PEGMA   | 88.3%          | 37500      | 1.19|

*aReaction conditions: [Monomer]₀:[EBiB]₀:[CTA]₀:[TPMA]₀ = 75:2:1:0.7 with 4.4 wt% ZnO in 50% (v/v) DMSO; Ultrasonic bath (33 °C, 40 kHz, 110 W). React for 8 hours.

*bConversion determined by ¹H NMR.

*cDetermined by GPC in THF.

*dReact for 4 hours.

Table S3. Results for weight percentage of cured resin after drying.

| Sample name | US-ZnO | Light-ZnO | Light |
|-------------|--------|-----------|-------|
| Percentage of cure (%) | 95.4%  | 31.3%     | 58.8% |
Figure S1. $^1$H NMR spectra of CTA in CDCl$_3$.

Figure S2. $^{13}$C NMR spectra of CTA in CDCl$_3$. 
Figure S3. Photograph of representative experimental set-up for piezo-RAFT polymerization: a) Schlenk flask, and b) ampoule.

Figure S4. $^1$H NMR spectra of polymerization mixture sonicated in the presence of ZnO at (a) t = 0 h, (b) t= 6 h, (c) purified PBA.
Figure S5. $^1$H NMR spectrum for PBA-$b$-PMA in CDCl$_3$.

Figure S6. 600 MHz $^1$H DOSY spectra for PBA, and PMA in CDCl$_3$. 
Figure S7. (a) $^1$H NMR and (b) LC-MS spectra of ultrasound agitation produced free radical. Reaction conditions: $[\text{EBiB}]_0:[\text{TPMA}]_0 = 2:0.7$, loading 4.4 wt% ZnO in 2 mL DMSO with and without 1 eq TEMPO; Ultrasonic bath (33 °C, 40 kHz, 110 W). React for 8 hours.

Figure S8. Images of ZnO before and after ultrasound agitation: (a) pure ZnO; (b) ZnO/TPMA before ultrasonication and (c) ZnO/TPMA after ultrasonication. (d) XPS wide survey spectra; (e) XPS N1s spectra; (f) PXRD patterns and (g) UV–Vis spectra with ZnO at different sonication times.
|                      | US-ZnO | Light-ZnO | Light |
|----------------------|--------|-----------|-------|
| **Before curing**    | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| **After curing**     | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |

Figure S9. Photograph of (a) US-ZnO, (b) Light-ZnO, and (c) Light samples before and after curing.

Figure S10. Photograph of the thickness of (a) US-ZnO, (b) Light-ZnO, and (c) Light samples after the curing.
Figure S11. The storage modulus ($G'$, solid symbols) and loss modulus ($G''$, open symbols) of US-ZnO and Light sample as a function of time obtained at 25 °C.

Figure S12. Photographs show incomplete curing for resin (Light-ZnO) after UV exposure, and complete curing for resin (Light & US-ZnO) using UV curing and subsequent piezo-curing.
Figure S13. The storage modulus (G’) and loss modulus (G”) of Light & US-ZnO sample as a function of time obtained at 25 °C.

Reference
(1) Stache, E. E.; Kottisch, V.; Fors, B. P., Photocontrolled Radical Polymerization from Hydridic C–H Bonds. J. Am. Chem. Soc. 2020, 142 (10), 4581-4585.