Piezoelectrically Mediated Reversible Addition-Fragmentation Chain Transfer Polymerization

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Abstract

A well-controlled piezoelectrically mediated reversible addition-fragmentation chain transfer polymerization (piezo-RAFT) was carried out under ultrasound agitation with piezoelectric ZnO nanoparticles as the mechano-chemical trans-ducer. The resulting polymer had predictable molecular weight, high end-group fidelity, low dispersity, and capacity for chain extension. This chemistry was further adopted in curing composite resins to circumvent the light penetration limit of UV curing. This work opened a new avenue of piezoelectrically mediated chemistry and showed its good potential in curing applications.

Main text

Biological materials, such as bones and muscles can sense and respond to the mechanical signal *via* a process called mechanotransduction.[1] Synthetic materials are also subject to mechanical vibrations that often leads to the damage of material. Mechanically mediated reactions that harness mechanical energy for constructive purposes have gained renewed interest in recent years.[2-5] For example, ultrasound (US) can initiate or enhance the reaction *via* acoustic cavitation in liquid (sonochemistry).[6-8] More recently, piezoelectrically mediated reactions that use the redox activities of piezoelectric nanoparticles under mechanical agitation was reported. It showed advances in both solution and bulk reactions where acoustic cavitation is not sufficient to promote the reaction.[9-15] Great efforts have been made for piezoelectrically mediated small molecular reactions, including water splitting, oxidative dye degradation, and C–C coupling.[12,15-19]

Piezoelectric means to activate the polymerization (piezo-polymerization) process expand the scope of piezoelectrically mediated reactions and show successes in various chemical bond formations.[14,20] Esser-Kahn *et al*. have demonstrated the piezoelectrically mediated atom transfer radical polymerization (mechano-ATRP) by piezoelectric activation of Cu(II) deactivator and bulk-scale free radical polymerization initiated by piezoelectric generation of alkyl radicals.[20-22] Later on, they disclosed piezoelectrically activated thiol–ene polymerization and disulfide bond cross-linking that opened up new avenues for sulfur-based polymer chemistry.[23,24] However, the further development of piezo-polymerization is deterred, as the less attention was put on the reversible deactivation radical polymerization (RDRP) techniques other than ATRP.[25-28]

RAFT polymerization is one of the most popular RDRP techniques that shows good control over molecular weight and high end-group fidelity.[29-33] However, the piezoelectric activation of RAFT agent *via* iniferter mechanism is still challenging. Herein, we show that the piezoelectrically

mediated reduction of alkyl bromides can (1) initiate polymerization and (2) trigger the S-S bond cleavage of the bis(trithiocarbonate) bisulfide to yield RAFT agent *in situ* (Scheme 1).[34-35] We hypothesize that the adsorption of tris(2-pyridylmethyl)amine (TPMA) on ZnO surface could balance the screening charges and fuel the electron transfer to alkyl bromides.[20,22] We first investigated this piezoelectrically mediated RAFT (piezo-RAFT) polymerization of n-butyl acrylate (BA) under US (40 kHz). As a result, the resulting poly(n-butyl acrylate) (PBA) showed excellent control over molecular weight and high chain-end fidelity as evidenced by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). We also demonstrate the application of piezo-RAFT derived curing process (piezo-curing) that addresses the penetration issue of UV curing. This method gave a more complete curing of a cylindric sample (1.91 cm x 6.85 cm) than UV approach.

Piezo-RAFT of BA was conducted using TPMA modified
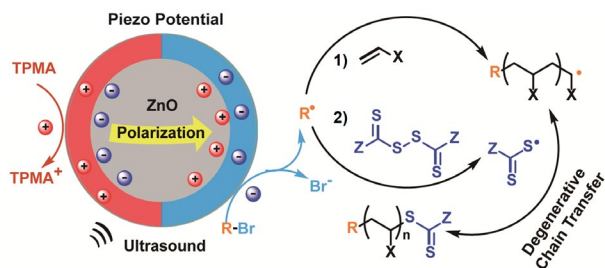
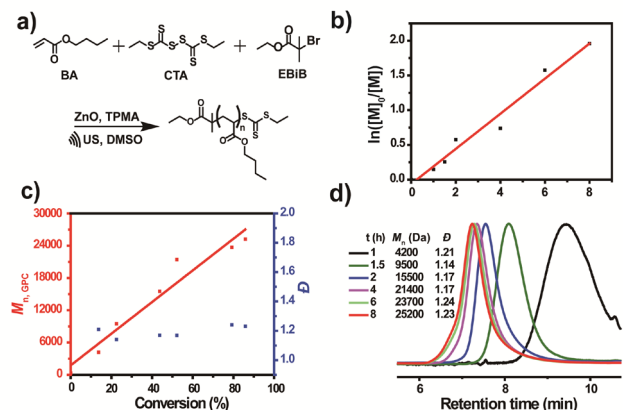**Scheme 1.** The proposed mechanism of piezo-RAFT polymerization.

Figure 1. (a) Piezo-RAFT polymerization of n-butyl acrylate under US; (b) semilogarithmic kinetic plots of evolution and (c) monomer conversion versus number average molecular weight (M_n) and molecular weight distribution ($Đ$); (d) GPC traces evolution.

ZnO as the mechano-chemical transducer, ethyl α-bromoisobutyrate (EBiB) as the radical source, bis(trithiocarbonate) bisulfide as the chain transfer agent precursor (CTA, Figure S1-2) in degassed DMSO under US (40 kHz, 110 W) (Figure 1a). Our experimental set-up (Figure S3) consists of a 5 L ultrasonic bath, a thermocouple, and a cryogenic cooling circulating pump. Temperature was maintained at 33 ± 0.2 °C to avoid thermal contribution. The semilogarithmic kinetic plot in the polymerization of BA followed a pseudo-first-order rate law as expected for RDRP (Figure 1b). The M_n obtained from GPC data increased linearly with conversion, while $Đ$ kept low during the polymerization (Figure 1c). The GPC traces of PBA were unimodal and shifted to the higher molecular weight region over time (Figure 1d). After 8 hours of US, the polymerization of BA reached a monomer conversion of 85.9%, and M_n of 25200 Da. In contrast, no polymerization was observed without ZnO nanoparticles (Table S1), excluding the effect of solvent cavitation.

The structure of PBA was characterized by ^{1}H NMR. The peak assignments were shown in Figure S4.[22] Peaks at δ = 3.31 and 4.16 ppm were assigned to the protons of -CH$_2$- from EBiB and CTA derived group. The PBA structure was also further confirmed by MALDI-TOF MS (Figure 2). The experimental value of the mass to charge ratio, m/z, agreed with the theoretical value of PBA with chain end groups derived from the CTA and EBiB. Main peak series with intervals of 128.08 Da corresponded to the molar mass of BA unit. The secondary peak series between the main peak series
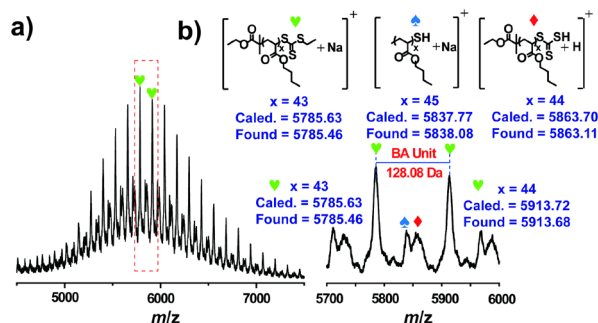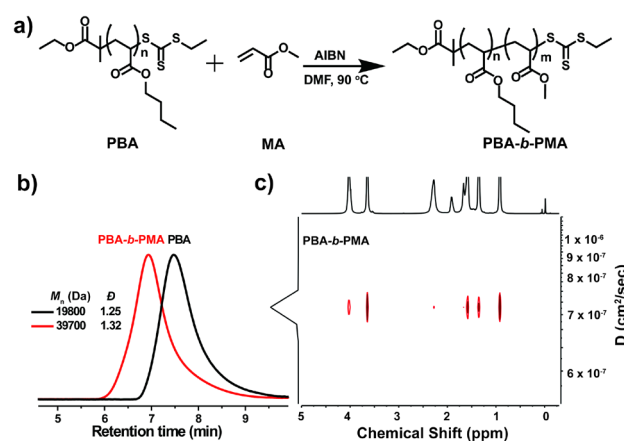
Figure 2. MALDI-TOF-MS analysis of PBA.

Figure 3. a) GPC chromatograms of PBA (red) and PBA-*b*-PMA block copolymer prepared via chain extension of PBA macro chain transfer agents (black); b) 600 MHz ^{1}H DOSY spectrum for PBA-*b*-PMA in CDCl$_3$.

was assigned to the fragmentation of polymer in the spectrometer. The piezo-RAFT polymerizations of different monomers, including tert-butyl acrylate (tBA), methyl acrylate (MA), methyl methacrylate (MMA) and polyethylene glycol methacrylate (PEGMA) were attempted. High monomer conversions (>75 %) were obtained for all the monomers. Among them, PEGMA exhibited the highest activity, giving a conversion of 88.3% and M_n of 37500 Da (Table S1).

To clarify the living character of piezo-RAFT polymerization, chain extension experiments of initially formed PBA were carried out under classic thermal initiation condition. The resulting

PBA-*b*-PMA block copolymer was then characterized by GPC and ^{1}H NMR to identify its structure (Figure 3 and Figure S5). The ^{1}H DOSY experiment was conducted to further confirm the copolymer structure (Figure 3b). All the protons from PMA and PBA block had the same diffusion coefficient (*D*) and thus from the same polymer chains. In comparison, the physical blend of PBA and PMA homopolymer showed different *D* values (Figure S6). These results suggested a living character of this RAFT polymerization and efficient chain transfer to prevent the formation of PMA homopolymer.

We propose that the initiation of piezo-RAFT involves the alkyl radical generation through electron transfer from piezoelectric nanoparticle to EBiB (Scheme 1). This piezoelectric-mediated initiation was first verified *via* (2,2,6,6-tetramethylpiperidine-1-oxyl) (TEMPO) trapping experiment. The reduction of EBiB forms alkyl radical that was subsequently quenched by TEMPO to form alkoxyamine. The ^{1}H NMR of the reaction mixture under US suggested the formation of alkoxyamine (δ 1.16 ppm, –CH$_3$ for TEMPO) (Figure S7a).[36] The LC-MS further confirmed the formation of alkoxyamine from EBiB derived alky radical (Figure S7b).

To further investigate the impact of other components, we conducted polymerizations by selectively removing EBiB, TPMA, and CTA. The polymerization results were summarized in Table S2. Negligible reactivity was observed when ZnO nanoparticle, EBiB, or TPMA was removed from the reaction mixture, suggesting the essential role of each component in the polymerization. In the absence of CTA, the fission-based radical processes took place. This led to the high molecular weight polymer (M_n = 72200 Da) and broad molecular weight distribution ($Đ$ = 1.69) with low monomer conversion (25.3%) due to the severe chain terminations. This uncontrolled polymerization result also highlights the importance of CTA in our experimental design.

The surface of ZnO plays a pivotal role in determining the piezo-reactivity.[11] After US, the color of ZnO sample (ZnO/TPMA) became gray (Figure S8a-c). We speculated that TPMA could balance the screening charges by forming TPMA cation (TPMA$^+$) on the ZnO surface.[20] The deposition of TPMA was further confirmed by the X-ray photoelectron spectroscopy (XPS) analysis. Zn, O, and C peaks were detected as shown in the wide survey spectra (Figure S8d). The N1s XPS spectra showed the peak of nitrogen appeared at 399.5 eV (nitrogen in TPMA) for ZnO/TPMA (Figure S8e). In addition, the sulfur from CTA was not detected, indicating that the polymer did not grow directly from ZnO surface. The powder X-ray diffraction (PXRD) analysis results confirmed the wurtzite structure of ZnO after US (Figure S8f). Thus, the deposition of TPMA and US treatment has little effect on the ZnO structure. Furthermore, the decrease of UV absorbance at 280 nm after US further supported the deposition of TPMA on the ZnO surface (Figure S8g).

Light curing was a widely used technique in the curing industry.[37-38] But curing thick or filled samples (composites) was challenging when using light as the radiation source. In-spired by the high penetration depth of mechanical vibration (usually >10 cm for US)[39], we anticipated that the piezo- curing method could be a good alternative to light curing. To demonstrate this concept, we used piezo-RAFT
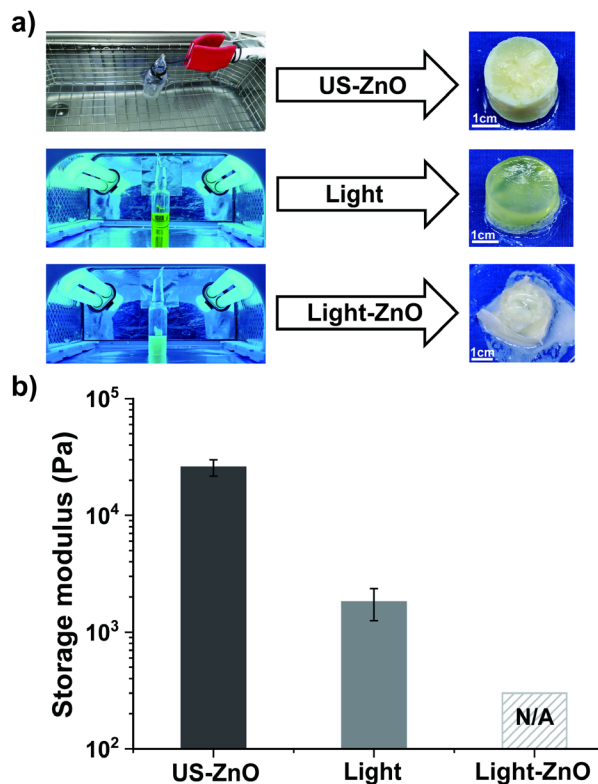
Figure 4. a) The photographs of different experimental set-up and three resulting samples used for rheology measurements. b) The storage modulus of different samples after curing. Data were collected at oscillation frequency of 1 Hz, and time of 300 s.

crosslinking polymerization as the tool to cure an acrylic composite resin with 10 wt% of ZnO as the filler (**US-ZnO**). Two control experiments, one used UV light (6.35 W/m^2) for curing the composite resin (**Light-ZnO**) and the other used UV light for curing acrylic resin without fillers (**Light**), were carried out at a distance of 2 cm between the light source and the vial to ensure that all samples received consistent light (Figure 4a). The pictures of the samples before and after curing were also shown in Figure S9. Although the surface of the samples was easily cured after exposure to US or light, the curing behavior below the surface had a significant difference (Table S3). We measured the weight of cured resin by removing the residual monomer and solvent. The results showed a high percentage of cure (Mass $_{cured\ resin}$ /Mass $_{total\ resin}$) for **US-ZnO** (95.4%) that

far exceeds **Light** (58.8%) and **Light-ZnO** (31.3%). We also characterized the in-depth curing by vernier caliper, as shown in Figure S10. **US-ZnO** sample became a physical solid (6.83 mm thickness) after 4 hours of US (Figure S10a, Video 1). In comparison, **Light-ZnO** sample was cured only at the surface (1.02 mm thickness) with a significant amount of flowing resin still presented after post-curing by light for 4 hours (Figure S10b, Video 2). **Light** sample became gelled semi-solid (2.74 mm thickness) with uncured resin still at the center of the sample. (Figure S10c, Video 3). The inefficient post-curing was mainly attributed to the vitrified surface that blocked the light and prevented the resin inside from curing.

The viscoelastic properties of the gels were further analyzed by rheometry to demonstrate the difference between UV and piezo-curing (Figure 4b and Figure S11). Figure 4b showed the storage modulus of **US-ZnO** (26 kpa) was 10 times higher than the light cured sample (2 kpa). This was mainly attributed to the difference in degree of cure and reinforcement effect of ZnO filler. The **Light-ZnO** sample was not suitable for this measurement due to the incomplete curing as shown in Figure 4a.

To overcome this issue, we proposed to use US as the new post-curing method. The resin was UV cured first and then put under US to get a fully cured sample (**Light & US-ZnO**) (Figure S12). The mechanical strength of the sample was further characterized by the rheology, and a similar storage modulus (29 kpa) compared to piezo-curing was obtained (Figure S13). These results showed the advantage of applying US as a potential method on resin curing, and post-curing treatment. Though the speed of piezo-curing was relatively low in this report, we plan to couple it with other efficient radical processes and high energy US equipment in the future work.

In conclusion, we showed a piezoelectrically mediated reduction of alkyl bromide to activate the RAFT agent *in situ*. Using this piezo-RAFT methodology, the well-controlled polymerizations

were achieved. The resulting polymer had the controlled molecular weight and capacity for chain extension. We also demonstrated the use of this piezo-chemistry for curing composite resin that showed higher penetration depth compared with conventional UV curing. We envision that this chemistry adds new to the piezo-chemistry repertoire and provides new insight in fabricating mechanoresponsive polymeric materials.

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