

Alternating Sulfone Copolymers Depolymerize in Response to Both Chemical and Mechanical Stimuli

Kaushlendra Kumar and Andrew P. Goodwin*

Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO 80303.

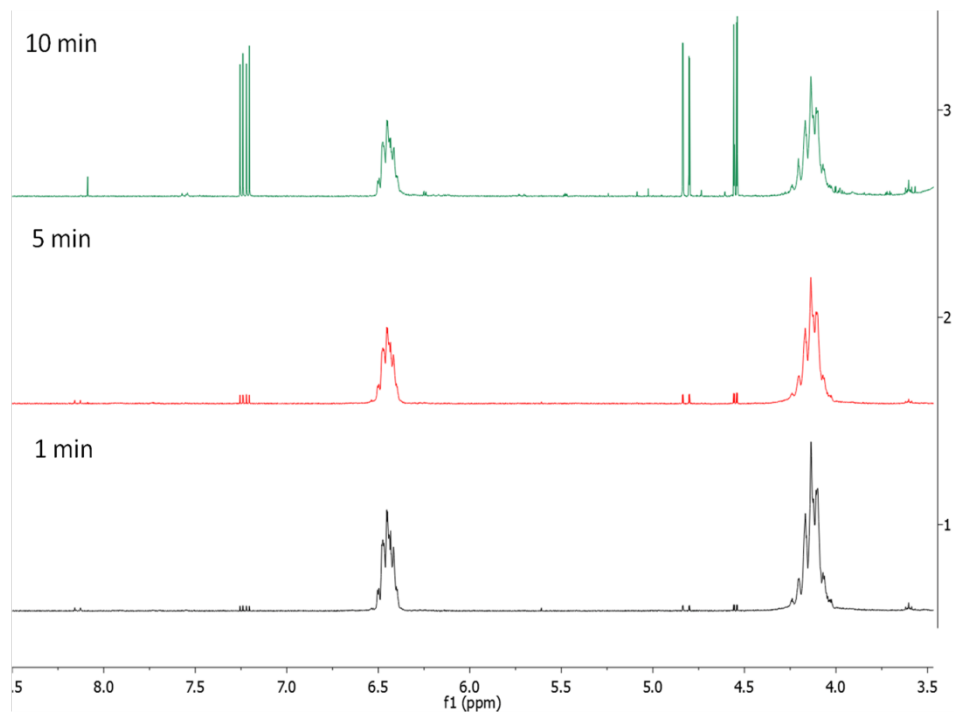


Figure S1: ¹H NMR spectra of 10 mg/mL PVAS in acetone-d₆ irradiated at 320-390 nm and 32-34 mW.

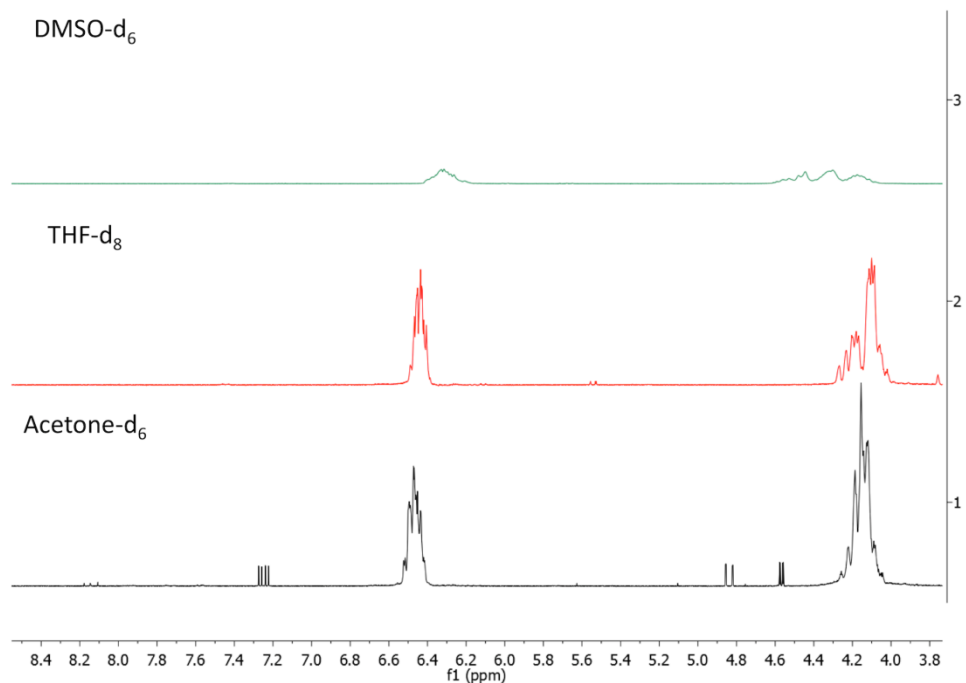


Figure S2: ¹H NMR spectra of 10 mg/mL PVAS in various solvents irradiated at 365 nm for 10 min.

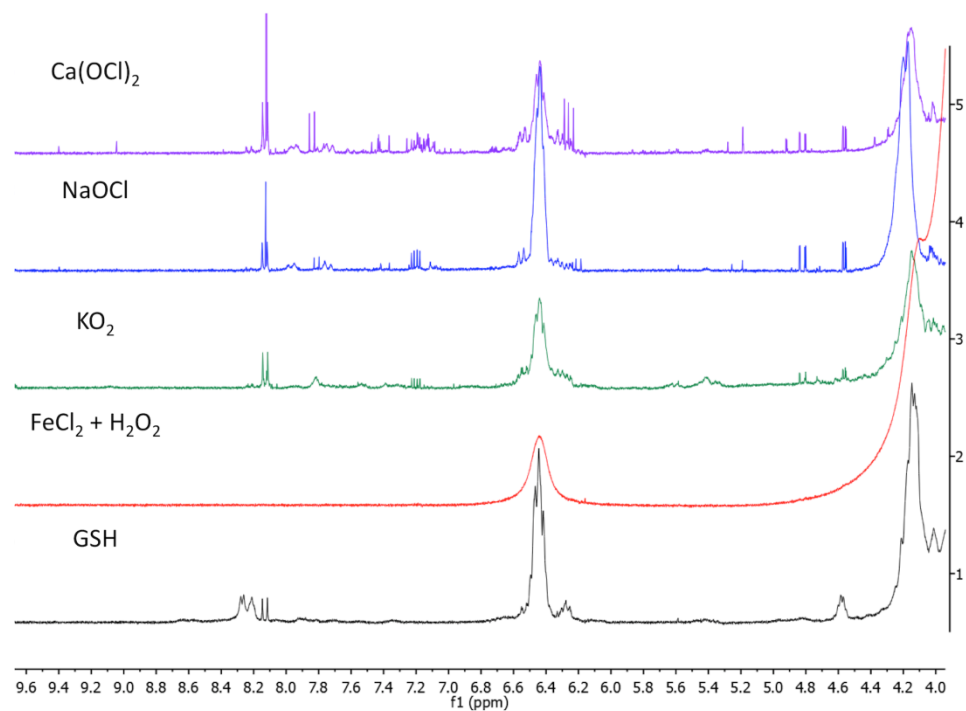


Figure S3: ¹H NMR spectra of 10 mg/mL PVAS in acetone-d₆ incubated with various 10 mM ROS for 20 min.

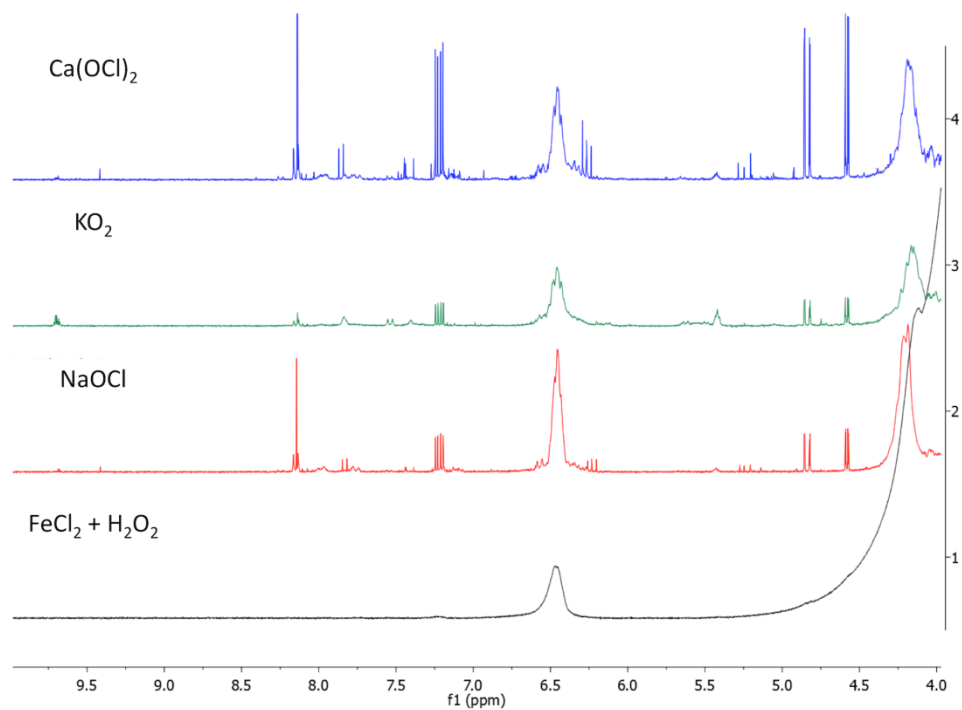


Figure S4: ^1H NMR spectra of 10 mg/mL PVAS in acetone- d_6 incubated with various 10 mM ROS for 24 h.

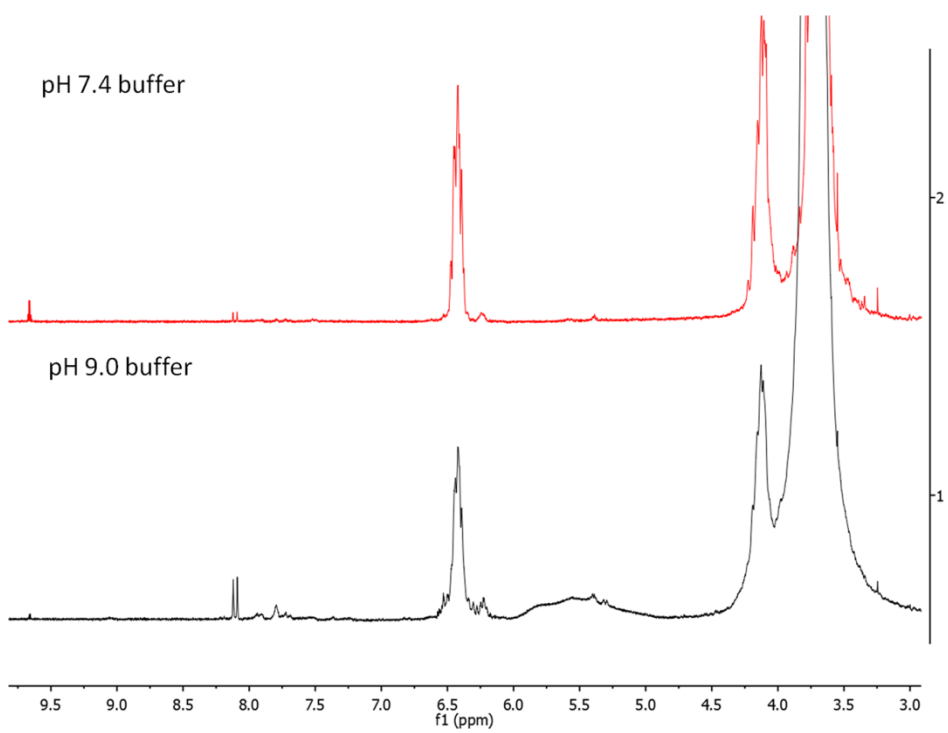


Figure S5: ^1H NMR spectra of 10 mg/mL PVAS in acetone- d_6 incubated with indicated buffers for 20 min.

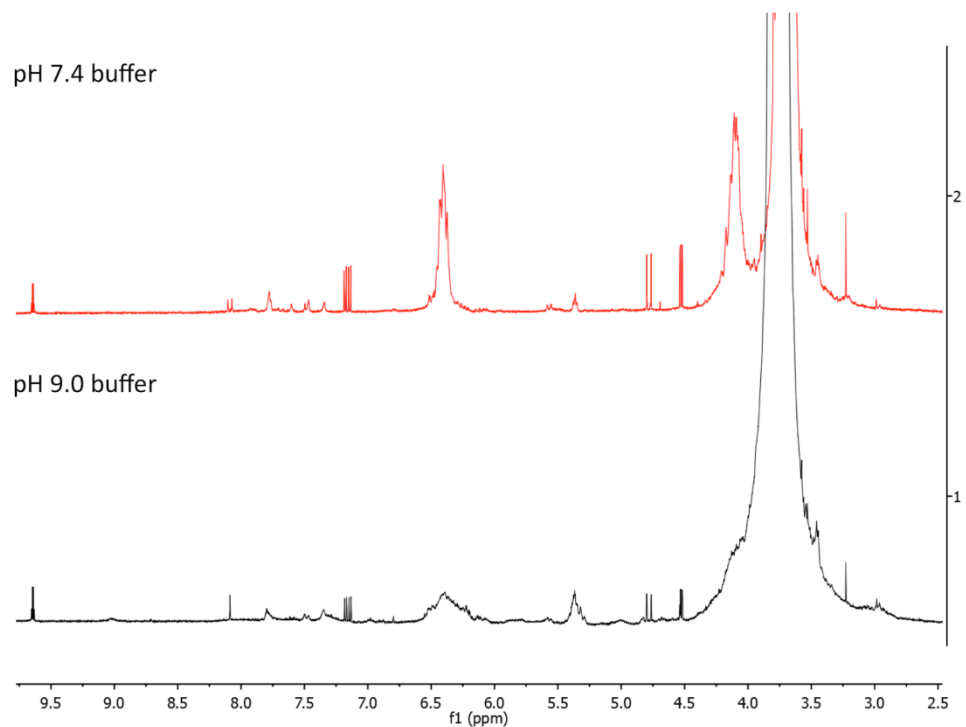


Figure S6: ^1H NMR spectra of 10 mg/mL PVAS in acetone- d_6 incubated with indicated buffers for 24 h.

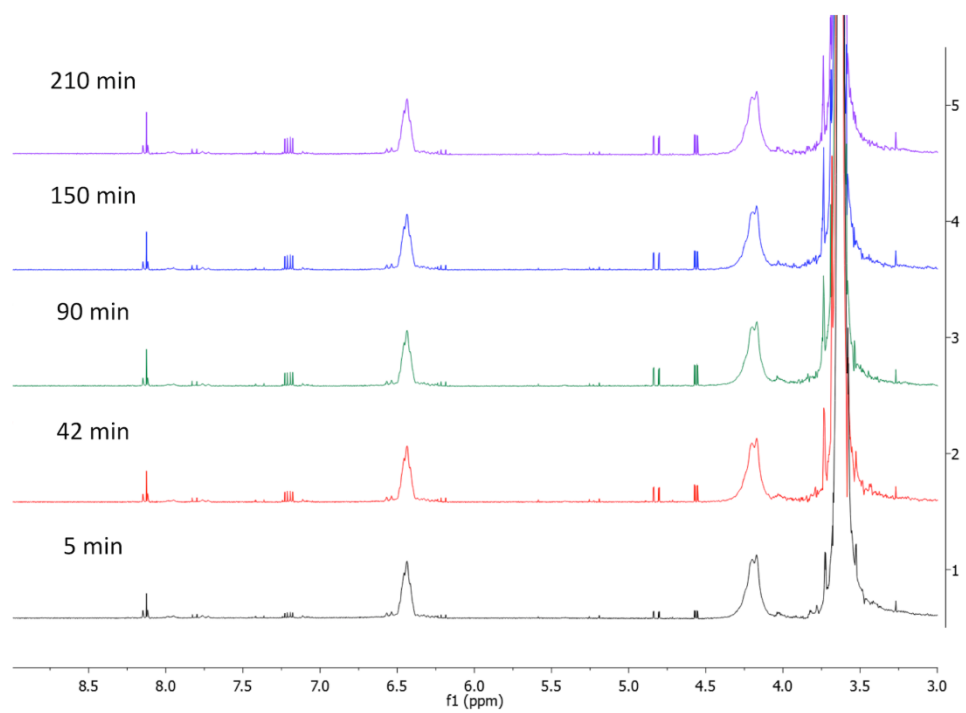


Figure S7: ^1H NMR spectra of 10 mg/mL PVAS in acetone- d_6 incubated with sodium hypochlorite at various times.

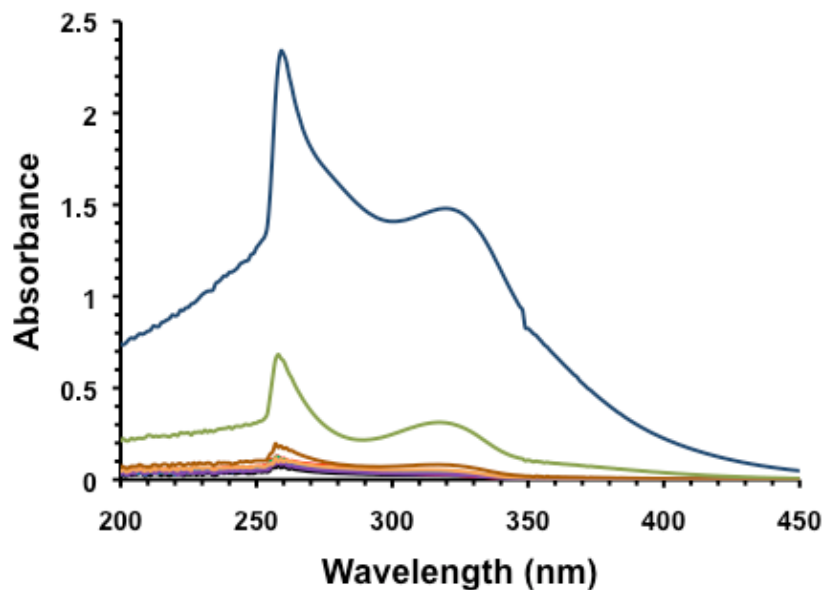


Figure S8: UV-Vis spectra of PVAS in DMSO with varying amounts of KO_2 as depicted in Figure 4a.

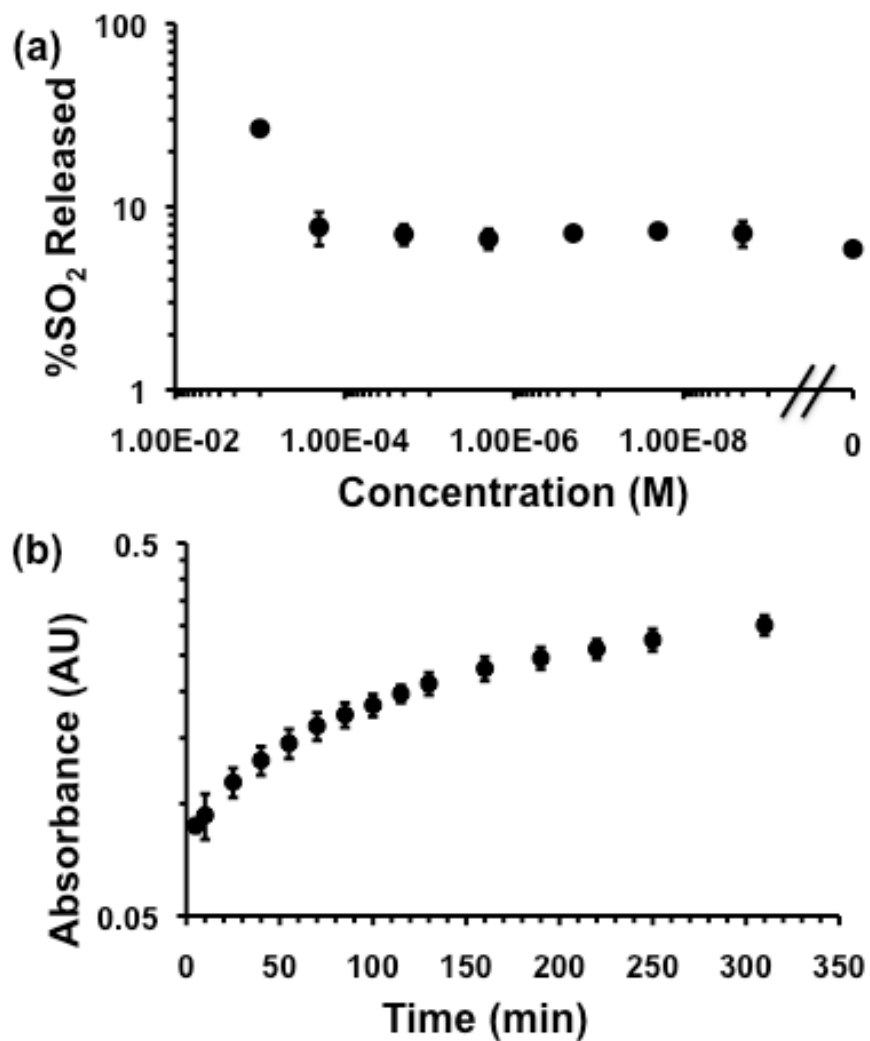


Figure S9: (a) Sulfur dioxide release from PVAS after 24 h, incubated with varying concentrations of NaOCl, as measured at 260 nm and compared to 100% release (Figure S9). Error bars represent standard deviation of two trials. (b)

Absorbance at 260 nm vs. time for PVAS incubated with 200 μM NaOCl. Error bars represent standard deviation of two trials.

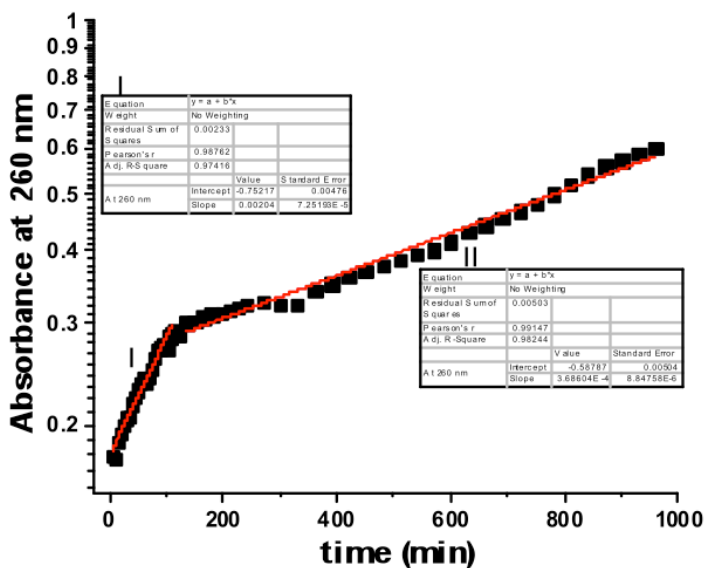


Figure S10: First-order kinetic fit of PVAS reaction with 200 μM potassium superoxide. Initial phase (I) has a slope of $2.0\text{E-}3$ AU/min, second phase has a slope of $3.7\text{E-}4$ AU/min based on first-order kinetics.

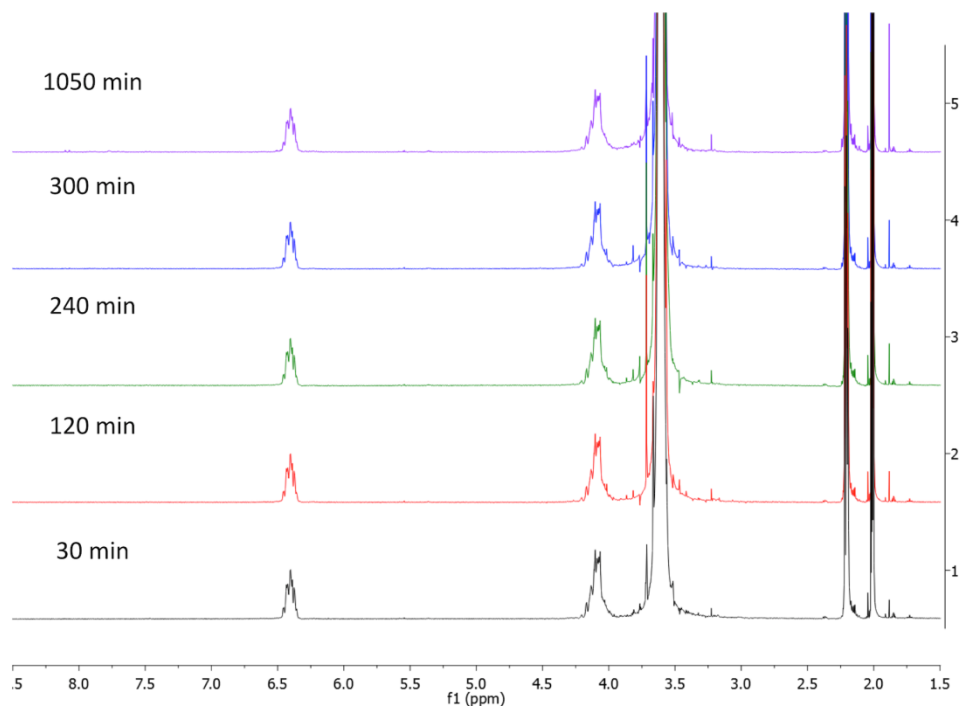


Figure S11: ^1H NMR spectra of 10 mg/mL PVAS in acetone- $\text{d}_6/\text{H}_2\text{O}$ at various times.

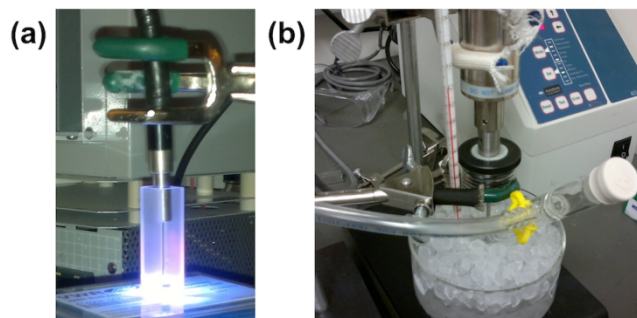


Figure S12: (a) Experimental setup for UV-irradiation of PVAS. (b) Experimental setup for ultrasonication of PVAS.

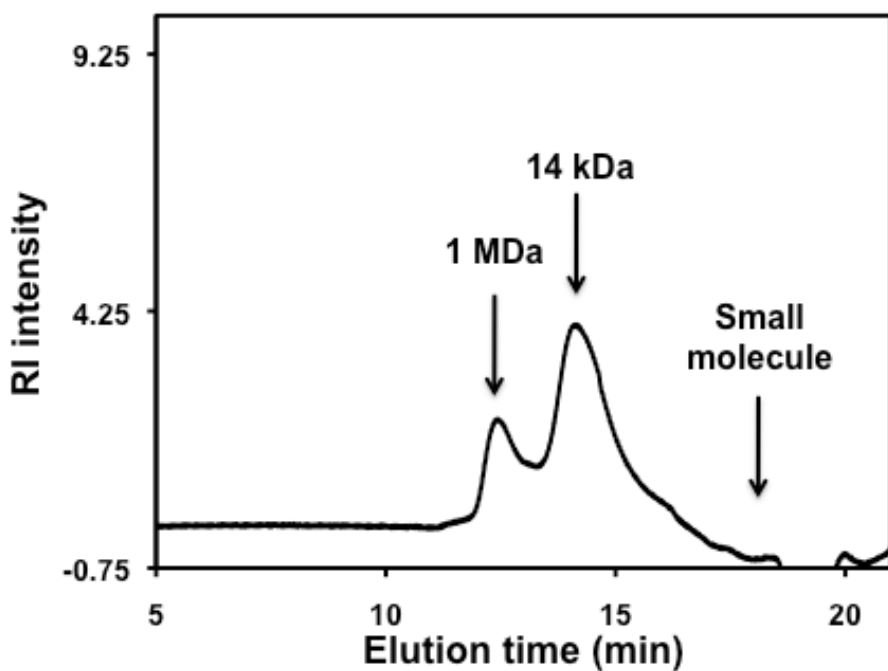


Figure S13: GPC chromatogram of unreacted or unsonicated PVAS. Arrows indicate maximum molecular weight for each peak.

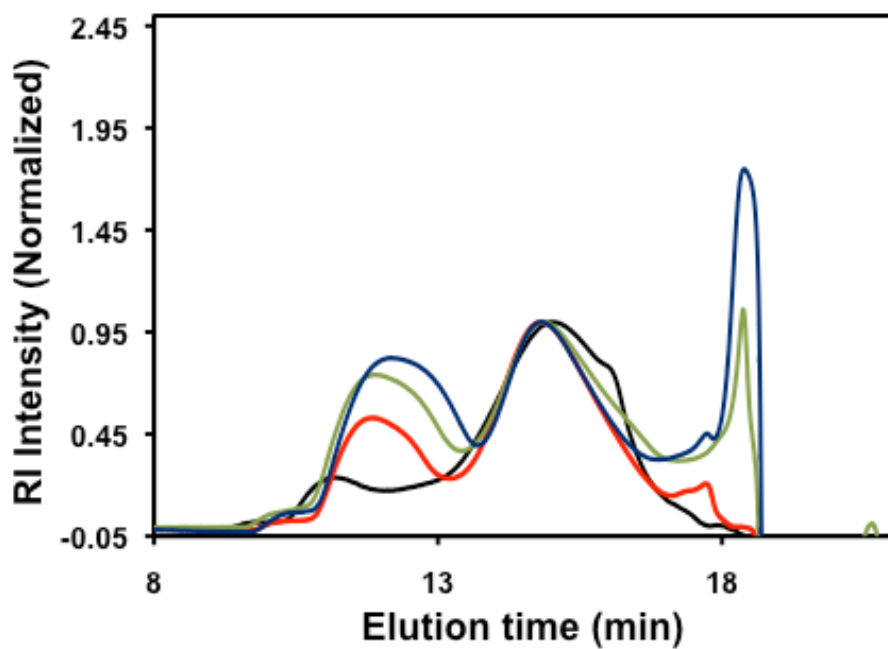


Figure S14: GPC chromatogram of PVAS compared before and after sonication for different times. No sonication (black), 15 min sonication (red), 30 min sonication (green) and 60 min sonication (blue).

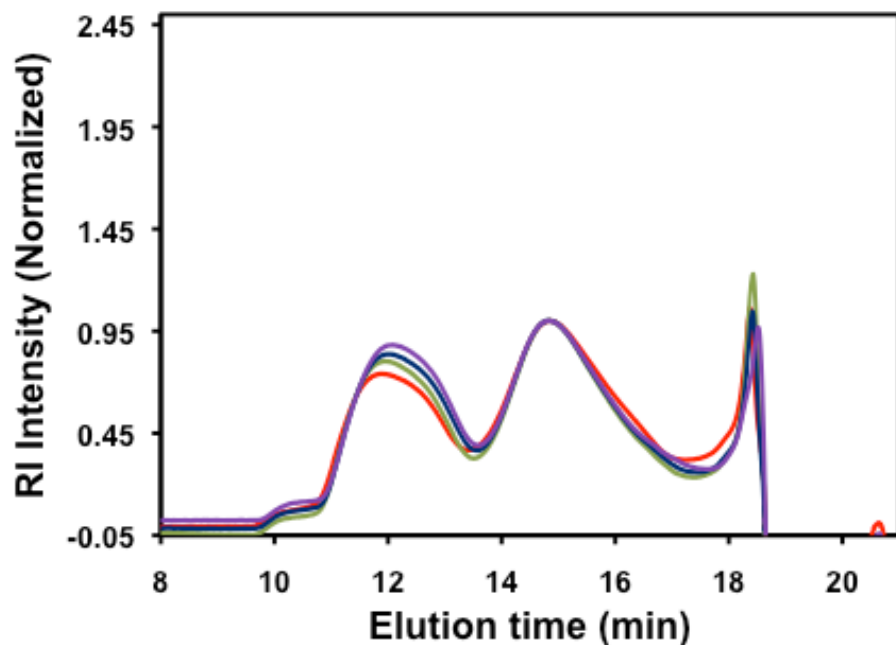


Figure S15: GPC chromatograms of PVAS after 30 min sonication (red), then 30 min (green), 1 h (blue), and 2 h (purple) post-sonication.

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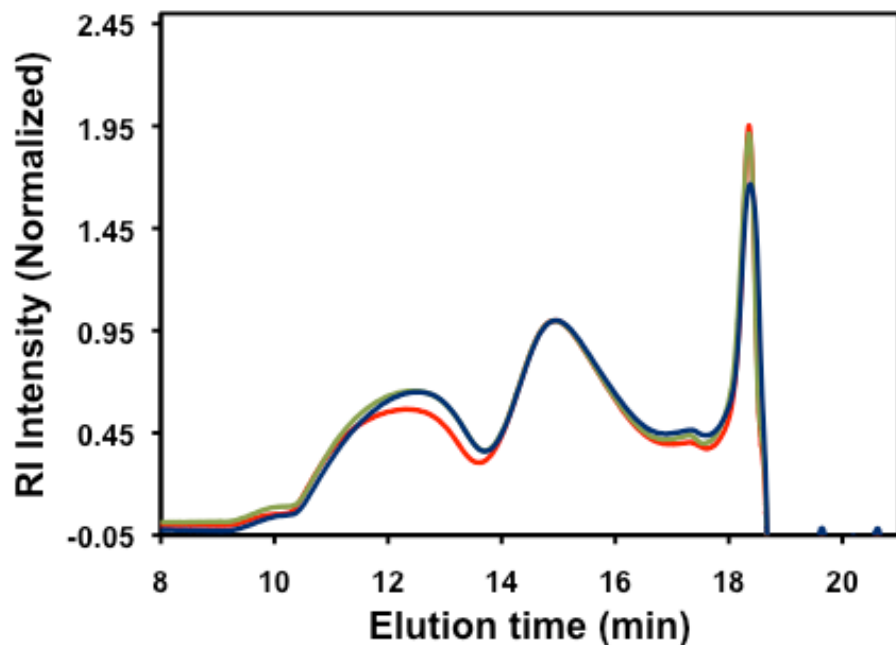


Figure S16: GPC chromatograms of PVAS after 60 min sonication (red), then 1 h (green) and 2 hr (blue) post-sonication.

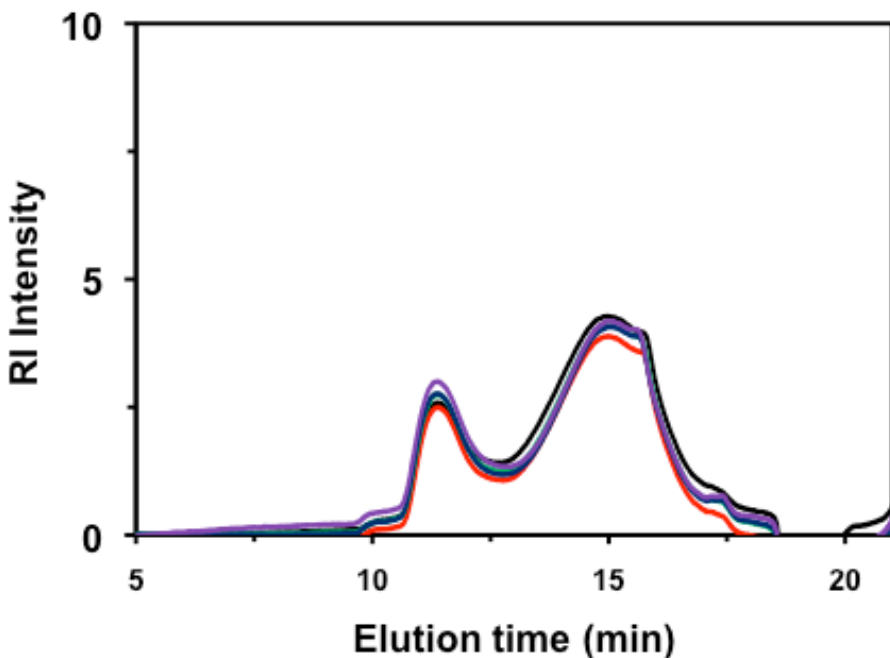


Figure S17: GPC chromatograms of PVAS in DMSO without sonication for freshly prepared sample (black), after 1 h (red), 2 h (green), 3 h (blue), and 4 h (purple).

Experimental Section

Materials

Vinyl acetate (VA), Sulfur dioxide (SO₂), and tert-butyl hydroperoxide as a solution in decane (TBHP) were purchased from Sigma Aldrich. Vinyl acetate was passed through alumina column prior to use. SO₂ was passed through calcium sulfate dessicant just before transferring to reaction vessel. Calcium hypochlorite with 65 % available chlorine (Ca(OCl)₂), sodium hypochlorite with 5 % active chlorine (NaOCl), potassium superoxide (KO₂), glutathione, and ferrous chloride (FeCl₂) were purchased from Acros Organics and used without any further purification. 30% aqueous solution of hydrogen peroxide (H₂O₂) was purchased from Macron Fine Chemicals. Methanol was purchased from EMD Chemicals. Deuterated solvents acetone-d₆, tetrahydrofuran-d₈ (THF-d₈) and dimethyl sulfoxide (DMSO-d₆) were purchased from Cambridge Isotope Laboratories and used without further purification.

Instrumentation

The ¹H-NMR spectroscopy studies were carried out using Bruker AV-III 400 MHz NMR spectrometer, using ICON NMR in automation. The chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard. Ultraviolet (UV) irradiation studies were carried out with an EXFO Acticure 4000 Spot Curing System using a 365 nm filter for narrow wavelength and 320-390 nm filter for broad wavelength. The lamp intensity was measured by radiometer/photometer, Model IL1400A, supplied by International Light. UV-Vis measurements were obtained on an Agilent Cary 100 operating in double-beam mode with an equivalent solvent composition contained in the reference cuvette. The molecular weight of the polymer was determined by Gel Permeation Chromatography (GPC) from ECOSEC HLC-8320 GPC instrument supplied by TOSOH Bioscience LLC. Dimethyl sulfoxide was used as elution solvent and the system was calibrated using polymethyl methacrylate (PMMA) standards. Sonication studies were carried out with Branson Sonicator, Model 4C15, further details below.

Synthesis of poly(vinyl acetate-alt-sulfur dioxide)

The polymer was synthesized using literature procedure.¹ A 50 ml round bottom flask was evacuated, backfilled with argon, and placed in a cooling bath (dry ice-ethylene glycol/ethanol (30:70)) at -71°C. 10 mL SO₂ was passed through a drying tube containing calcium sulfate and condensed into dried 10 mL graduated cylinder, then transferred into the round bottom flask by canula. Under argon environment and constant stirring, 1 mL VA was added to the round bottom flask. 0.15 ml of TBHP solution was added to the reaction contents and the reaction was carried out for 2 h while maintaining a bath temperature between -71 and -65°C. The reaction was stopped by pouring the reaction contents in methanol held at RT. The white precipitate was dissolved in small amount of tetrahydrofuran

(THF) and reprecipitated in methanol. Yield: 1.5 g (92.5%). $M_n = 2.00 \times 10^4$, PDI = 4.3. $^1\text{H NMR}$ (acetone- d_6): 6.42-6.52 (b m, 1H, $-\text{CHCH}_2\text{-SO}_2$), 4.08-4.22 (b m, 2H, $-\text{CHCH}_2\text{-SO}_2$), 2.28 (s, 3H, $\text{CH}_3\text{-COO-}$).

Depolymerization studies using UV irradiation

For the UV irradiation experiments, separate 10 mg/mL solutions of PVAS were prepared in 1 mL acetone- d_6 , DMSO- d_6 , and THF- d_6 . For each UV irradiation experiment, each solution was divided in two portions: 0.5 ml of the solution was kept for irradiation and 0.5 was reserved as an unirradiated control. The polymers were irradiated using either a broad filter (light 320-390 nm) or a narrow wavelength (365 nm) filter for 1, 5, 10, or 20 min in the UV cuvet from the top (Figure S12a) and immediately transferred to NMR tubes for $^1\text{H-NMR}$ spectroscopic measurements of the irradiated samples. The experiments were repeated at least three times.

Depolymerization studies using Reactive Oxygen Species (ROS)

For initial screening studies, PVAS was dissolved in acetone- d_6 to a final concentration of 10 mg/mL. For each experiment, 0.5 mL solution was mixed with stock solutions of ROS in Millipore water to produce final concentrations of 0 (blank), 1 μM , 10 μM , 100 μM , 1 mM or 10 mM ROS. $^1\text{H-NMR}$ spectra were recorded after 20 min and 24 h. For concentration studies, PVAS was diluted to 0.20 mg/mL in DMSO, and either potassium superoxide or sodium hypochlorite was added as a solution in Millipore water. UV-Vis spectra were recorded using a split beam with an equivalent solvent mixture contained in the reference cuvette. For depolymerization kinetics, a sample was prepared with 0.20 mg/mL PVAS and 200 μM potassium superoxide. Only the absorbance at 260 nm was read to increase the number of data points in the study. Spectra were recorded at the times indicated in the text. Sodium hypochlorite kinetics were run using 0.20 mg/mL PVAS and 200 μM sodium hypochlorite. Figure S7 shows the $^1\text{H NMR}$ spectra at discrete times in acetone- d_6 at 10 mg/mL for sodium hypochlorite kinetics.

Depolymerization studies using probe sonication

For sonication studies, the sonicator (Branson spe) was operated at 40 kHz with a 1/8" diameter probe. The sonication conditions were: amplitude: 70%, on time: 1 sec, off time: 2 sec, total sonication time: 30 min. The total power output was measured by calibration and found to be 5.97 ± 0.37 J/s using the thermal calibration studies as described by Koda, *et al.*² For sonication studies described below, the internal temperature was maintained with a bath; for these studies a submerged thermocouple indicated that the temperature did not increase more than 3°C over the length of any sonication experiment.

For sonication studies followed by $^1\text{H NMR}$ spectroscopy, PVAS solutions were prepared in acetone- d_6 at concentrations indicated in the text. The sonication experiments were carried out in a Suslick cell (Ace Glass).³ The tube was thoroughly purged with argon and the solution was transferred to the tube. The flask was placed in a cooling bath (-5 to -10°C) and sonication commenced (Figure S12b). After completion of sonication in 30 min, the solution was transferred to an NMR tube and $^1\text{H-NMR}$ spectra were recorded at regular time intervals to check the kinetics of depolymerization. Unsonicated polymer solutions were also run at discrete time intervals as negative controls.

For sonication studies followed by GPC, PVAS solutions were prepared and purged as above but in DMSO. The flask was placed in a RT bath (22 to 25°C) and sonication commenced. The PVAS solutions (2.5 mg/mL) were prepared freshly for all the experiments and the sonication was carried out for 15 min, 30 min, or 60 min. The GPC was obtained immediately. For the 30 min and 60 min samples additional chromatograms were obtained without additional sonication at times as indicated in the text. GPCs of unsonicated polymer solutions in DMSO were also run at discrete time intervals as negative controls.

References.

- (1) Jiang, Y.; Frechet, J. M. J. *Macromolecules* **1991**, *24*, 3528.
- (2) Koda, S.; Kimura, T.; Kondo, T.; Mitome, H. *Ultrason. Sonochem.* **2003**, *10*, 149.
- (3) Suslick, K. S.; Goodale, J. W.; Schubert, P. F.; Wang, H. H. *J. Am. Chem. Soc.* **1983**, *105*, 5781.