Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information to:

Nitroxide Polymer Gels for Recyclable Catalytic Oxidation of Primary Alcohols to Aldehydes

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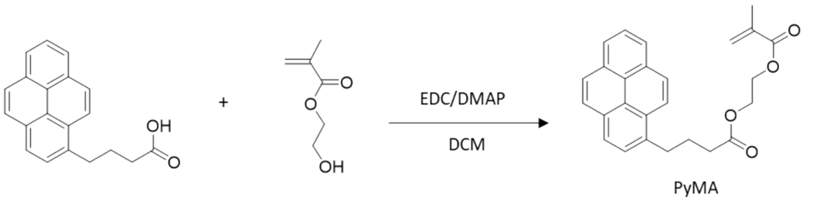
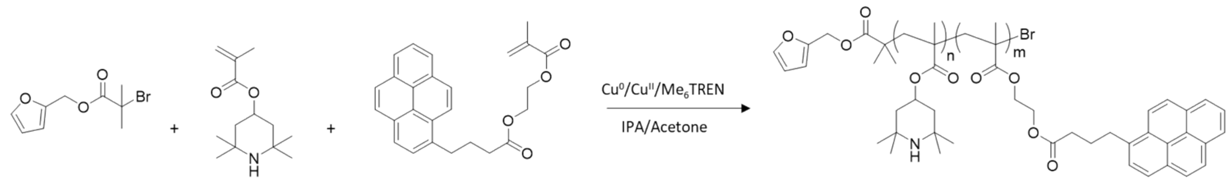
Synthesis of 2-(methacryloyloxy)ethyl 4-(pyren-1-yl)butanoate (PyMA).



To a round bottom flask, 1-pyrenebutyric acid 1.00 g (3.47×10^{-3} mol), 2-hydroxyethyl methacrylate 0.54 g (4.16×10^{-3} mol) in 5 mL THF were added with magnetic stirring. Subsequently, EDC 0.64 g (4.16×10^{-3} mol) and DMAP 0.04 g (3.47×10^{-4} mol) were added. The mixture was stirred at room temperature overnight. The mixture was washed with water to remove salt and the DCM phase was dried over $MgSO_4$, fileted and concentrated. The residual was purified by column chromatography with EtOAc/petroleum spirit (1/1, v/v) as eluent. The product with R_f= 0.8 was collected and dried. 1.12 g product was obtained with a yield of 80%. 1H NMR spectrum was shown in Figure S6.

Copolymerization of TMPM and PyMA by SET-LRP[1]



A 10 mL Schlenk flask was charged with monomer TMPM 0.87 g (3.88×10^{-3}mol), PyMA 0.22g (5.6×10^{-4} mol) and purged under argon for 0.5 h. $CuBr_2$ 3 mg (1.33×10^{-5} mol), Me_6TREN 21.3 µL (8.0×10^{-5} mol) were dissolved together in isopropanol/acetone (1/4) mixture 2.0 mL and prepurged under argon for 5 min before added to the monomer. Finally, a furan functional initiator (furan group was for NMR characterization) 21.8 mg (8.88×10^{-5} mol) with 0.5 ml of acetone was added to the mixture via syringe. The mixture was further purged under argon for another 5 min. A magnetic stir bar wrapped with copper wire (freshly activated) (5 cm, Φ=0.893 mm) was dropped in to start the reaction at 25 °C. The reaction mixture was then taken out by using a syringe at predetermined time intervals for kinetics. The samples were firstly diluted in $CDCl_3$ for the ^{1}H NMR characterization to obtain monomer conversion. The solution was then passed through a short column of basic alumina to remove copper and dried by airflow. The residual was then re-dissolved in methanol and precipitated in petroleum spirit before characterization.

The polymerization kinetics and the ^{1}H NMR of the final product were shown in Figure S7 and S8. The kinetics data in Figure S7 indicated that the two monomers were polymerized with the same rate, and a random copolymer should be produced. The monomer to initiator ratio

TMPM/PyMA/initiator was 43.7/6.3/1, with the pyrene of 12.6%. After the monomer conversion of 86%, the ^{1}H NMR of the purified copolymer in Figure S8 showed the ratio of TMPM/PyMA was 46/7.8, with a pyrene content of 14.5%.

Characterization.

Size exclusion chromatography (SEC). SEC was performed to determine the molecular weight distribution of the as-synthesized polymers using a Waters 2695 separations module, equipped with a Waters 410 refractive index detector at 35 °C, a Waters 996 photodiode array detector (PAD), and two Ultrastyragel linear columns (7.8 × 300 mm) arranged in series. SEC calibration was performed by using a PS standard (PDI = 1.1) ranging from 500 to 2 000 000 g/mol. The samples were used THF as eluent at a flow rate of 1.0 mL/min.

Nuclear magnetic resonance (NMR). All NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer at 25 °C using an external lock ($CDCl_3$ or CD_3CN) and referenced to the residual nondeuterated solvent ($CHCl_3$ or MeCN).

Electron Spray Ionizationmass spectra (ESI-MS). All ESI-MS spectra were carried out on a Waters LC-MS system. Samples were dissolved in MeOH at the concentration of 1-3 mg/ml. (source parameters included: the capillary voltage 3.0 KV, extractor voltage 2.0 V, RF Lens 0.5 V, source temperature at 120 ^oC, desolvation temperature 200 ^oC, desolvation gas flow 500 L/hr, pump flow 20 µL/min, the cone voltage was varied from 15 to 80V depending on the sample).

Attenuated total reflection- Fourier transform infrared spectroscopy (ATR-FTIR). IR spectra were obtained using a diamond/ZnSe crystal ATR accessory on a Perkin-Elmer 400 FT-IR/FT-FIR Spectrometer. Spectra were recorded between 4000 and 750 cm^{-1} by acquiring 64 scans at 4 cm^{-1} resolution with an OPD velocity of 0.2 cm s^{-1}. Samples were pressed onto the diamond internal reflection element of the ATR without further sample preparation.

Matrix Assisted Laser Desorption/Ionization-Time-of-Flight (MALDI-TOF). MALDI-TOF mass spectra were obtained using a Bruker Autoflex III Smartbeam operated in reflection mode. Ions were accelerated at a potential of 20 kV with a nitrogen laser emitting at 337 nm. Three stock solutions were made: (i) a polymer solution in THF (1 mg/mL), (ii) sodium trifluoroacetate (NaTFA) in THF (1 mg/mL), and (iii) 2,5-dihydroxybenzoic acid (DHB) in THF (20 mg/mL). A solution containing 20 µL of the polymer solution, 20 µL of the DHB solution, and 2 µL of the NaTFA solution was mixed in an Eppendorf tube, vortexed, and centrifuged. A 1 µL aliquot of this solution was placed on the sample plate spot, dried at ambient conditions, and placed in the machine for measurement.

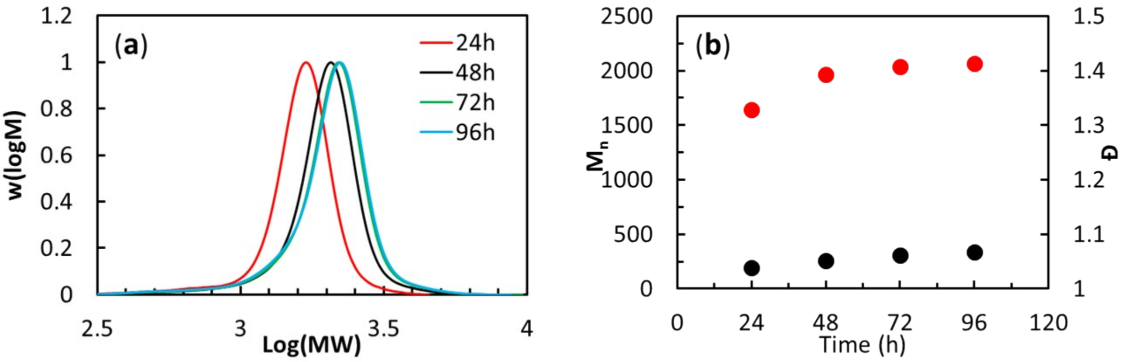


Figure S1. Anionic polymerization of GTEMPO with [GTEMPO]/[I] ratio of 25/1, 65^{o}C in THF. (a) SEC traces at different polymerization time, (b) molecular weight (M_n) and the dispersity (Đ) vs polymerization time.

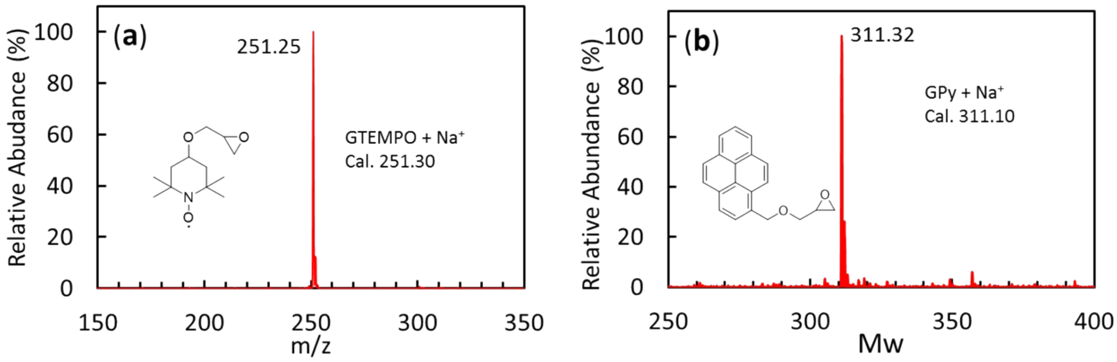


Figure S2. ESI-MS spectra of monomers (a) GTEMPO and (b) GPy.

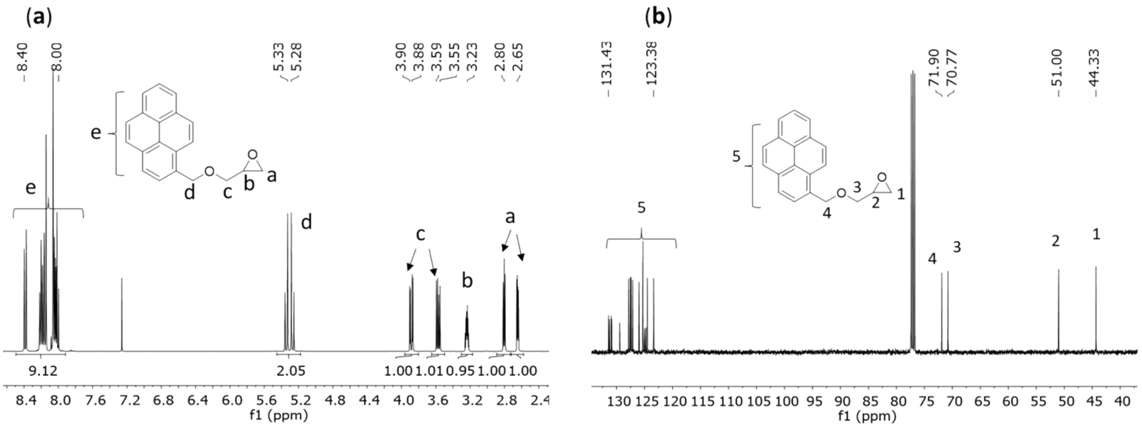


Figure S3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of monomer GPy in $CDCl_3$.

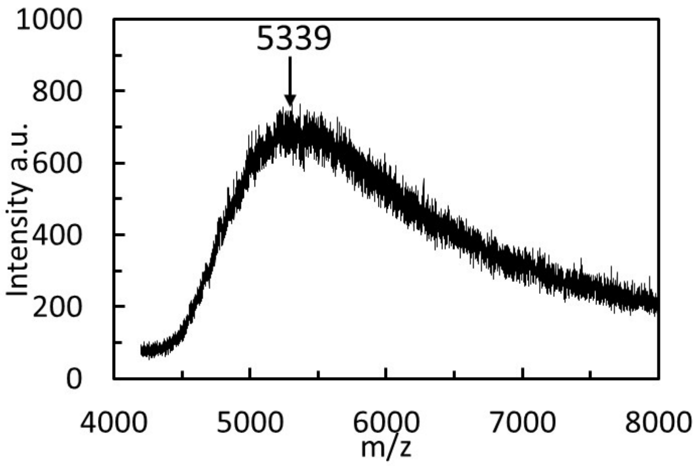


Figure S4. MALDI-TOF MS spectrum of P(GTEMPO-co-GPy), Entry 3 in Table 1.

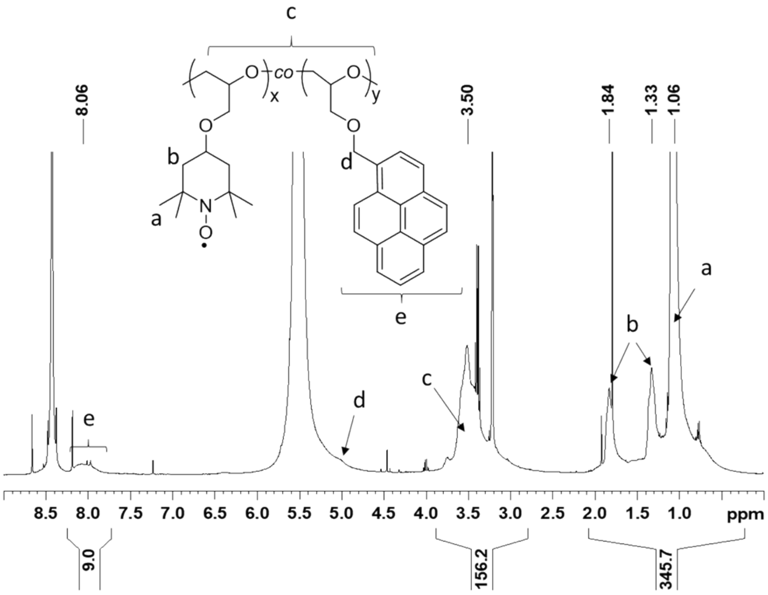


Figure S5. ^{1}H NMR spectrum of P(GTEMPO-co-GPy) in CD_3OD with the addition of Pd/C and ammonium formate, Entry 3 in Table 1.

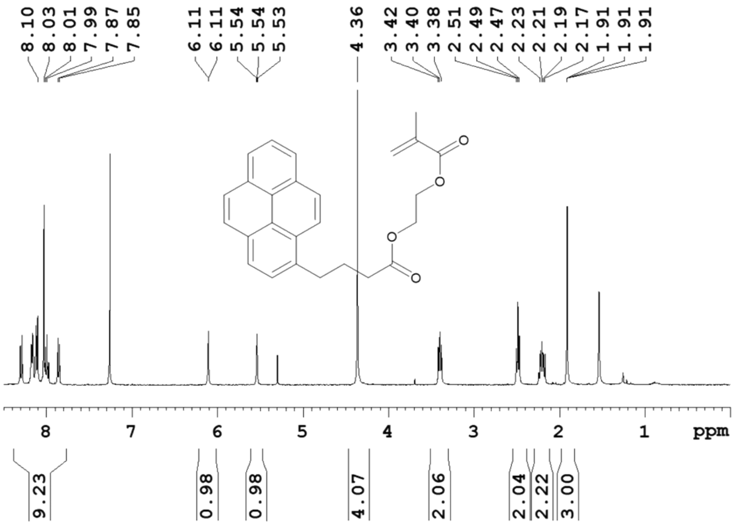


Figure S6. ^{1}H NMR spectrum of pyrene functional methyl methacrylate monomer in $CDCl_3$.

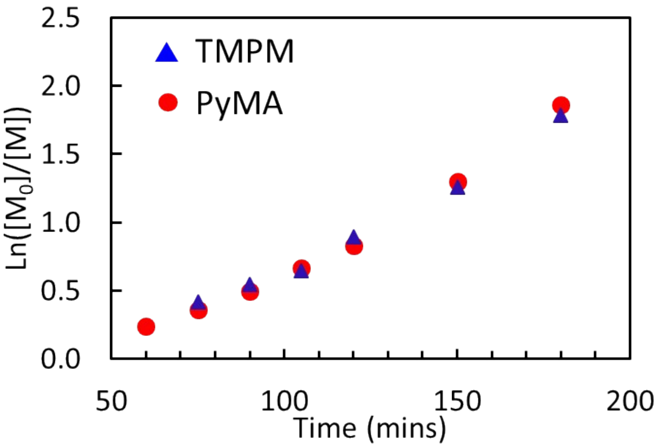


Figure S7. Copolymerization kinetics of TMPM with PyMA.

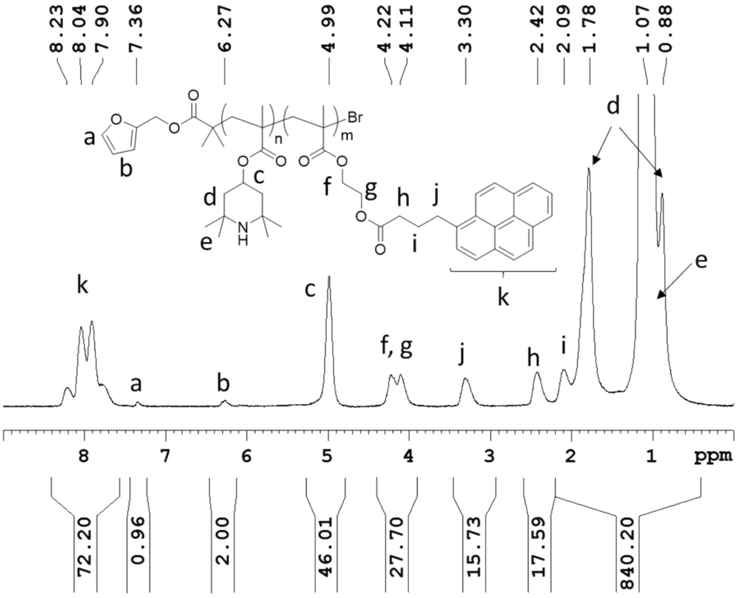


Figure S8. ^{1}H NMR spectrum of P(TMPM$_{46}$-co-PyMA$_{7.5}$) in CDCl$_3$.

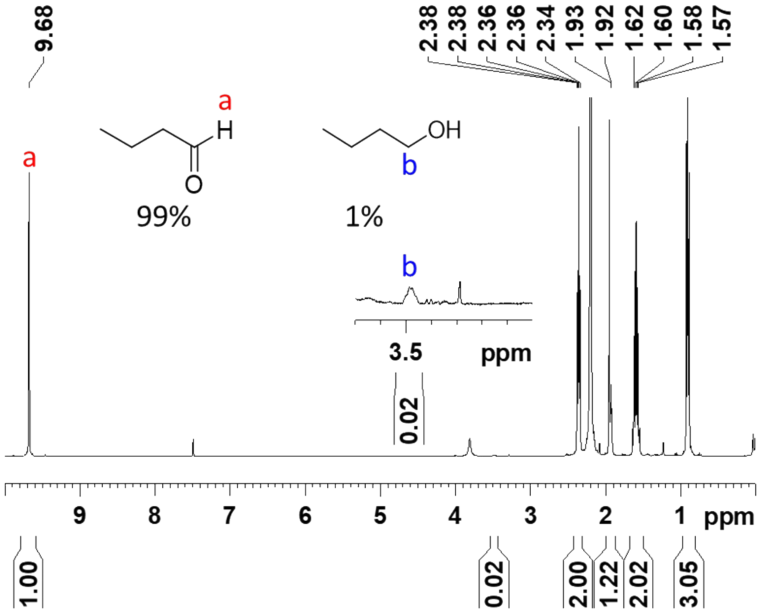


Figure S9. ^{1}H NMR spectrum of butyraldehyde oxidized from 1-butanol.

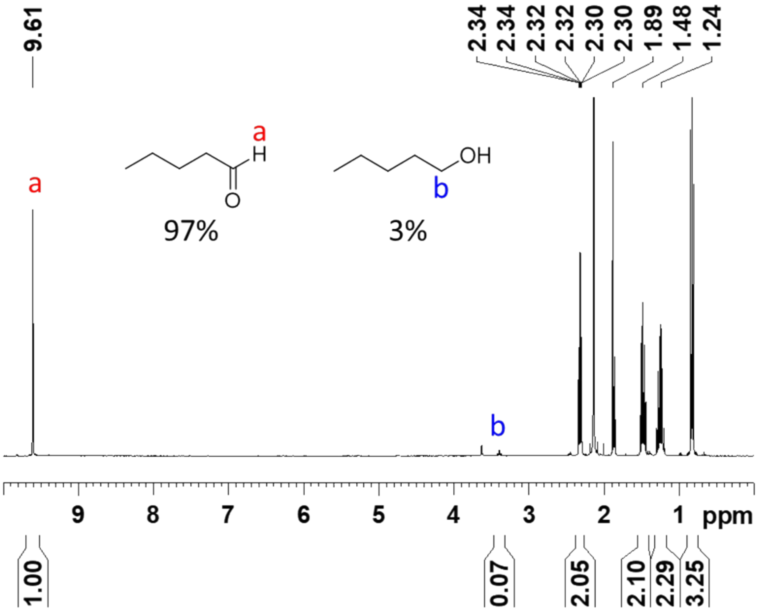


Figure S10. ^{1}H NMR spectrum of valeraldehyde oxidized from 1-pentanol.

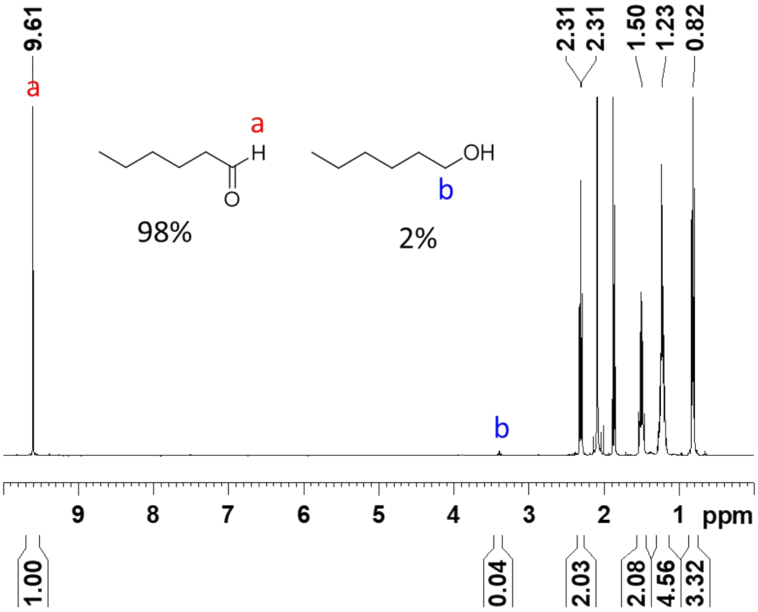


Figure S11. ^{1}H NMR spectrum of caproaldehyde oxidized from 1-hexanol.

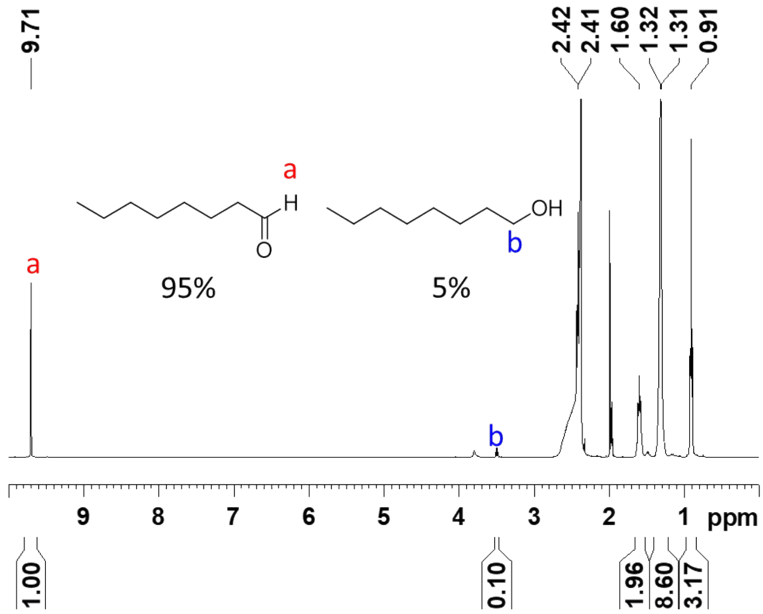


Figure S12. ^{1}H NMR spectrum of octyl aldehyde oxidized from 1-octanol.

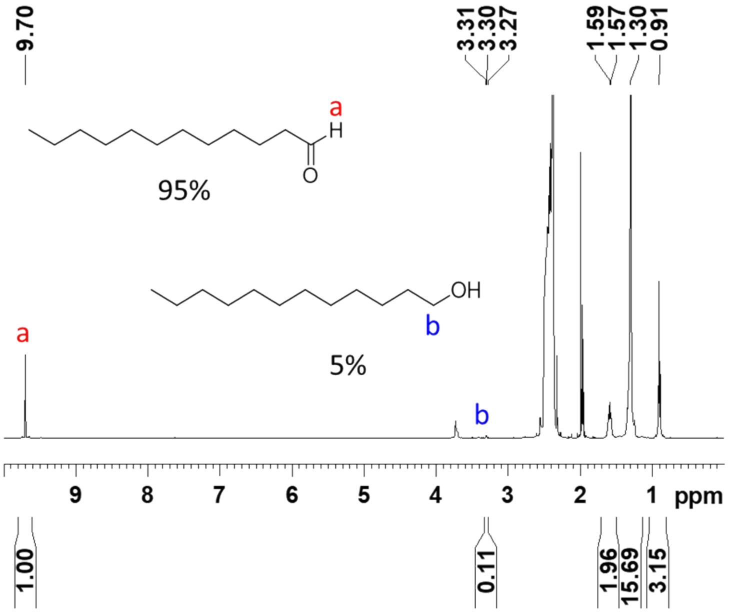


Figure S13. ^{1}H NMR spectrum of lauraldehyde oxidized from 1-dodecanol.

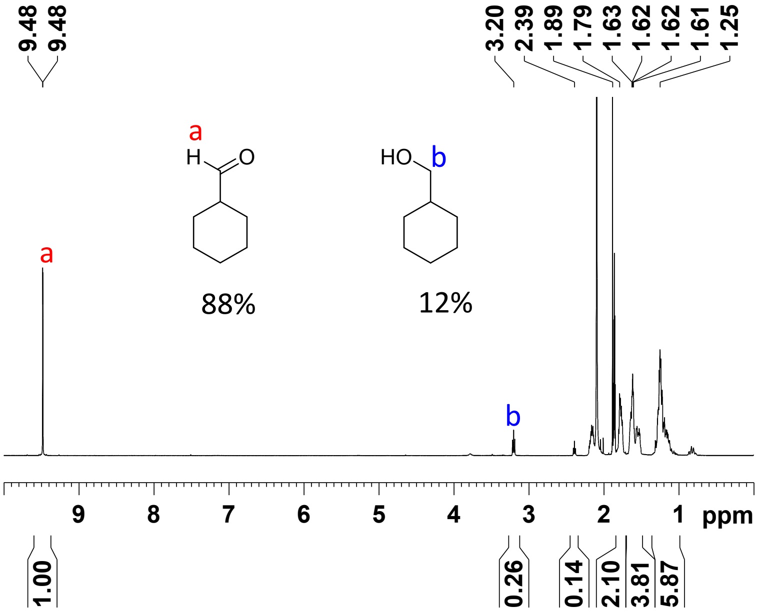


Figure S14. ^{1}H NMR spectrum of cyclohexanecarboxaldehyde oxidized from cyclohexylmethanol.

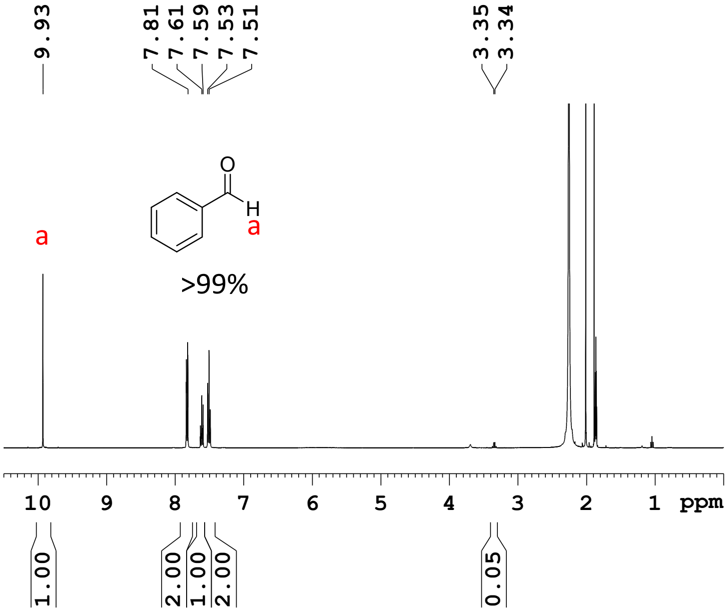


Figure S15. ^{1}H NMR spectrum of benzyl alcohol oxidized from benzaldehyde.

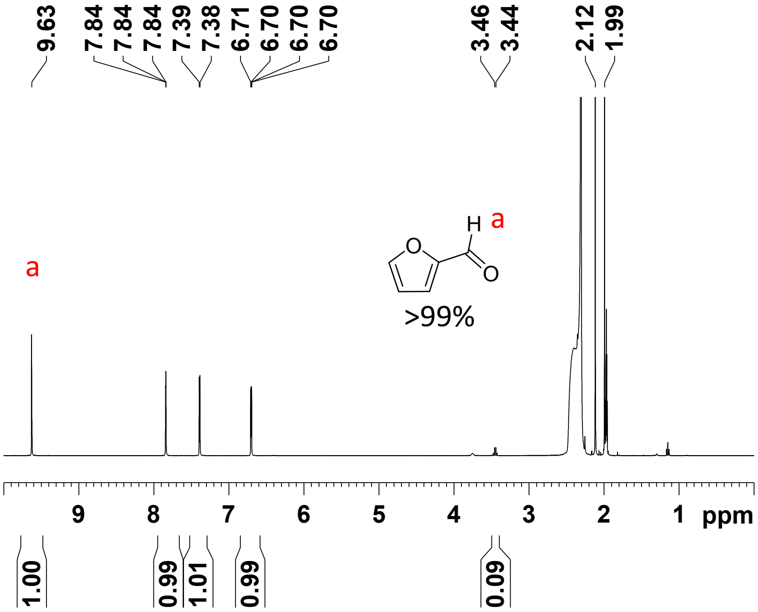


Figure S16. ^{1}H NMR spectrum of 2-furanmethanol oxidized from 2-furaldehyde.

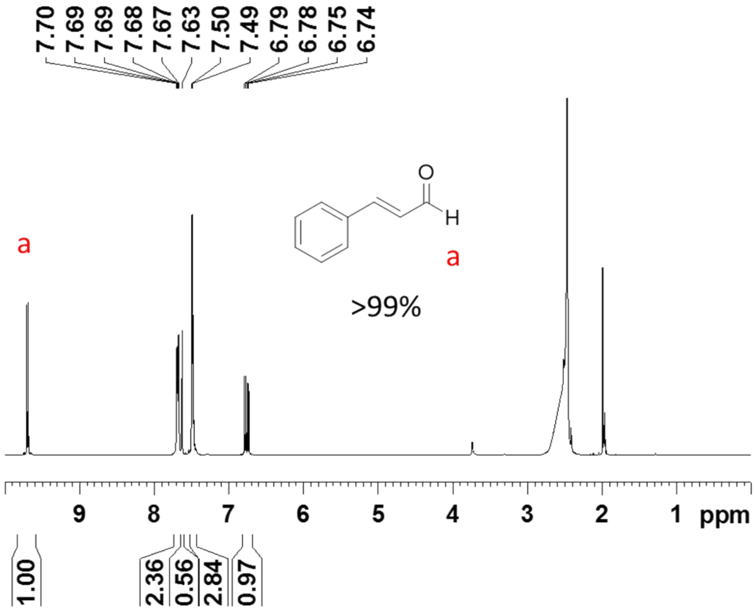


Figure S17. ^{1}H NMR spectrum of cinnamaldehyde oxidized from cinnamyl alcohol.

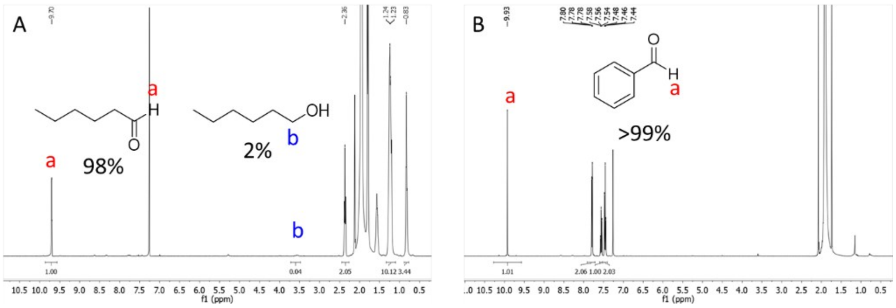


Figure S18. ^{1}H NMR spectra of the oxidation products (A) 1-octanol, (B) benzyl alcohol to the corresponding aldehydes. The ratio of [alcohol]/[gel]/[Cu(OTf)]/[bpy]/[NMI] was 100/15/5/5/10; The crude products were passed through a neutral alumina.

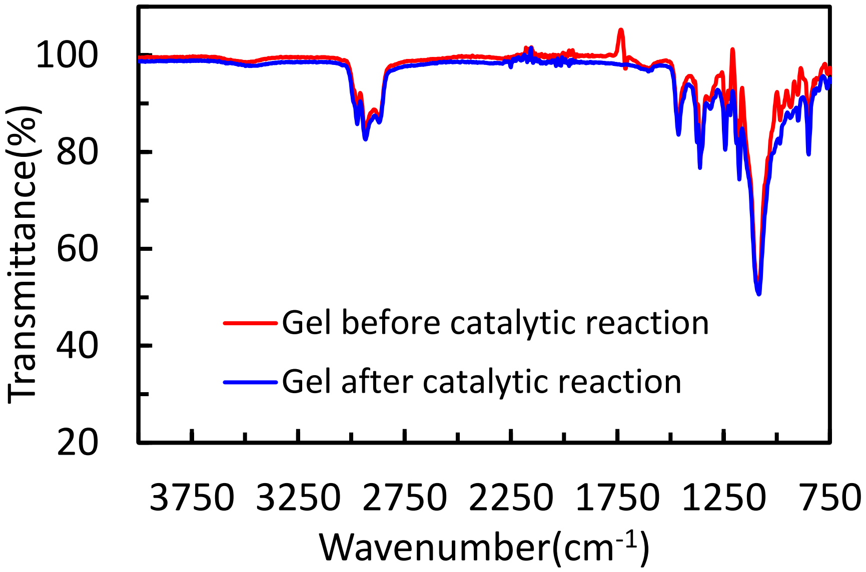


Figure S19. ATR-IR spectra of polymer gels (Entry 4) before (red) and after (blue) the catalytic reaction of 1-octanol. The gel after the catalytic reaction was washed by fresh acetonitrile for two times and air-dry for 30 min. Note that the bp of 1-octanol is 195 °C and the bp of octyl aldehyde is 171 °C.

1. Zhang, K.; Hu, Y.; Wang, L.; Fan, J.; Monteiro, M. J.; Jia, Z., The impact of the molecular weight on the electrochemical properties of poly(TEMPO methacrylate). *Polym. Chem.* **2017,** *8* (11), 1815-1823.