Supporting Information

Water Soluble Polyperoxides from 2-(2-Methoxyethoxy)ethyl Methacrylate: Influence of Molecular Oxygen on Thermoresponsive Properties and Thermal Degradation

Sunirmal Pal and Priyadarsi De[*]

Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research, Kolkata, PO: BCKV Campus Main Office, Mohanpur - 741252, Nadia, West Bengal, India.

Experimental Section

Materials. 2-(2-methoxyethoxy)ethyl methacrylate (MEO_2MA, Sigma, 95%) was purified prior to polymerization by passing through a column of basic alumina. The 2,2′-azobisisobutyronitrile (AIBN, Sigma, 98%) was recrystallized twice from methanol. High purity oxygen (BOC, 99.99%) was used for all the experiments. $CDCl_3$ (99% D) and D_2O (99% D) were received from Cambridge Isotope, USA and used as received. The solvents, petroleum ether (boiling range, 60–80 ^oC), tetrahydrofuran, chloroform, etc., were purified by standard procedures.

Polymerization. The bulk polymerizations of MEO_2MA were carried out in the presence of AIBN (0.04 mol L^{-1}) initiator in a Parr reactor (Parr Instrument Co., USA) equipped with a digital pressure transducer, temperature controller and mechanical stirrer at 50 ^oC at different oxygen pressures (10, 50, 100, 200 and 300 psi). The O_2 consumption during the polymerization reactions was measured as a function of time using a pressure transducer. Polyperoxides were separated from the reaction mixture by precipitating it with petroleum ether. It was isolated as white sticky material after repeated precipitation from chloroform solution followed by the removal of the solvent by vacuum drying at room temperature. CAUTION!! Polyperoxide polymers should be handled with extreme care to avoid explosive decomposition and should be stored in the dark and in a refrigerator to minimize degradation.

Methods. Molecular weights and molecular weight distributions of polyperoxides were determined by gel permeation chromatography (GPC) using Waters 515 HPLC pump, Waters 2414 refractive index detector and two columns (Styragel HT4 and Styragel HT3). The eluent was tetrahydrofuran at 30 ^oC and the flow rate was 0.3 mL/min. Narrow molecular weight polystyrene standards were used to generate the calibration curve. The ^1H NMR spectroscopy was conducted with a Bruker Avance^{III} 500 spectrometers operating at 500 MHz. The thermal analysis was carried out using a Mettler Toledo DSC1 STARe differential scanning calorimeter (DSC) at various heating rates (5, 10, 15, 20 and 25 ^{o}C min^{-1}) with sample sizes of 4-8 mg in nitrogen atmosphere. The thermogravimetric analysis (TGA) was accomplished on a Mettler Toledo TGA/SDTA 851e instrument at a heating rate of 10 ^{o}C min^{-1} with a sample weight of ~4 mg in nitrogen atmosphere. The elemental analysis was carried out on a Perkin-Elmer Series-II, CHNO/S Analyzer-2400. The FT-IR spectrum was recorded on KBr pellets using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Positive mode electrospray ionization mass spectrometry (ESI-MS) was performed on a Q-Tof Micro YA263 high resolution (Waters Corporation) mass spectrometer. UV-Visible spectroscopic measurements were obtained from Perkin-Elmer Lambda 35 UV/VIS Spectrometer. For DLS measurements, PMEO$_2$MAP was dissolved in DI water (0.5 mg/mL) and cooled at 4 °C for ~16 h to ensure complete dissolution of the PMEO$_2$MAP. The solution was transferred to a cuvette and DLS measurements were carried out at different temperatures with 20 min equilibration time at each temperature from 2 °C to 32 °C.

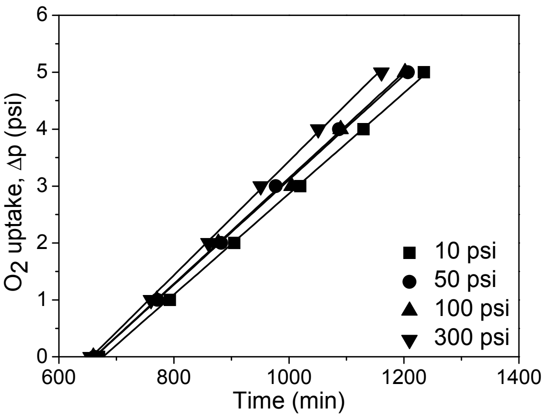

Figure S1. Fall of oxygen pressure as a function of time for the oxidation of MEO$_2$MA at 50 ^{o}C under different oxygen pressure.

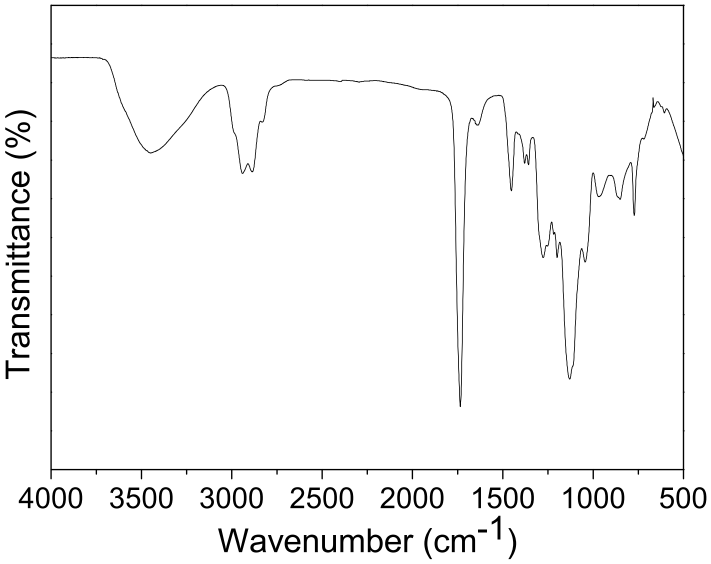

Figure S2. The FT-IR spectrum of PMEO$_2$MAP.

Synthesis of PMEO$_2$MA **via Conventional Radical Polymerization.** Polymerization reaction was performed in a 20 mL glass vial under a dry nitrogen atmosphere. AIBN (0.9 mg, 5.32 μM), MEO$_2$MA (0.5 g, 2.67 mM) and DMF ([MEO$_2$MA]/[AIBN] = 50:0.1, 0.5 g MEO$_2$MA and 1 mL DMF) were sealed in a 20 mL vial equipped with a magnetic stir bar and purged with dry nitrogen for 20 min. The reaction vial was placed in a preheated reaction block at 70 ºC. After 90 min (^{1}H NMR measurement showed 60 % monomer conversion), the polymerization was quenched by cooling in ice water bath and exposing the solution to air. The solution was diluted with acetone and precipitated into cold hexane. The polymer was reprecipitated four times form acetone/hexane and dried under vacuum at room temperature for 6 h. $M_{n,GPC}$ = 16,500 g/mol and PDI = 1.73.

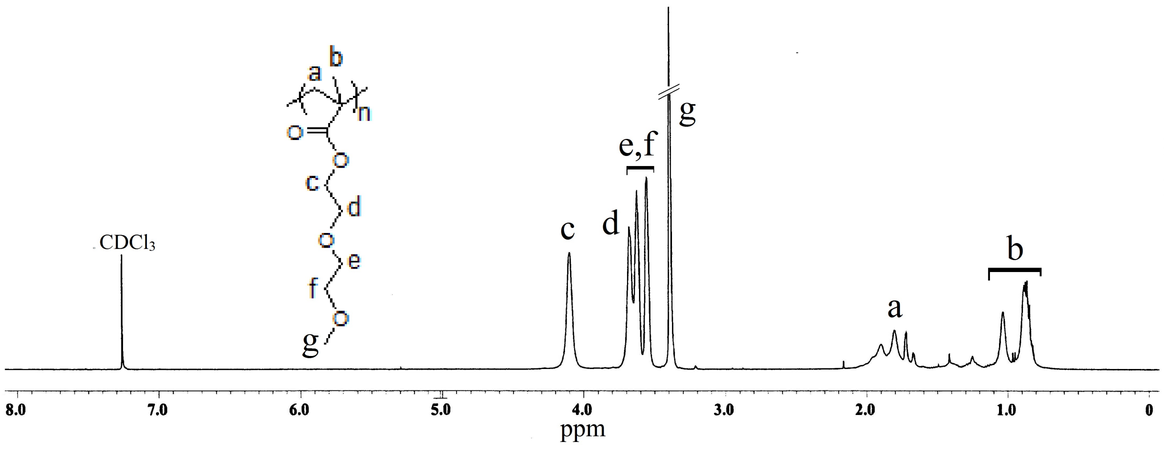

Figure S3. ^{1}H NMR spectrum of PMEO$_2$MA in CDCl$_3$.

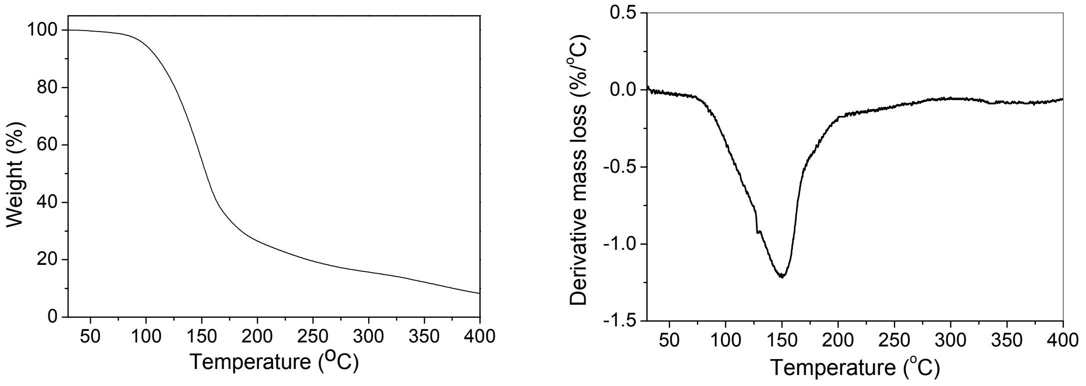

Figure S4. TGA (left side) and DTG (right side) curve of PMEO$_2$MAP at a heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere.

Table S1. The molecular ions identified in the ESI-MS of PMEO$_2$MAP.

Structure	*m/z*
CH_3-O-CH_2-CH_2-O-CH_2-CH_2	103
CH_3-CO-CO-O-CH_2-CH_2	115
CH_3-O-CH_2-CH_2-O-CH_2-CH_2-OH + Na^+, CH_3-O-CH_2-CH_2-O-CH_2-CH_3 + K^+	143
CH_3-CO-CO-O-CH_2-CH_2-O-CH_2-CH_2	159
CH_3-CO-CO-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3	191[a]
CH_3-CO-CO-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3 + Na^+	213
CH_3-CO-CO-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3 + K^+	229
HO-CH_2-C(CH_3)(OH)-CO-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3 + Na^+	245

[a] Observed as MH^+

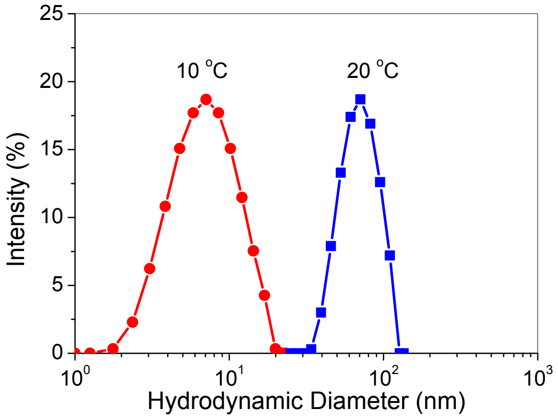

Figure S5. Hydrodynamic diameter distribution for PMEO$_2$MAP in water at 10 °C (red curve) and 20 °C (blue curve).

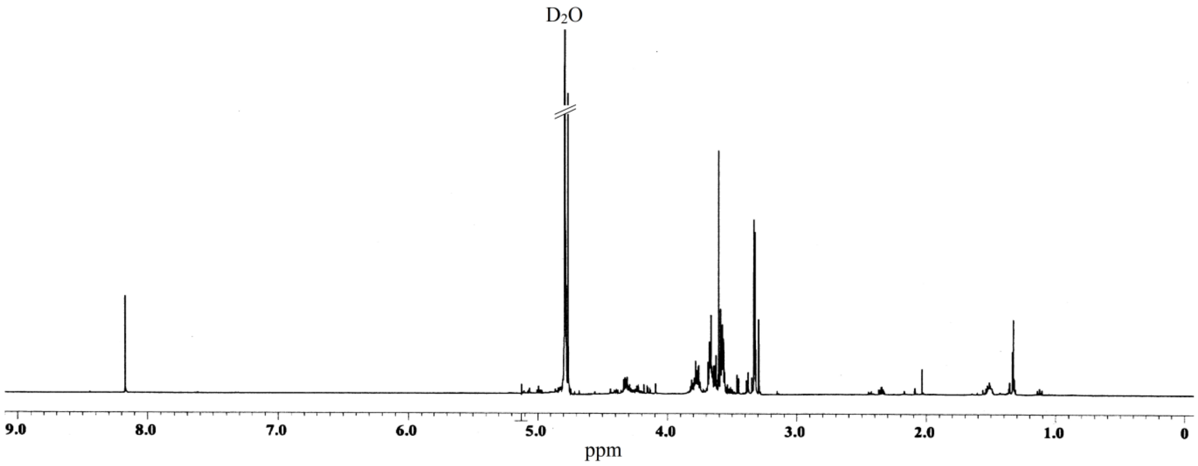

Figure S6. The ^{1}H NMR spectrum of PMEO$_2$MAP after heating in D_2O at 70 °C for 6 h.