

Synthesis and characterization of a biodegradable polymer prepared via radical copolymerization of 2-(acetoacetoxy)ethyl methacrylate and molecular oxygen

*Sunirmal Pal,^a Amit Das,^b Sankar Maiti^b and Priyadarsi De^{*a}*

^a Department of Chemical Sciences, ^b Department of Biological Sciences

Indian Institute of Science Education and Research, Kolkata, PO: BCKV Campus Main Office, Mohanpur - 741252, Nadia, West Bengal, India

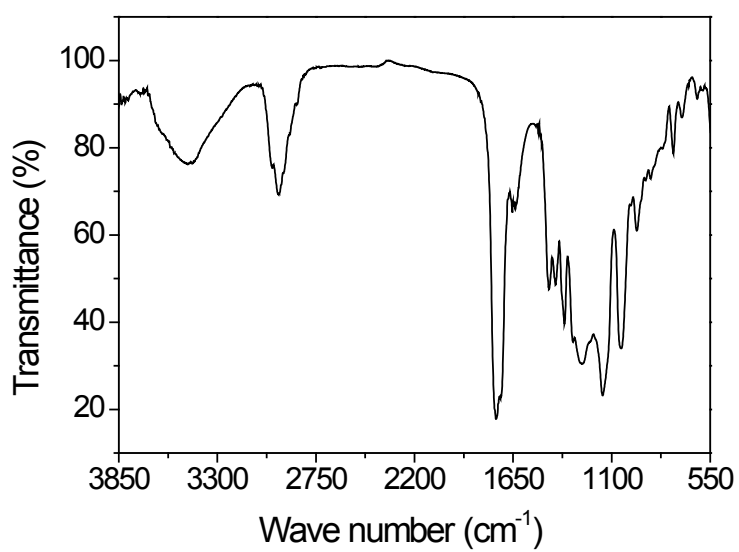


Figure S1. The FTIR spectrum of PAEMAP.

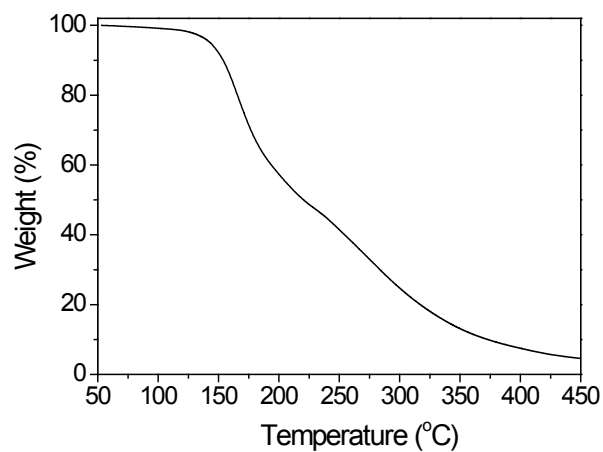
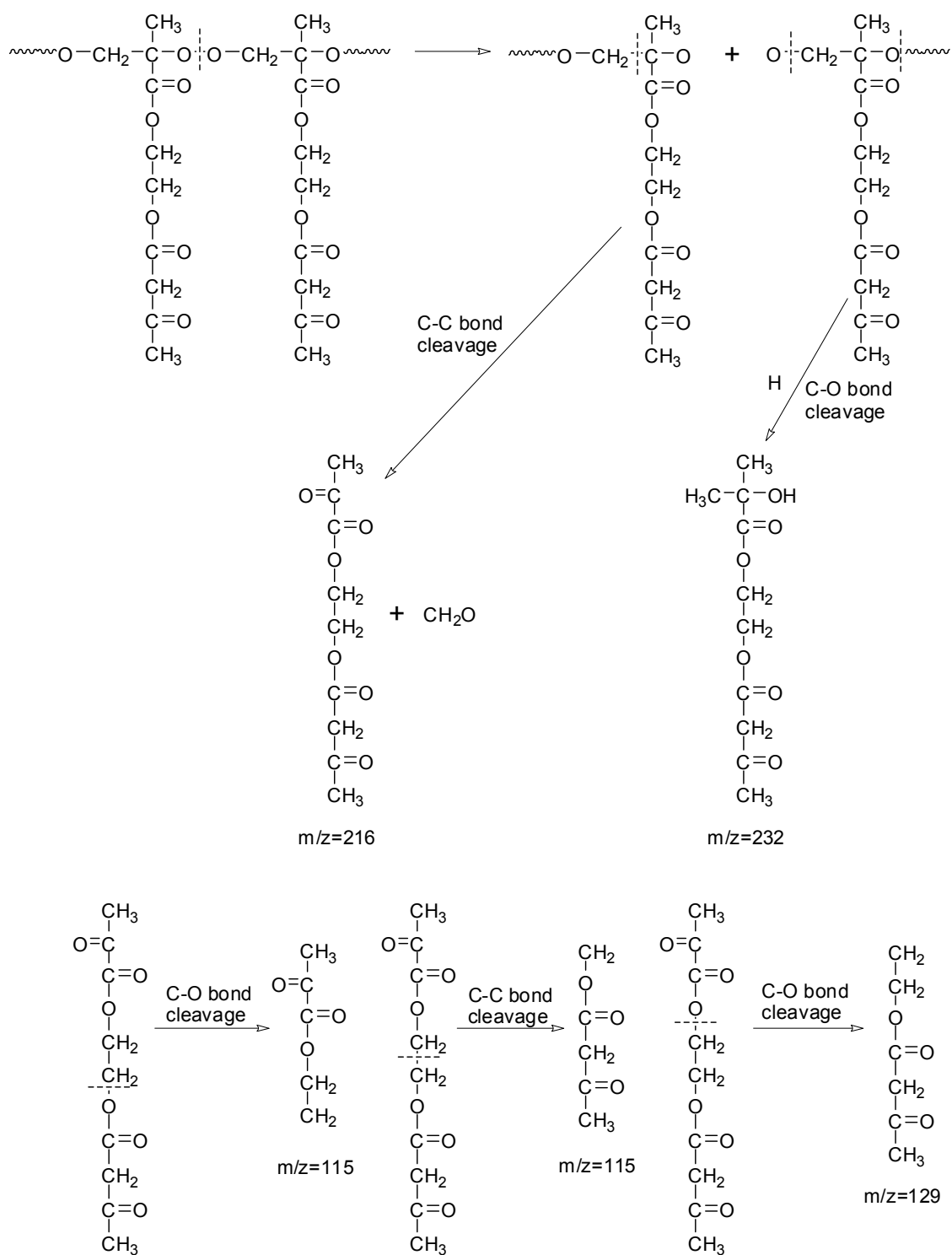


Figure S2. TGA curve of PAEMAP at a heating rate of 10 °C min⁻¹.



Scheme S1. Thermal degradation mechanism of PAEMAP.

Synthesis of PAEMA via RAFT Polymerization. Low molecular weight PAEMA was prepared by reversible addition-fragmentation chain transfer (RAFT) radical polymerization using 4-cyano-4-methyl-4-thiobenzoylsulfanyl butyric acid (CTP) as RAFT chain transfer agent and 2,2'-azobis(isobutyronitrile) (AIBN) as radical source in DMF at 70 °C. Polymerization was performed in a 20 mL glass vial under a dry nitrogen atmosphere. AIBN, CTP, AEMA and DMF ($[AEMA]/[CTP]/[AIBN] = 30:1:0.2$, 1 mL AEMA and 2 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 °C. After 7 h (^1H NMR measurement showed 92 % 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 from acetone/hexane and dried under vacuum at room temperature for 6 h.

The theoretical molecular weight ($M_{n,\text{theo}} = (\text{molecular weight (MW) of AEMA}) \times [AEMA]_0/[CTP]_0 \times \text{conversion} + (\text{MW of CTP})$); $M_{n,\text{theo}} = 6,220$ g/mol. Comparison of the integration areas from the terminal phenyl group at 7.85 ppm and backbone protons at 3.57 ppm (Figure S3) allowed calculation of the number-average molecular weight ($M_{n,\text{NMR}}$) from NMR spectroscopy; $M_{n,\text{NMR}} = 5,700$ g/mol. The number average molecular weight ($M_{n,\text{GPC}}$) and molecular weight distribution (PDI) were determined by organic gel permeation chromatography (GPC) in DMF at 35 °C using a flow rate of 0.9 mL min⁻¹ (Viscotek pump; columns: two ViscoGel I-Series G4000); calibration based on polystyrene standards. Detection consisted of a Viscotek refractive index detector operating at $\lambda = 660$ nm, and a Viscotek model 270 series platform, consisting of a laser light scattering detector (operating at 3 mW, $\lambda = 670$ nm with detection angles of 7° and 90°) and a four-capillary viscometer. $M_{n,\text{GPC}} = 6,500$ g/mol and PDI = 1.47.

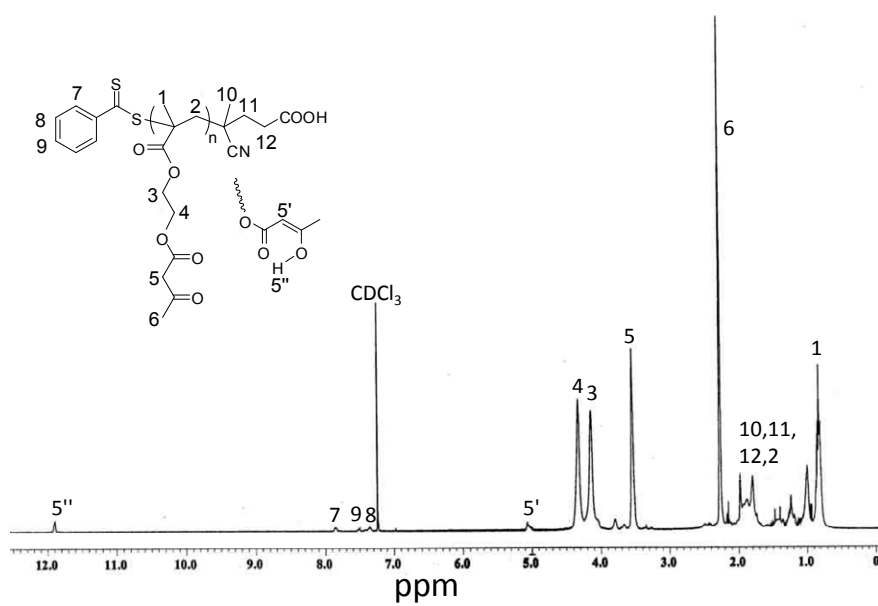


Figure S3. ¹H NMR spectrum of PAEMA in CDCl₃.