

Electronic Supplementary Information (ESI)

Lipase-catalyzed synthesis of azido-functional aliphatic polyesters towards acid-degradable amphiphilic graft copolymers

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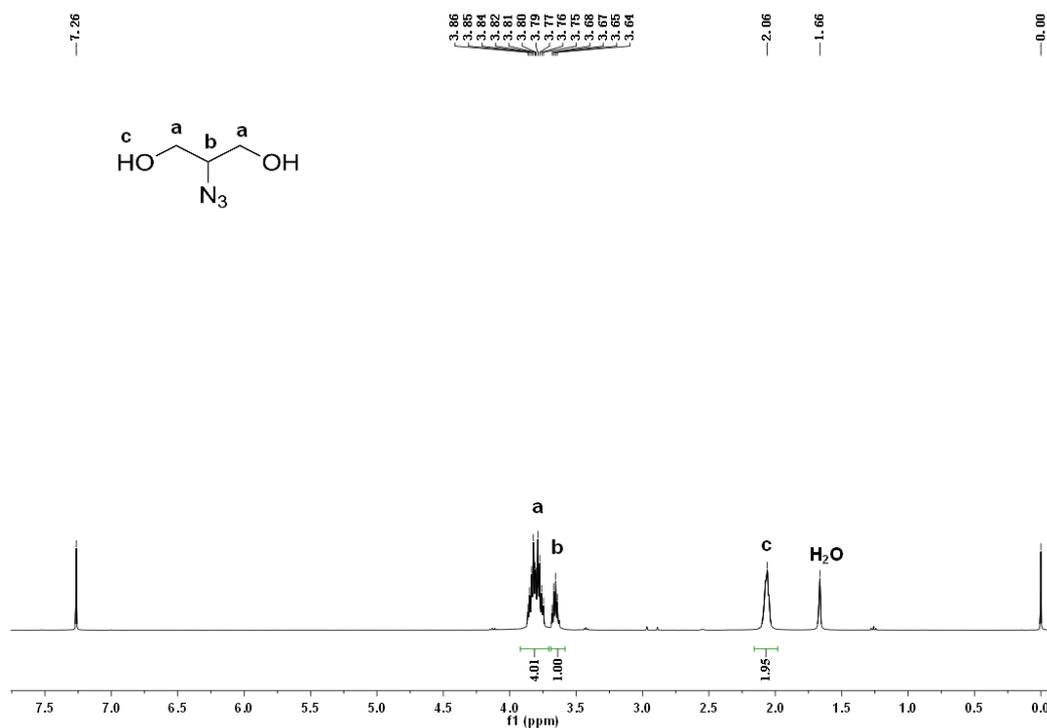


Fig. S1. ^1H NMR spectrum of 2-azido-1,3-propanediol in CDCl_3 .

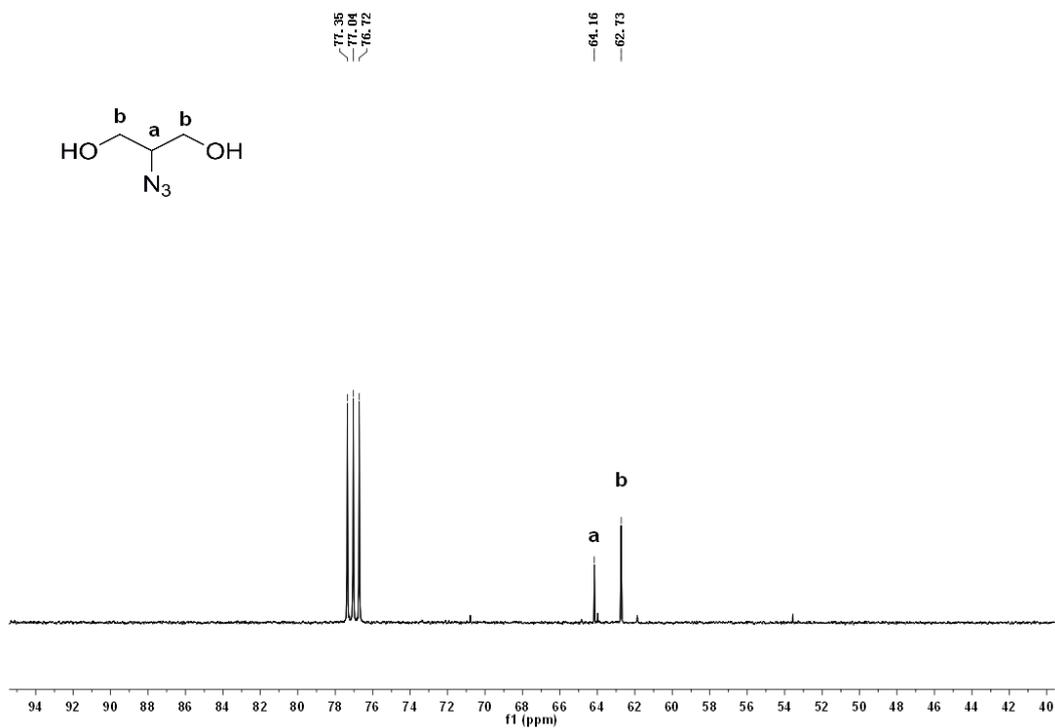


Fig. S2. ^{13}C NMR spectrum of 2-azido-1,3-propanediol in CDCl_3 .

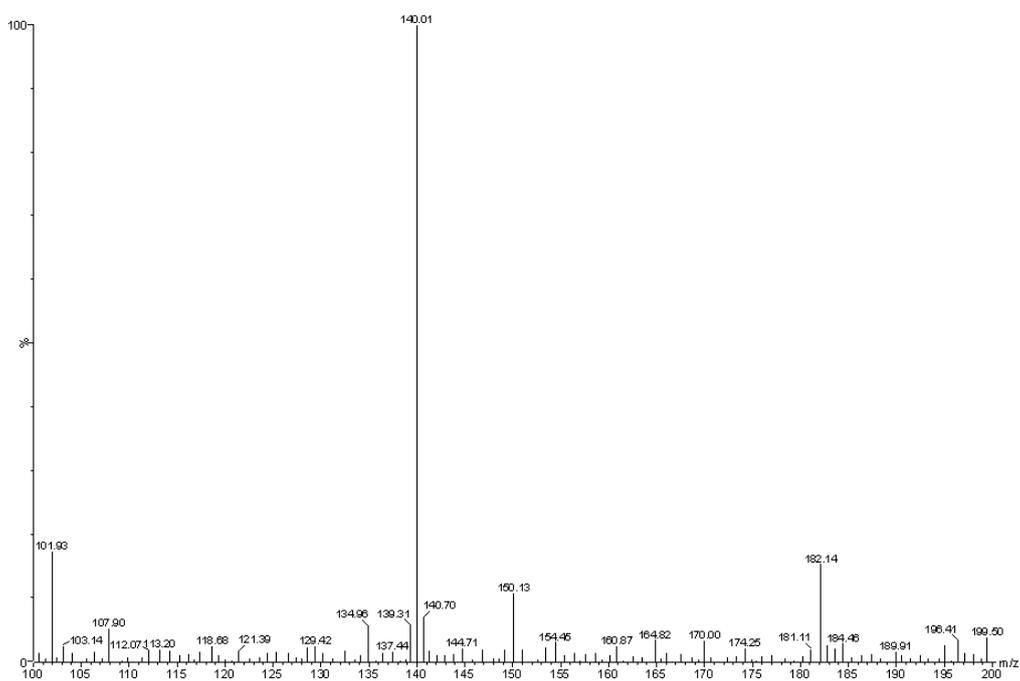


Fig. S3. ESI-MS (m/z) of 2-azido-1,3-propanediol.

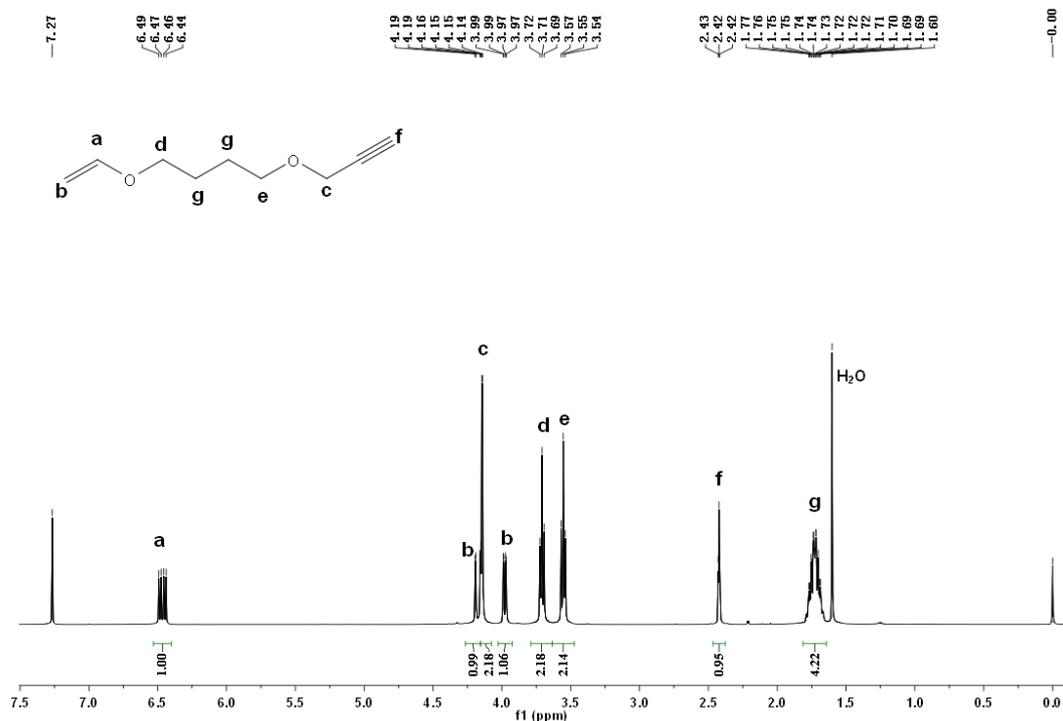


Fig. S4. ¹H NMR spectrum of 4-propargyloxybutyl vinyl ether in CDCl₃.

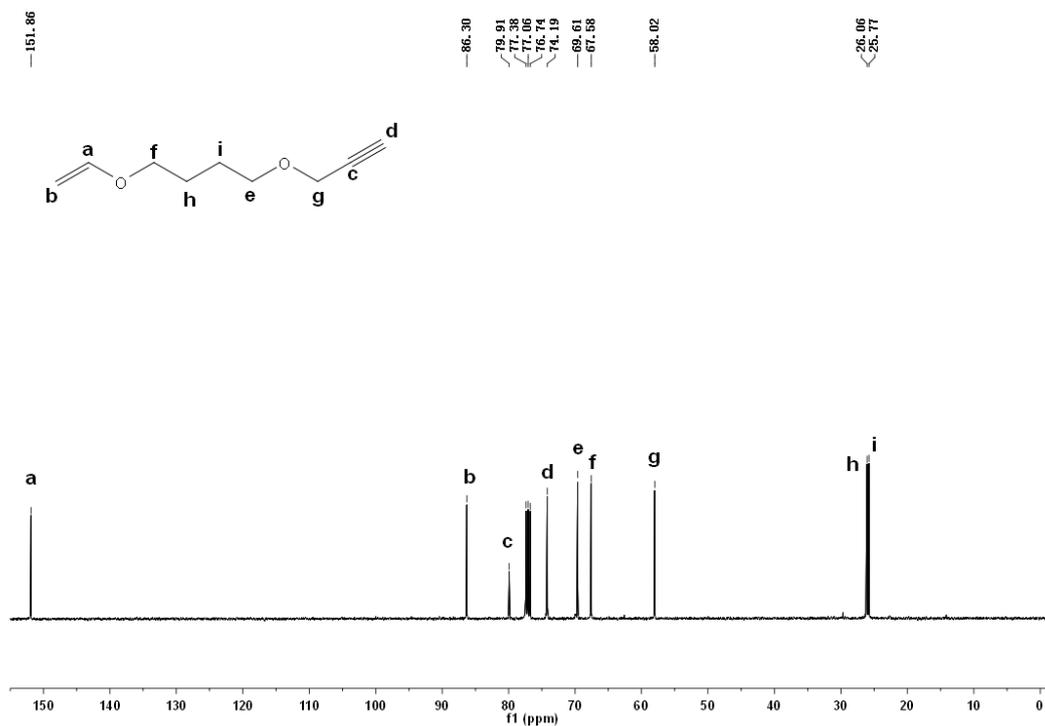


Fig. S5. ¹³C NMR spectrum of 4-propargyloxybutyl vinyl ether in CDCl₃.

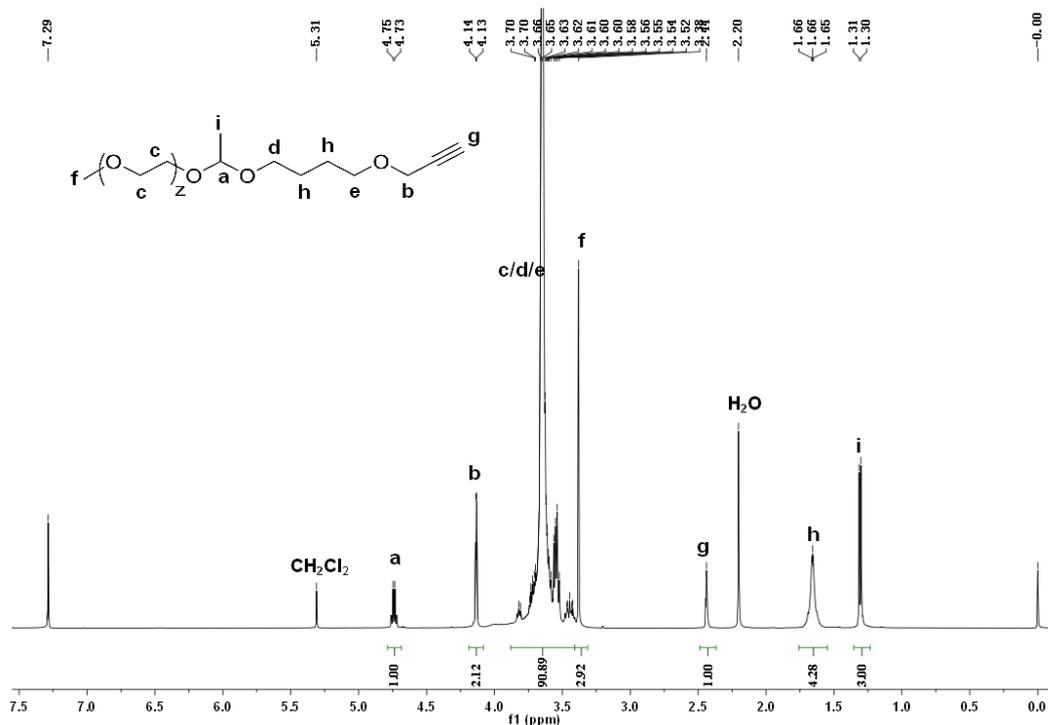


Fig. S6. ^1H NMR spectrum mPEG₁₀₀₀-acetal-alkyne of in CDCl_3 .

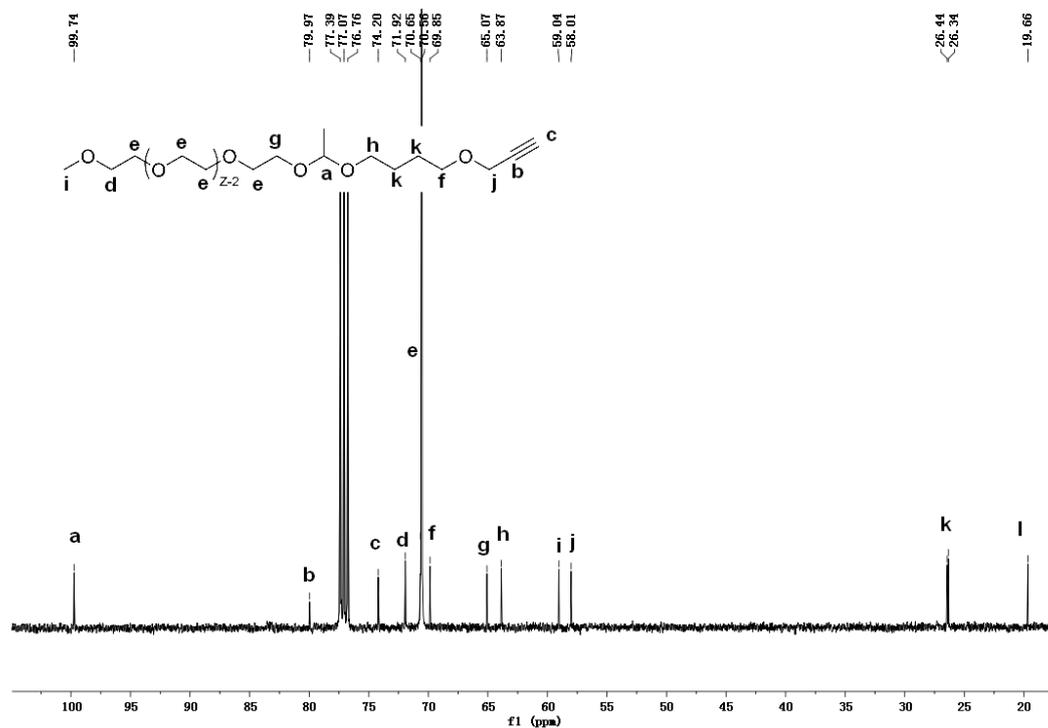


Fig. S7. ^{13}C NMR spectrum mPEG₁₀₀₀-acetal-alkyne of in CDCl_3 .

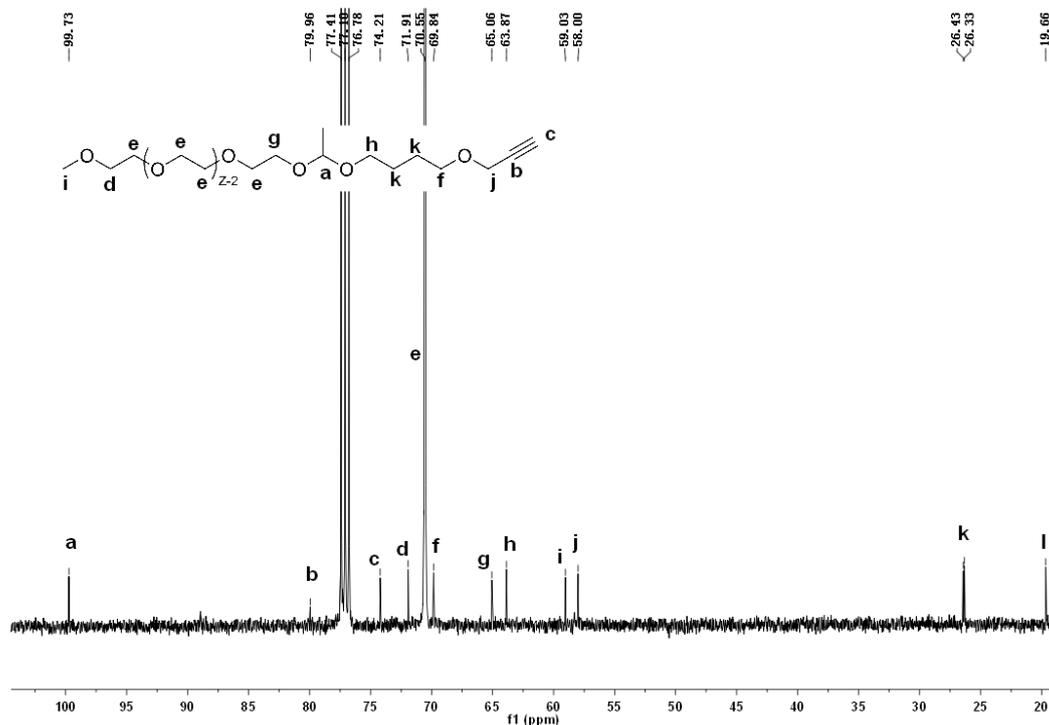


Fig. S8. ^{13}C NMR spectrum mPEG₂₀₀₀-acetal-alkyne of in CDCl_3 .

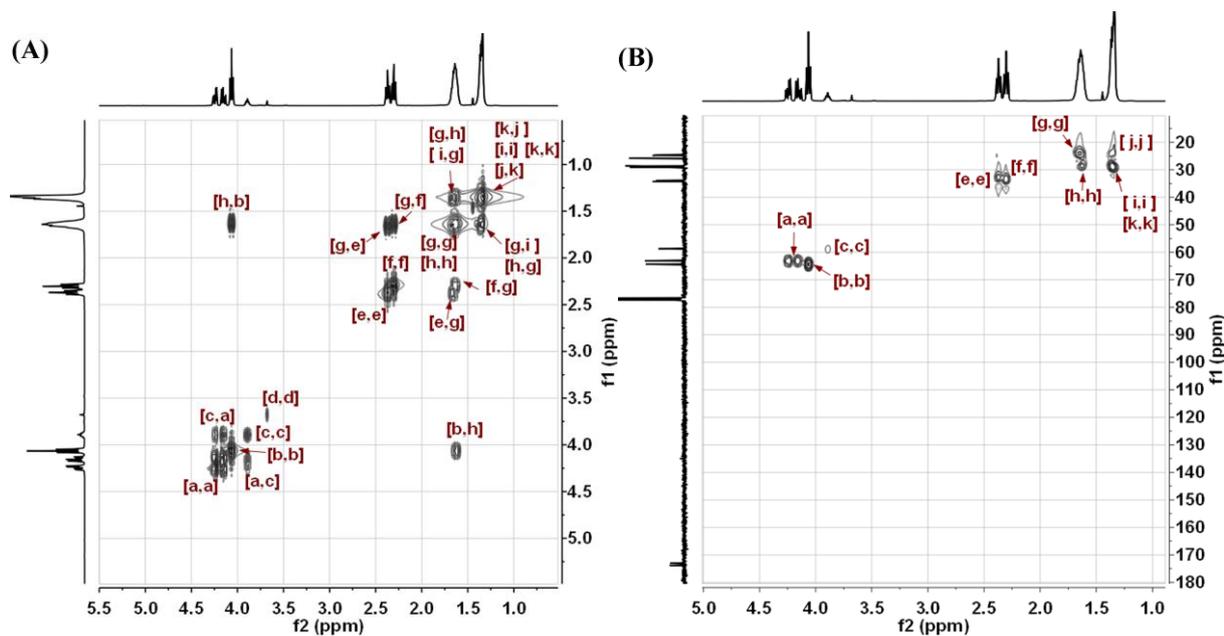


Fig. S9. 2D-NMR spectra of P(OSu_{0.51}-co-APSu_{0.49}) in CDCl_3 : (A) ^1H , ^1H -COSY spectrum; (B) ^{13}C , ^1H -HSQC spectrum.

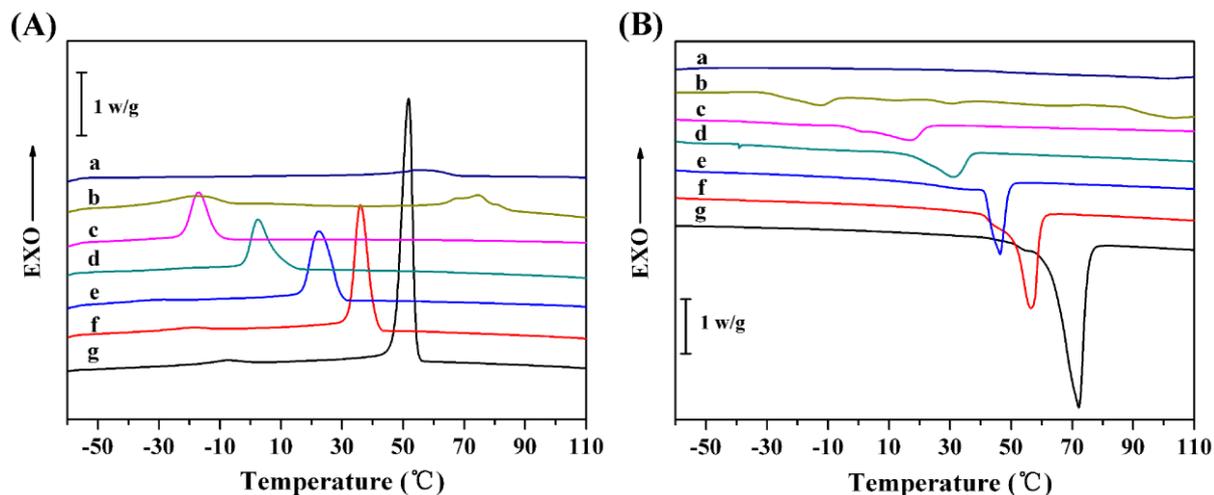


Fig. S10. DSC curves of P(OSu-co-APSu): (A) Cooling runs at 10 °C min⁻¹; (B) Heating runs at 10 °C min⁻¹ for (a) P(APSu), (b) P(OSu_{0.25}-co-APSu_{0.75}), (c) P(OSu_{0.36}-co-APSu_{0.64}), (d) P(OSu_{0.51}-co-APSu_{0.49}), (e) P(OSu_{0.63}-co-APSu_{0.37}), (f) P(OSu_{0.78}-co-APSu_{0.22}) and (g) P(OSu).

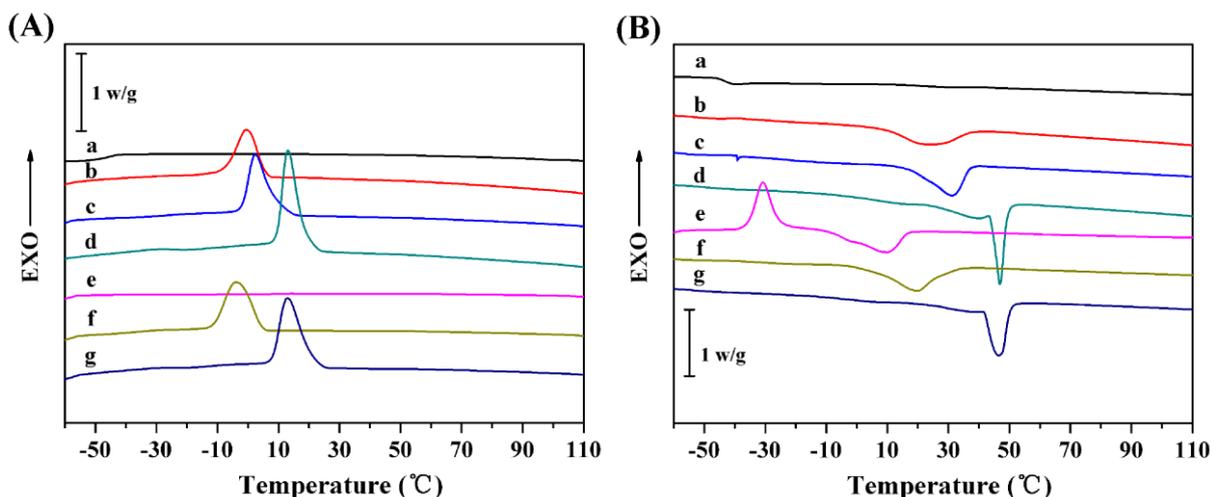


Fig. S11. DSC curves of the copolyesters from dialkyl diesters and diols with varying chain lengths: (A) Cooling runs at 10 °C min⁻¹; (B) Heating runs at 10 °C min⁻¹ for (a) P(OSc-co-APSc), (b) P(OAd-co-APAd), (c) P(OSu-co-APSu), (d) P(OSe-co-APSe), (e) P(BSu-co-APSu), (f) P(HSu-co-APSu) and (g) P(DSu-co-APSu).

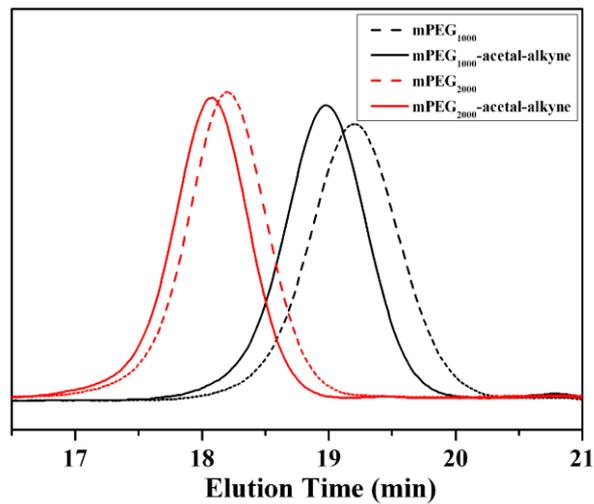


Fig. S12. GPC traces of mPEG and mPEG-acetal-alkyne .

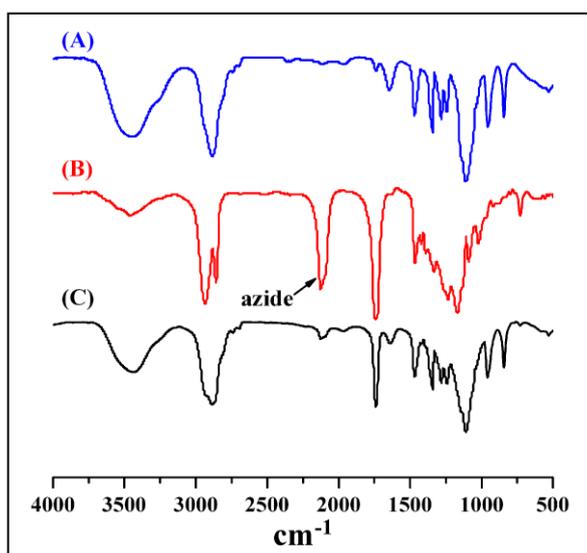


Fig.S13. FTIR of (A) mPEG₂₀₀₀-acetal-alkyne, (B) P(OSu_{0.51}-co-APSu_{0.49}) and (C) P(OSu_{0.51}-co-APSu_{0.49})-g-mPEG₂₀₀₀.

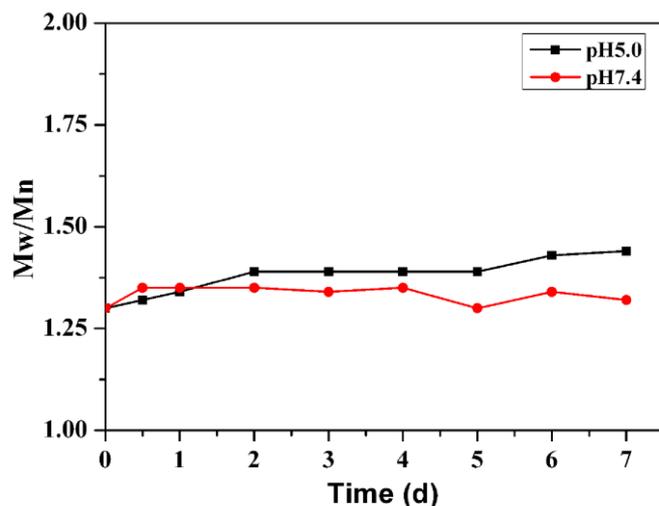


Fig. S14. Polydispersity (Mw/Mn) of P(OSu_{0.51-co}-APSu_{0.49})-g-mPEG₂₀₀₀ as a function of hydrolysis time by GPC.

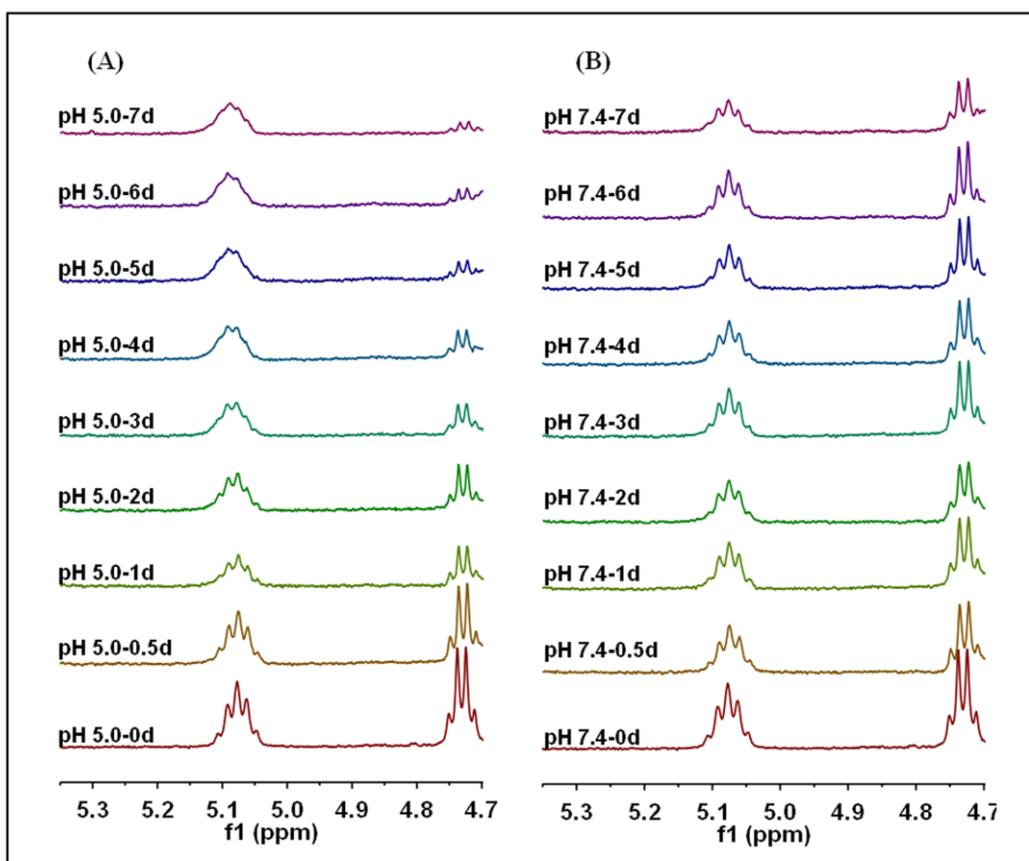


Fig. S15. ¹H NMR spectrum of acid-sensitive degradation of P(OSu_{0.51-co}-APSu_{0.49})-g-mPEG₂₀₀₀ with hydrolysis time in CDCl₃: (A) pH 5.0; (B) pH 7.4.

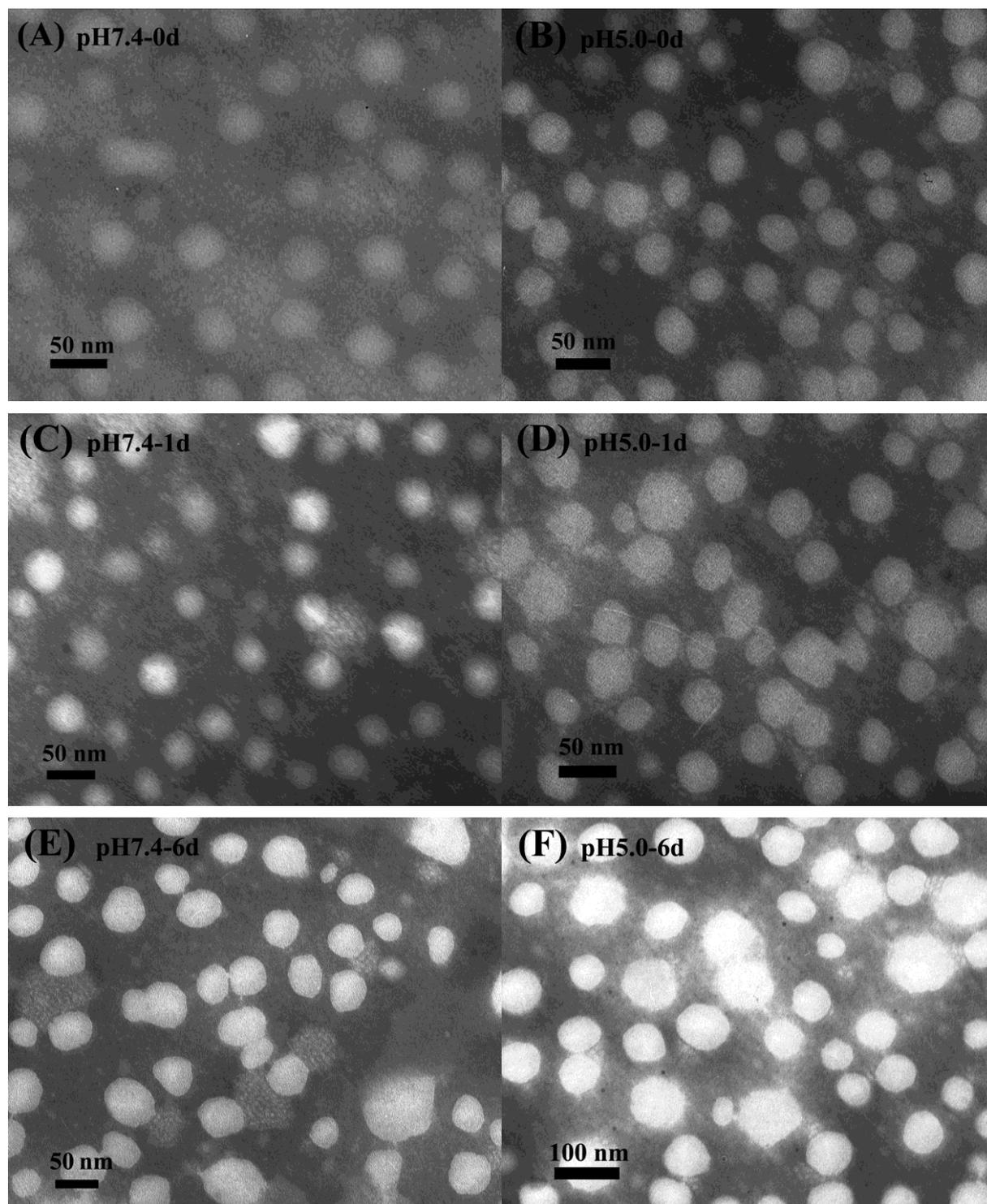


Fig. S16. TEM micrographs of the P(OSu_{0.51}-co-APSu_{0.49})-g-mPEG₂₀₀₀ micelles (0.5 mg mL⁻¹) at 37°C in phosphate buffer (0.1 M) under pH 7.4 at 0 day (A); pH 7.4 after 1 day (C); pH 7.4 after 6 days (E) and in acetate buffer (0.1 M) under pH 5.0 at 0 day (B); pH 7.4 after 1 day (D); pH 7.4 after 6 days (F).

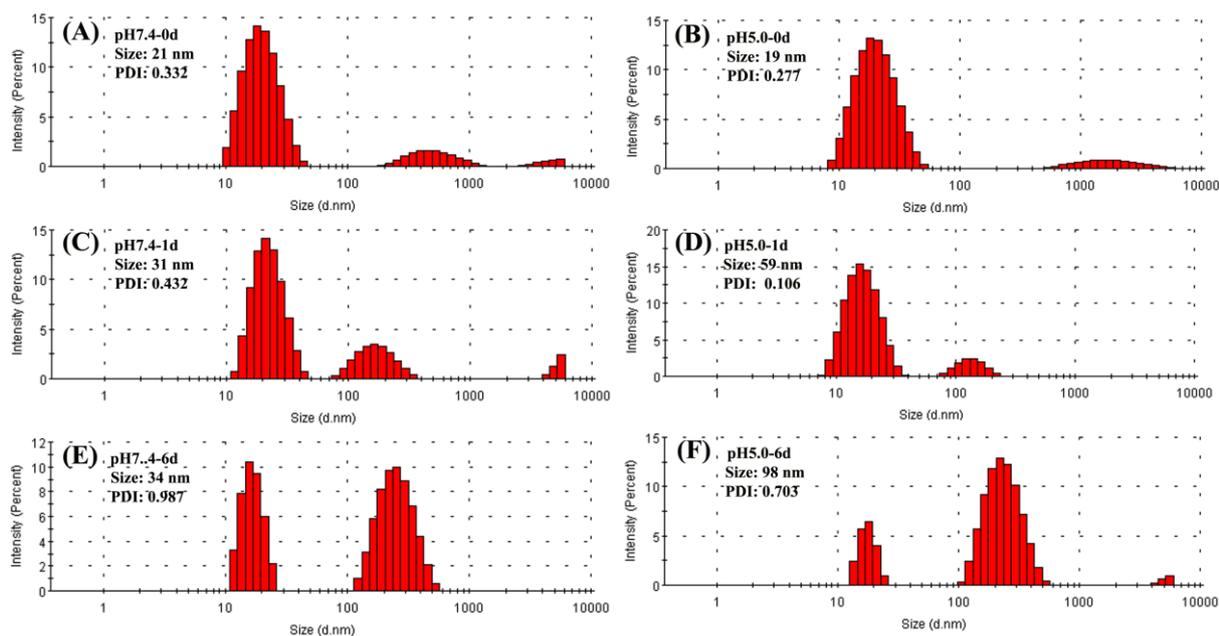


Fig. S17. Size distributions of the $P(\text{OSu}_{0.51}\text{-co-APSu}_{0.49})\text{-g-mPEG}_{2000}$ micelles (0.5 mg mL^{-1}) at 37°C in phosphate buffer (0.1 M) under pH 7.4 at 0 day (A); pH 7.4 after 1 day (C); pH 7.4 after 6 days (E) and in acetate buffer (0.1 M) under pH 5.0 at 0 day (B); pH 7.4 after 1 day (D); pH 7.4 after 6 days (F) determined by DLS.

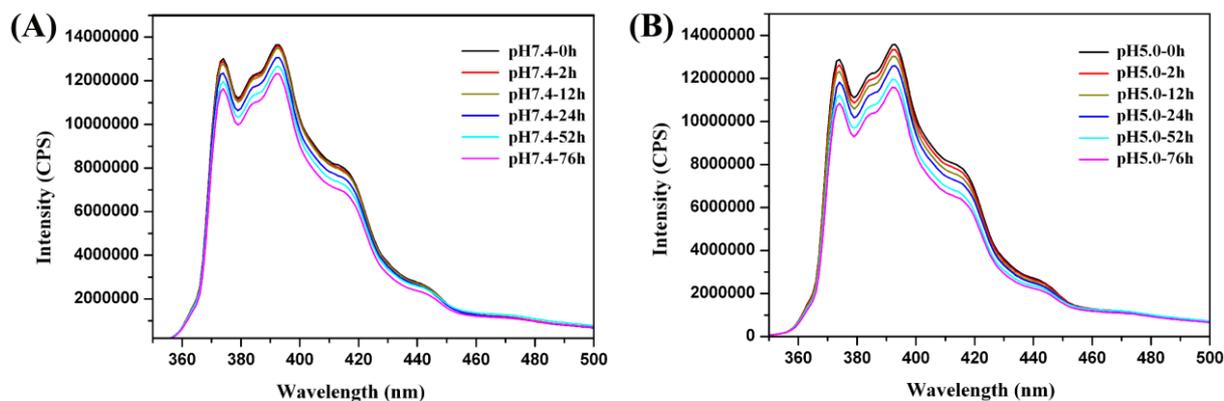


Fig. S18. Emission spectra changes of $P(\text{OSu}_{0.51}\text{-co-APSu}_{0.49})\text{-g-mPEG}_{2000}$ (0.1 mg mL^{-1}) micelle with pyrene (0.25 mg L^{-1}) excited at 335 nm at different time at pH 7.4 (A) and pH 5.0 (B).