Supplementary Information

Bioinspired amphiphilic phosphate block copolymers as non-fluoride material to prevent dental erosion

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Calculation of Mn of block copolymer by ^{31}P NMR spectroscopy

One mL of polymer solution in CDCl3 with a known polymer concentration (C1, mg/mL) and a known concentration of an external standard, trioctylphosphine oxide (TOPO) (C2, mg/mL), was prepared for 31P NMR measurement. The peak integration for PMOEP and TOPO within the 31P NMR spectrum is calculated to be A1 and A2, respectively. The mole of MOEP unit can be calculated by the equation as below,

$$\frac{A1}{A2} = \frac{Mole\ of\ MOEP}{C2/Mn_{TOPO}}\ ,$$

where Mn $_{TOPO}$ is the molecular weight of TOPO.

The Mn of block copolymer can be further calculated by the equation as below,

$$Mn\ of\ block\ copolymer = 1 * C1/(\frac{1 * C1 - Mn_{MOEP} * Mole\ of\ MOEP}{Mn_{PMMA}})\ ,$$

where Mn of MOEP and Mn of PMMA are the molecular weights of the MOEP monomer and PMMA-RAFT, respectively.

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Polymer/HAP binding

Five mL of polymer solution with different concentrations (0.06, 0.12, 0.25, 0.5 and 1.0 g/L) and different pH values were mixed with 100 mg of HAP powder for 2 h at room temperature. After centrifuging the mixture for 10 min at 10,000 rpm, the supernatant was tested using UV-Vis spectroscopy. The UV-Vis absorbance of the polymer solution before and after binding with the HAP powder was utilized to calculate the adsorbed polymer onto HAP powder. In order to compare the binding capability between phosphate and carboxylate groups, a poly(acrylic acid) based block copolymer with similar chain length was similarly synthesized as indicated in Scheme S1. Similar experiments were performed to compare the binding strength between phosphate groups and carboxylate groups.
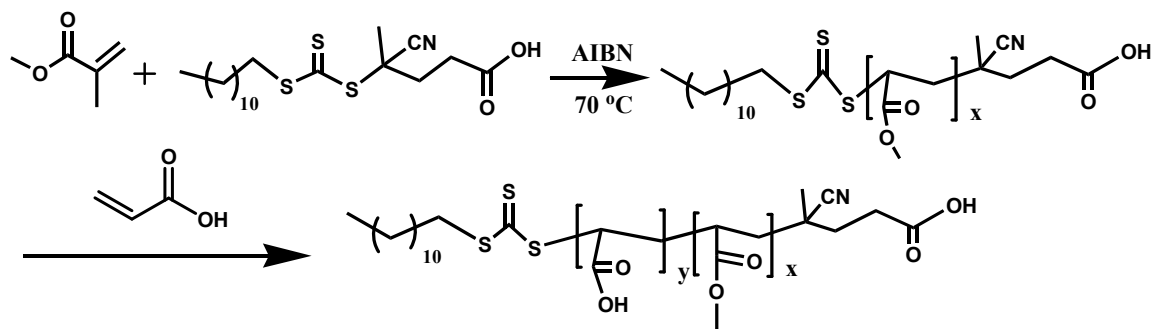
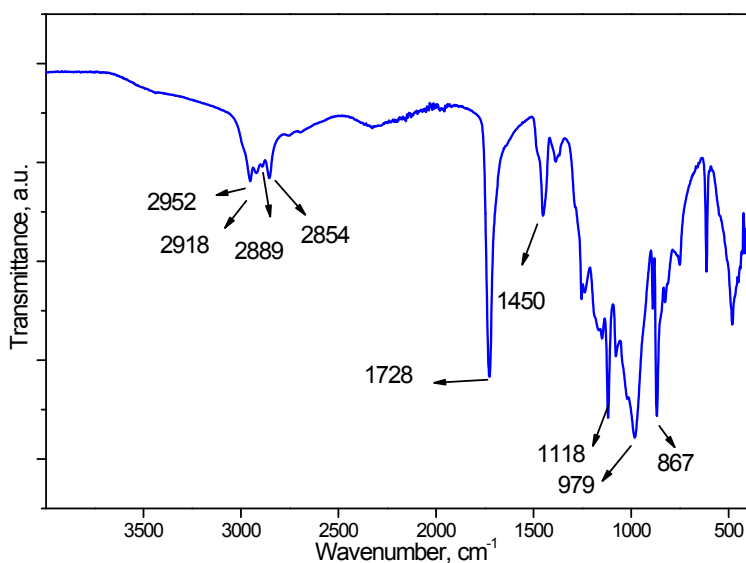**Scheme S1** Synthesis of PMMA-*b*-PAA block copolymer

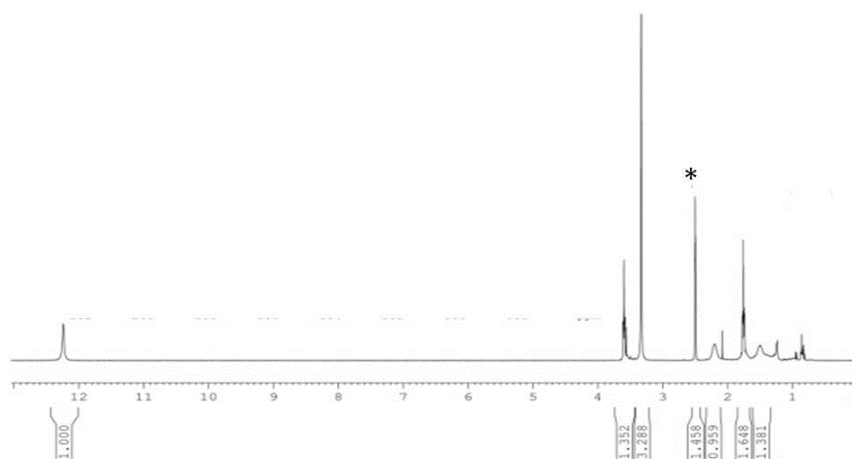**Figure S1** FTIR spectrum of PMMA-*b*-PAA

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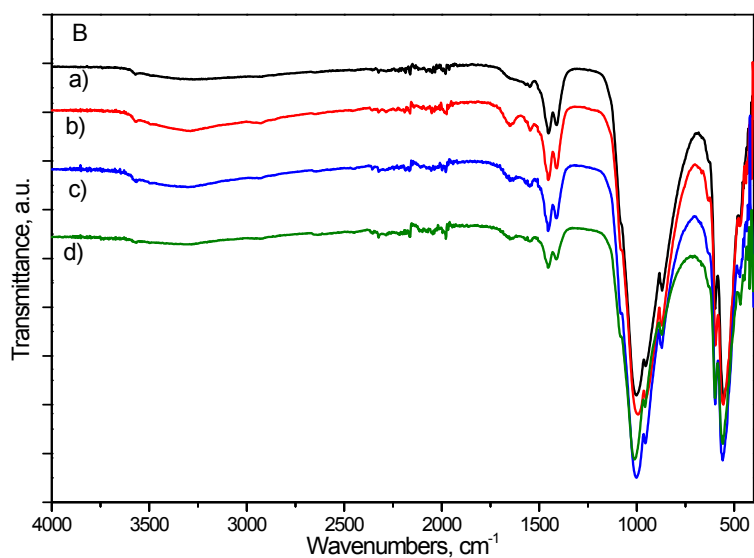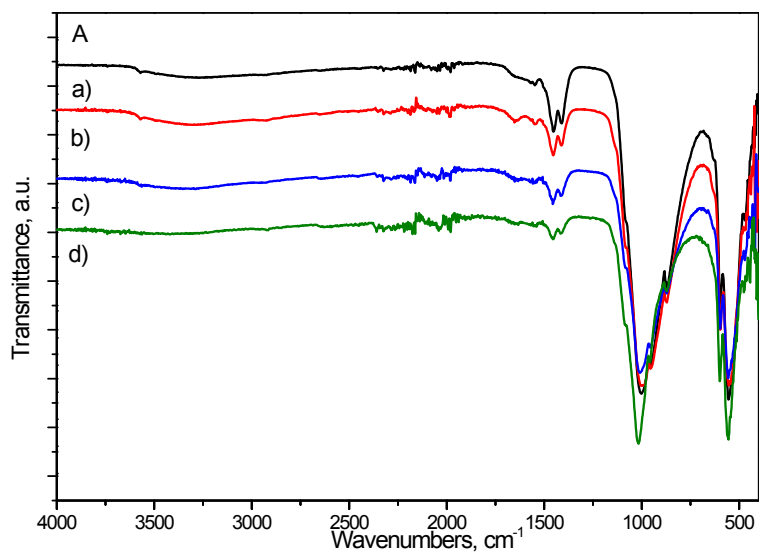**Figure S2** ^{1}H NMR spectra for PMMA-*b*-PAA (* marked peak at 2.5 ppm is due to DMSO)

Figure S3 FTIR spectra of enamel treated with PMMA-*b*-PAA with (A) 1.0 g/L at pH=3.1 or (B) pH=4.2. Each curve in the figures represents: curve a: enamel before treatment; curve b: polymer-treated enamel; curve c: polymer-treated enamel with acid challenge of 1 cycle; curve d: polymer-treated enamel with acid challenge of 2 cycles.
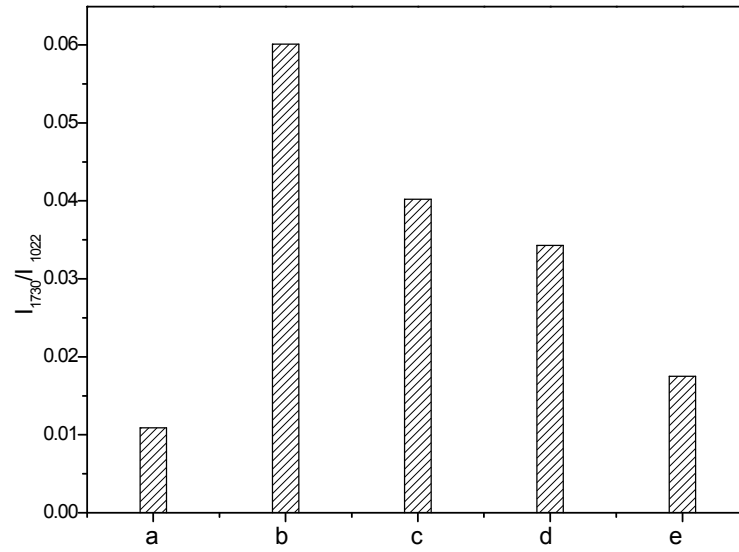
Figure S4 Relative ratio of I_{1730} to I_{1022}. a: blank enamel; b: polymer-treated enamel; c: polymer-treated enamel with acid challenge of 1 cycle; d: polymer-treated enamel with acid challenge of 2 cycles; e: polymer-treated enamel with acid challenge of 2 cycles and additional sonication of 2 min.
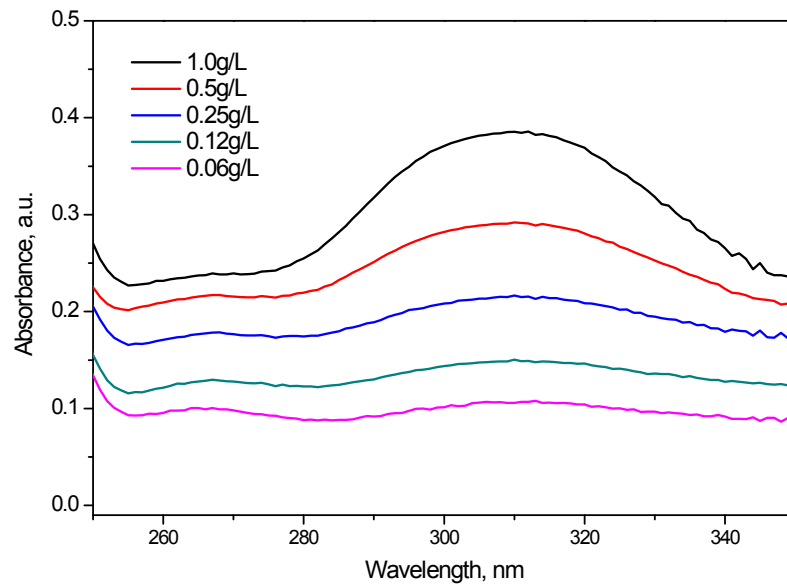

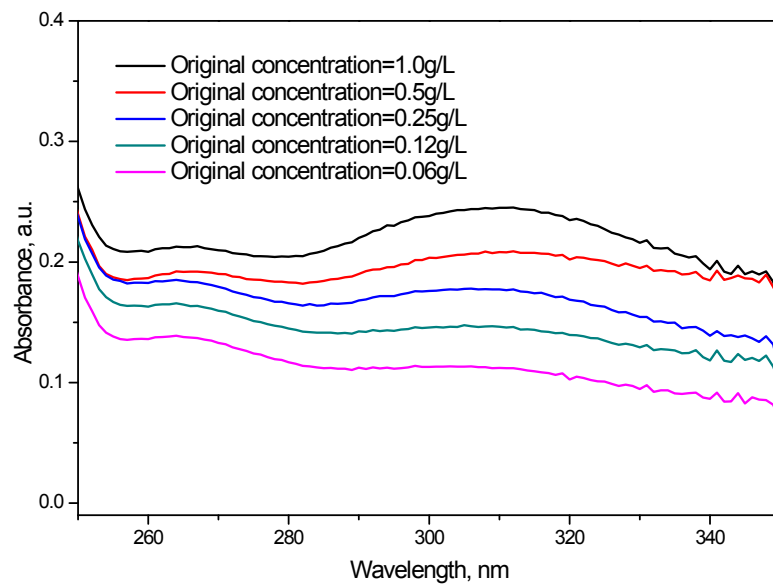**Figure S5** UV spectra of PMMA-*b*-PAA solution with standard concentrations

Figure S6 UV spectra of PMMA-*b*-PAA solutiosn after binding with HAP powder at pH=4
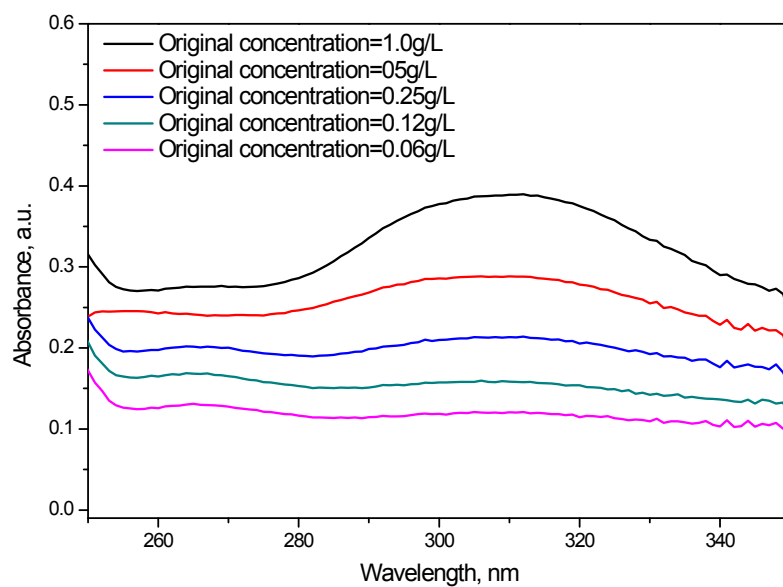

Figure S7 UV spectra of PMMA-*b*-PAA solution after binding with HAP powder at pH=7

References:

[1] Barner-Kowollik C. Handbook of RAFT Polymerization: WILEY-VCH Verlag GmbH & Co.; 2008.