Supporting Information

Specific Ion Effects on the Enzymatic Degradation of Polymeric Marine Antibiofouling Materials

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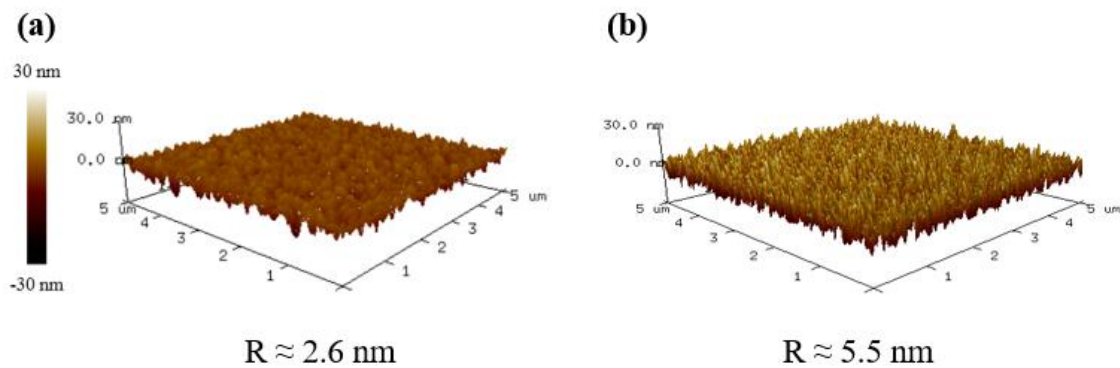
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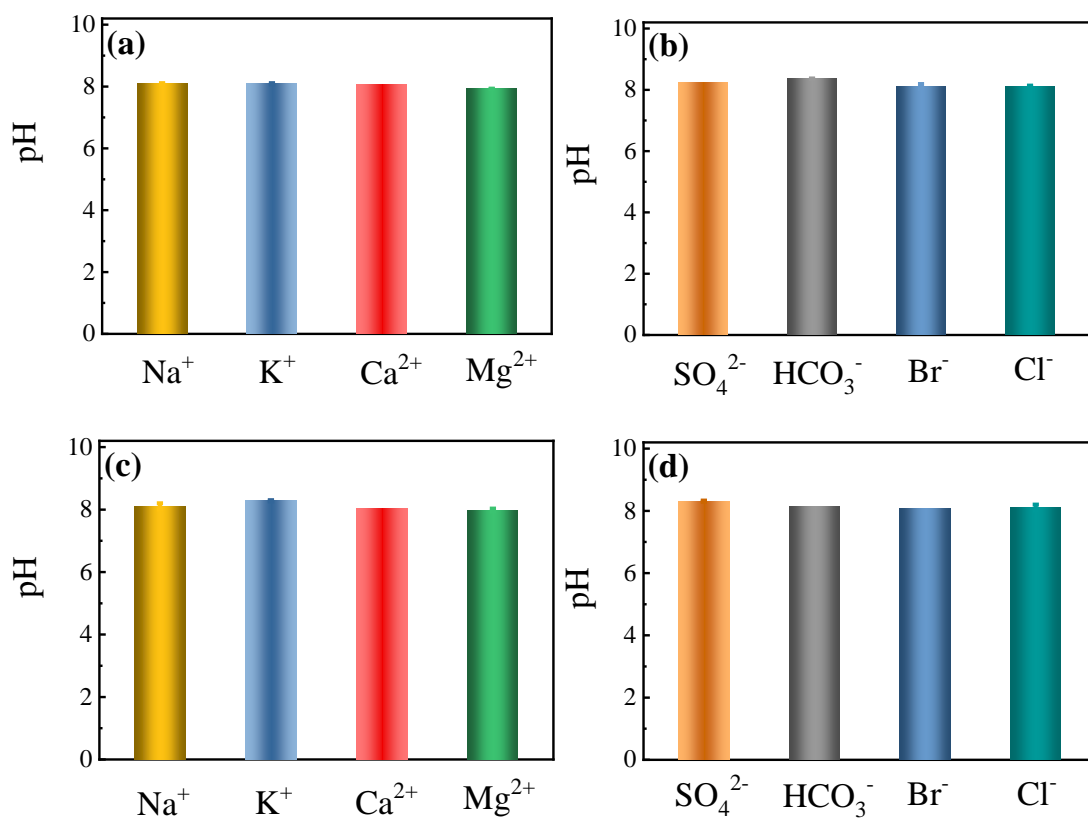
Figure S1. pH values of the salt solutions employed in this work. (a) The salt solutions with different types of cations in which the cations have the same concentrations as those in the natural seawater. (b) The salt solutions with different types of anions in which the anions have the same concentrations as those in the natural seawater. (c) The salt solutions with different types of cations at an ionic strength of 0.72 M. (d) The salt solutions with different types of anions at an ionic strength of 0.72 M.
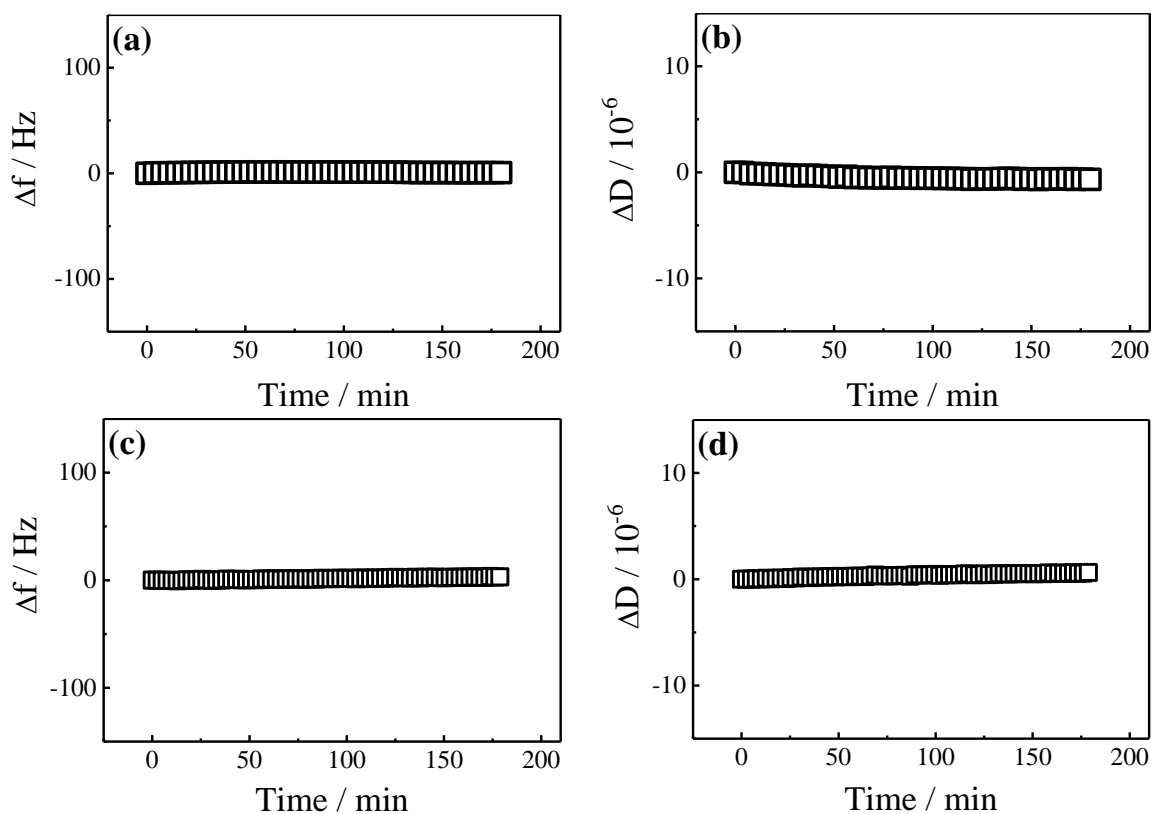
Figure S2. (a) The shift in frequency (Δf) as a function of time for the PCLPU film immersed in the Tris-HCl buffer in the absence of lipase. (b) The shift in dissipation (ΔD) as a function of time for the PCLPU film immersed in the Tris-HCl buffer in the absence of lipase. (c) The shift in frequency (Δf) as a function of time for the PCLPU film immersed in the artificial seawater in the absence of lipase. (d) The shift in dissipation (ΔD) as a function of time for the PCLPU film immersed in the artificial seawater in the absence of lipase.

(a)

30 nm

30.0 nm

0.0 nm

5 um
4
3
2
1

5 um
4
3
2
1

-30 nm

(b)

30.0 nm

0.0 nm

5 um
4
3
2
1

5 um
4
3
2
1

$R \approx 2.6$ nm

$R \approx 5.5$ nm

Figure S3. (a) The AFM image of the PCLPU film prior to the enzymatic degradation. (b) The AFM image of the PCLPU film at the time of enzymatic degradation of ~ 3 min in the Tris-HCl buffer, where the ΔD has the maximum value (see Figure S4).
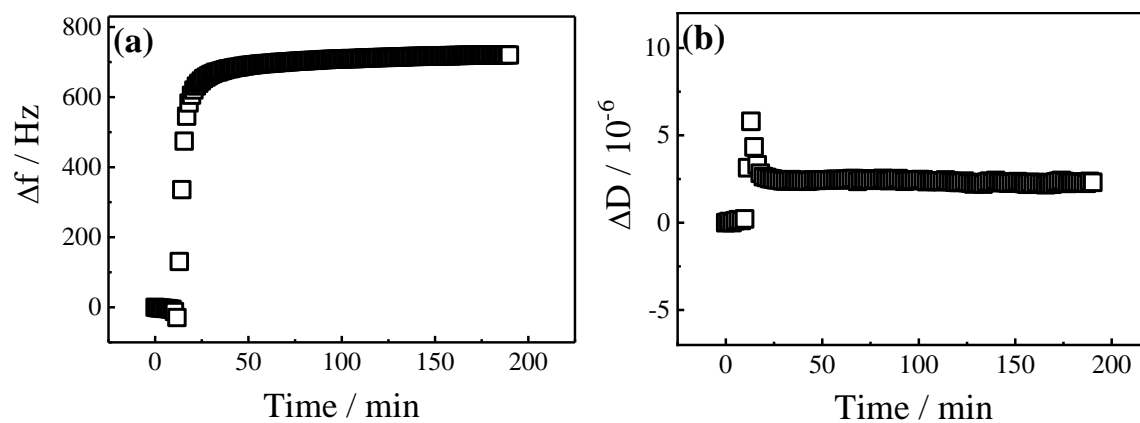
Figure S4. (a) The shift in frequency (Δf) as a function of time for the PCLPU film immersed in the Tris-HCl buffer in the presence of lipase. (b) The shift in dissipation (ΔD) as a function of time for the PCLPU film immersed in the Tris-HCl buffer in the presence of lipase.
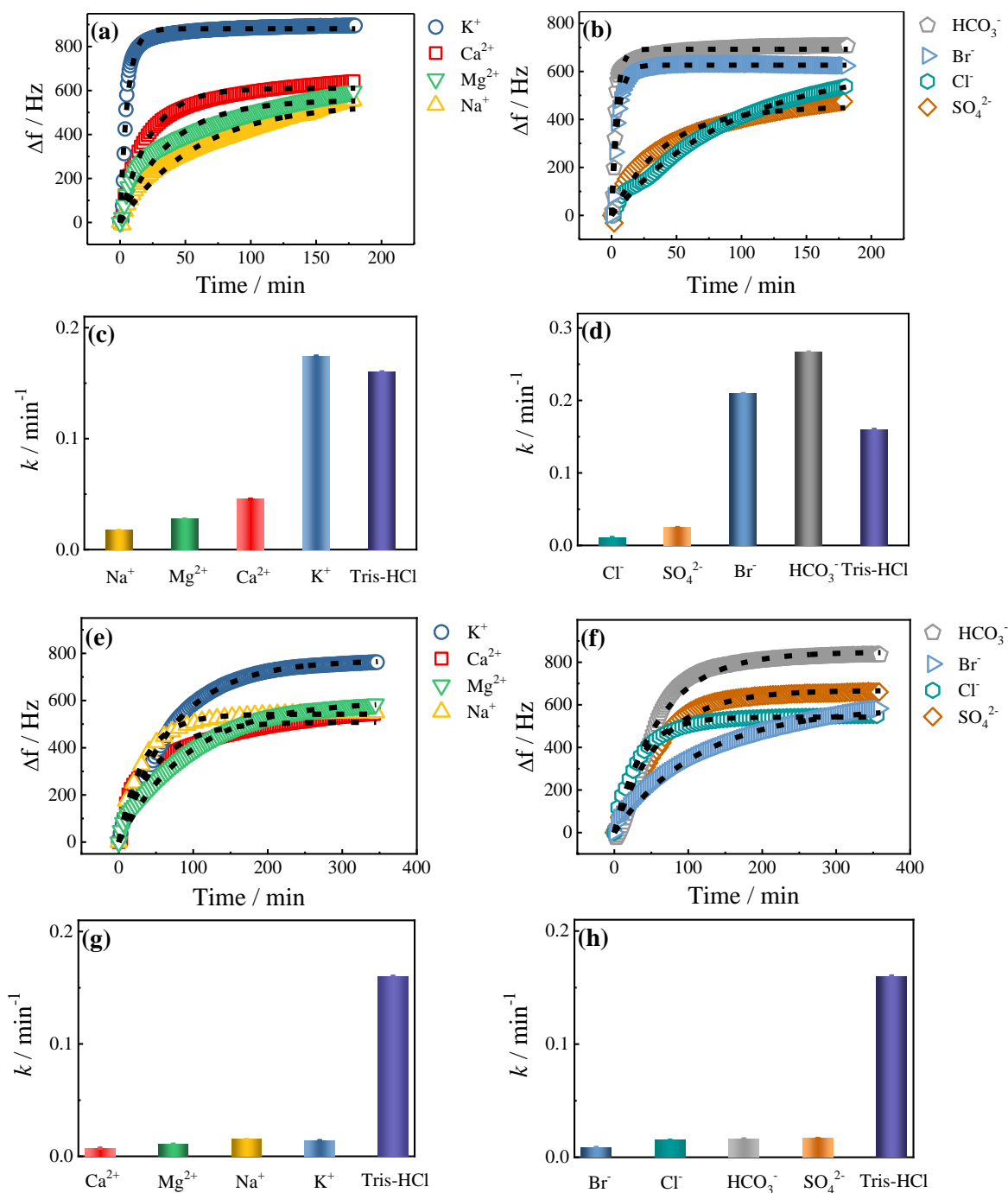
Figure S5. (a) Fitting of the time dependence of Δf for the enzymatic degradation of the PCLPU film in the presence of different cations using Equation 3. (b) Fitting of the time dependence of Δf for the enzymatic degradation of the PCLPU film in the presence of different anions using Equation 3. (c) The rate constant (k) obtained by fitting the time

dependence of Δf for the enzymatic degradation of the PCLPU film in the presence of different cations. (d) The rate constant (k) obtained by fitting the time dependence of Δf for the enzymatic degradation of the PCLPU film in the presence of different anions. (e) Fitting of the time dependence of Δf for the enzymatic degradation of the PCLPU film in the presence of different cations at an ionic strength of 0.72 M using Equation 3. (f) Fitting of the time dependence of Δf for the enzymatic degradation of the PCLPU film in the presence of different anions at an ionic strength of 0.72 M using Equation 3. (g) The rate constant (k) obtained by fitting the time dependence of Δf for the enzymatic degradation of the PCLPU film in the presence of different cations at an ionic strength of 0.72 M. (h) The rate constant (k) obtained by fitting the time dependence of Δf for the enzymatic degradation of the PCLPU film in the presence of different anions at an ionic strength of 0.72 M. Here, both the cations in (a) and (c) and the anions in (b) and (d) have the same concentrations as those in the natural seawater, and the dashed lines are the curve fits to the experimental data. In (c), (d), (g), and (h), the rate constant for the enzymatic degradation of the PCLPU film in the Tris-HCl buffer is also plotted for comparison.
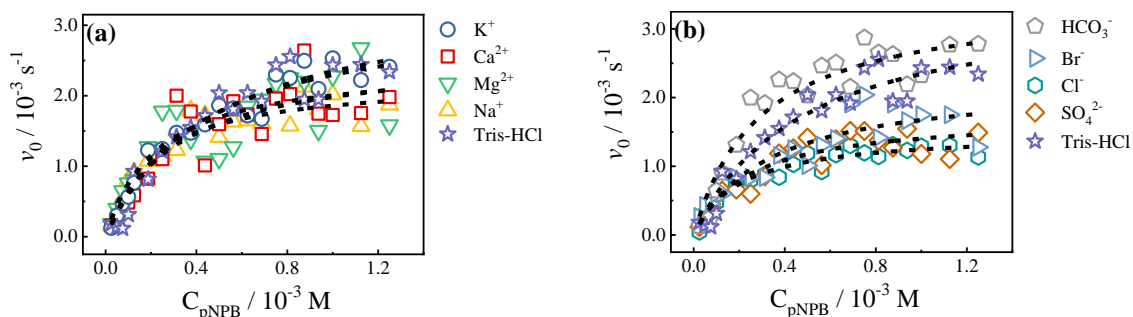
Figure S6. (a) The reaction rate (v_0) as a function of the substrate concentration (C_{pNPB}) in the presence of different cations with Cl⁻ as the common anion. (b) The reaction rate (v_0) as a function of the substrate concentration (C_{pNPB}) in the presence of different anions with Na⁺ as the common cation. Here, both the cations in (a) and the anions in (b) have the same concentrations as those in the natural seawater. The detailed information about the concentrations of cations and anions in the natural seawater are provided in the main text. The reaction rate (v_0) as a function of the substrate concentration (C_{pNPB}) in the Tris-HCl buffer is also plotted for comparison. The dashed lines are the curve fits to the experimental data.
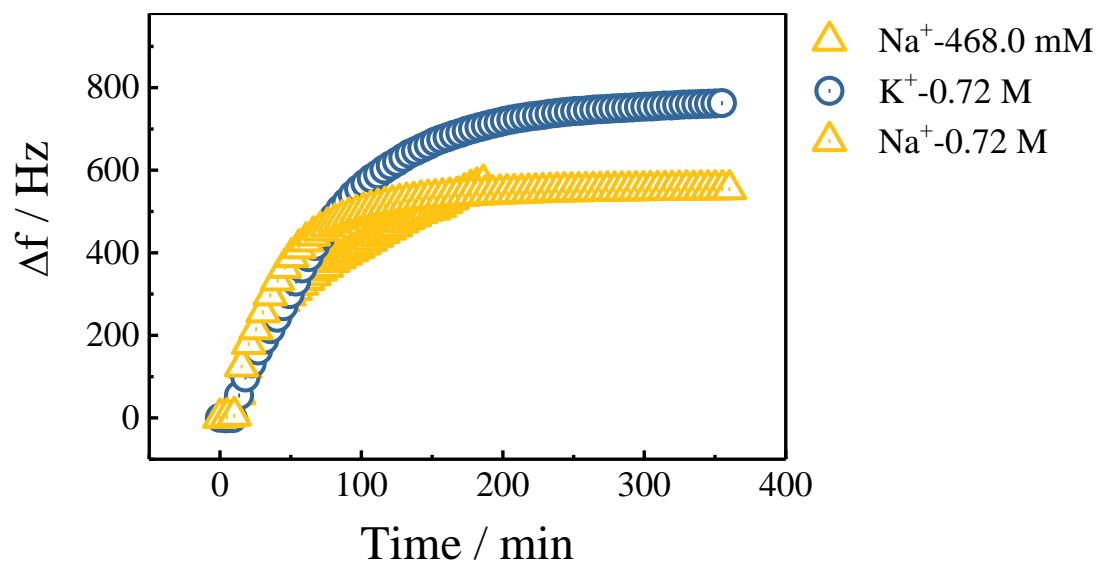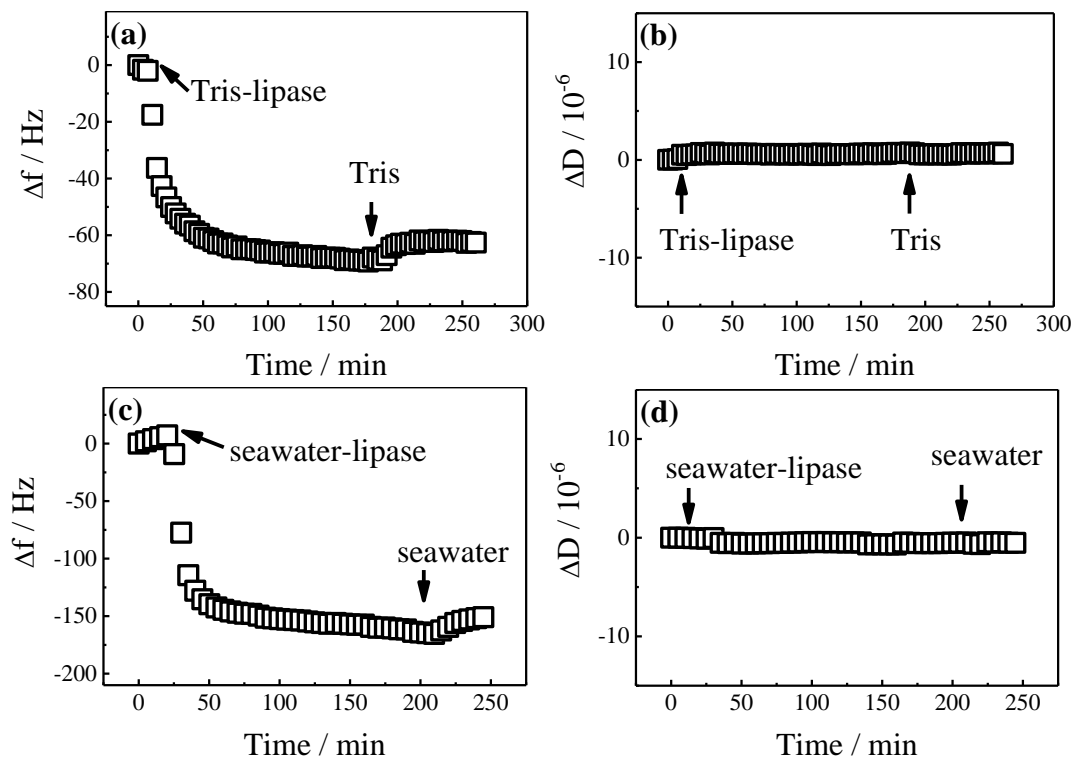
Figure S7. The shift in frequency (Δf) for the enzymatic degradation of the PCLPU film as a function of time in the presence of different cations with Cl⁻ as the common anion.
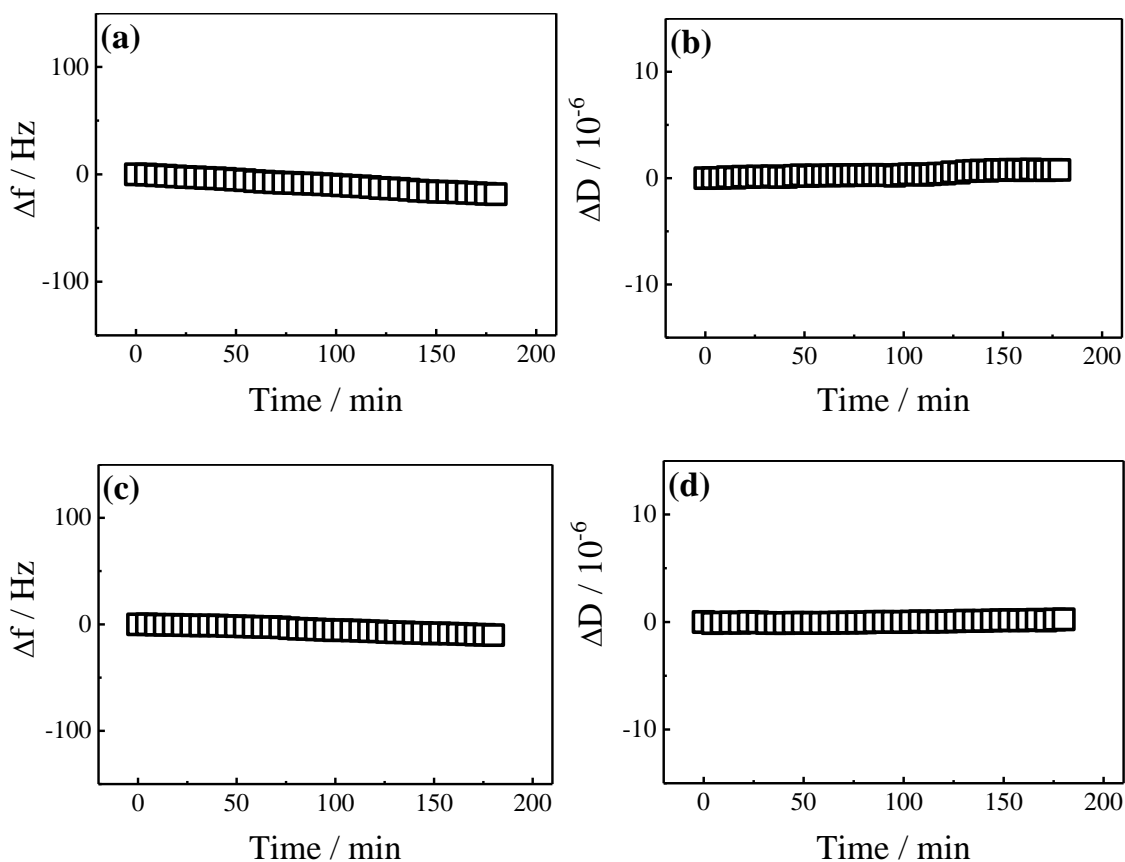
Figure S8. (a) The shift in frequency (Δf) as a function of time for the PTIO film immersed in the Tris-HCl buffer in the absence of lipase. (b) The shift in dissipation (ΔD) as a function of time for the PTIO film immersed in the Tris-HCl buffer in the absence of lipase. (c) The shift in frequency (Δf) as a function of time for the PTIO film immersed in the artificial seawater in the absence of lipase. (d) The shift in dissipation (ΔD) as a function of time for the PTIO film immersed in the artificial seawater in the absence of lipase.

Figure S9. (a) The shift in frequency (Δf) as a function of time for the poly(MMA-co-TIPSiMA) film immersed in the Tris-HCl buffer in the presence of lipase. (b) The shift in dissipation (ΔD) as a function of time for the poly(MMA-co-TIPSiMA) film immersed in the Tris-HCl buffer in the presence of lipase. (c) The shift in frequency (Δf) as a function of time for the poly(MMA-co-TIPSiMA) film immersed in the artificial seawater in the presence of lipase. (d) The shift in dissipation (ΔD) as a function of time for the poly(MMA-co-TIPSiMA) film immersed in the artificial seawater in the presence of lipase.

The M_n and PDI of the poly(methyl methacrylate-co-triisopropylsilyl methacrylate) (poly(MMA-co-TIPSiMA)) employed here are ~ 1.6×10^4 g/mol and ~ 1.7, respectively. As the PMMA is inert in the presence of lipase, the results shown in Figure S9 indicate that no obvious enzymatic hydrolysis of the silyl ester can be observed in both the Tris-HCl buffer and the artificial seawater during the time scale of our experiments. The decrease in

Δf shown in Figure S9a and S9c could be attributed to the adsorption of enzyme to the surface of polymer film.
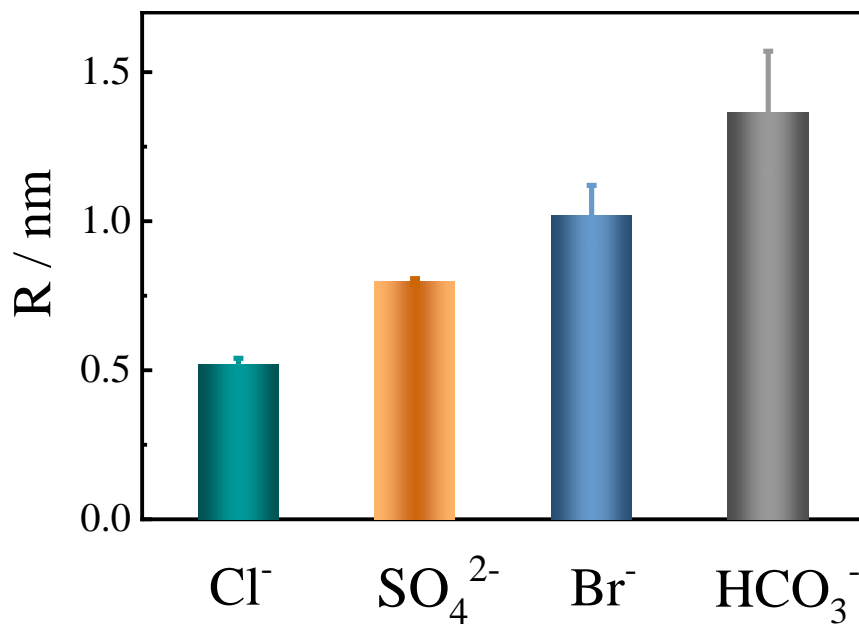
Figure S10. The RMS surface roughness (R) of the PTIO film after a certain time of enzymatic degradation in the presence of different anions with Na^+ as the common cation. For Cl^- and Br^-, the surface roughness is determined at the time of enzymatic degradation of ~ 90 min. For HCO_3^- and SO_4^{2-}, the surface roughness is determined at the time of enzymatic degradation of ~ 90 min and ~ 135 min, respectively, where the ΔD has the maximum values (Figure S11). Here, all the anions in the salt solutions have the same concentrations as those in the natural seawater.
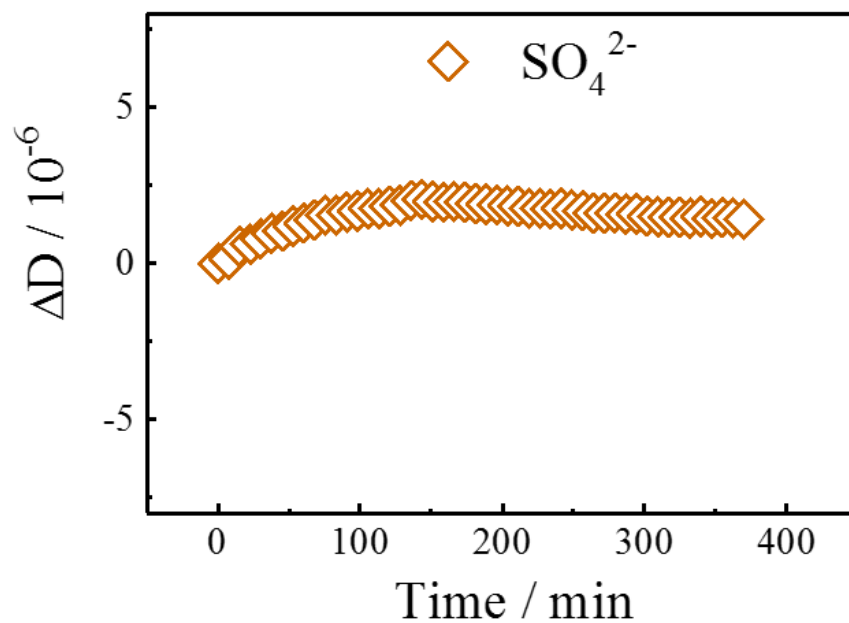
Figure S11. The shift in dissipation (ΔD) for the enzymatic degradation of the PTIO film as a function of time in the presence of SO_4^{2-}. Here, the SO_4^{2-} in the salt solution has the same concentration as that in the natural seawater.
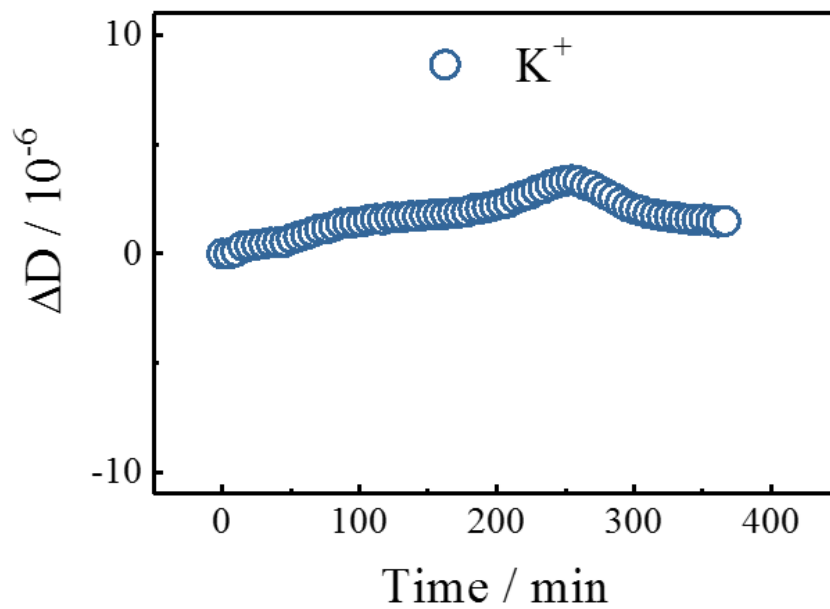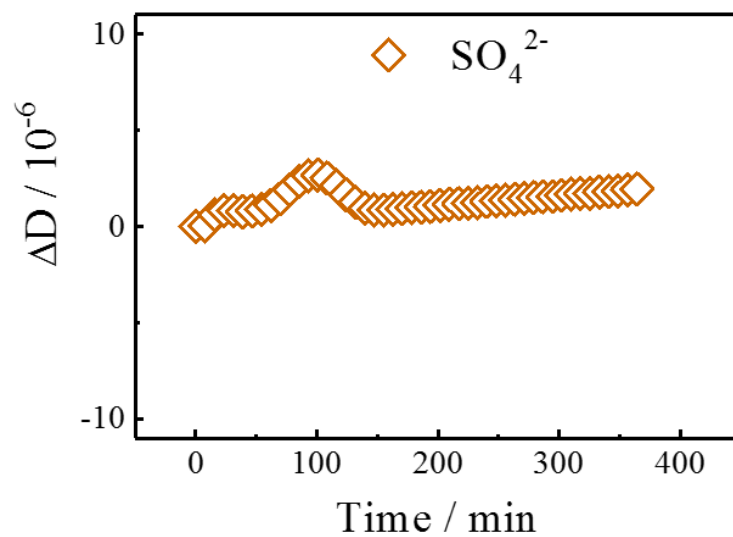
Figure S12. The shift in dissipation (ΔD) for the enzymatic degradation of the PTIO film as a function of time in the presence of K^+ at an ionic strength of 0.72 M.

(a)

10 nm

10.0 nm

0.0 nm

5 um

-10 nm

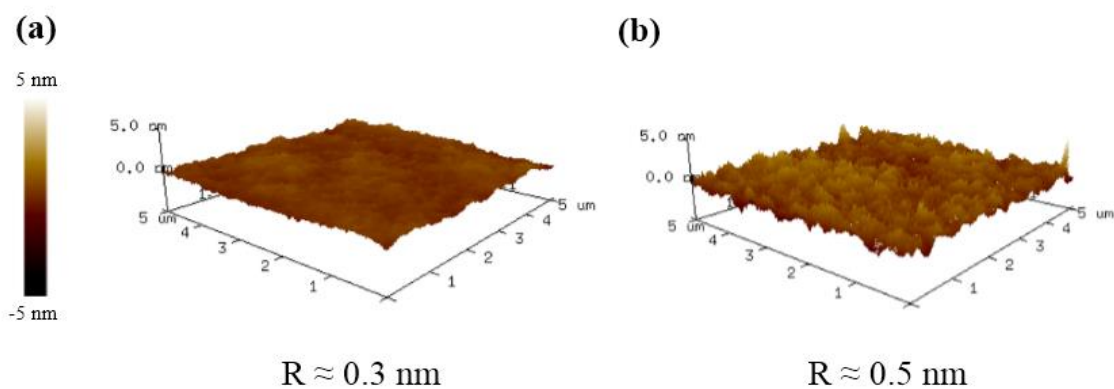R ≈ 0.3 nm

(b)

10.0 nm

0.0 nm

5 um

R ≈ 1.7 nm
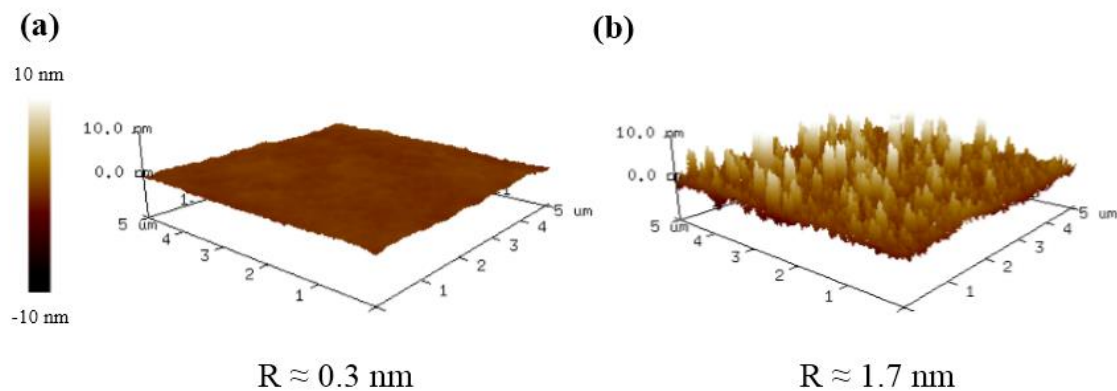
Figure S13. (a) The AFM image of the PTIO film prior to the enzymatic degradation. (b) The AFM image of the PTIO film at the time of enzymatic degradation of ~ 245 min in the presence of K^+ at an ionic strength of 0.72 M, where the ΔD has the maximum value (Figure S12).

Figure S14. The shift in dissipation (ΔD) for the enzymatic degradation of PTIO film as a function of time in the presence of SO_4^{2-} at an ionic strength of 0.72 M.

(a)

5 nm

5.0 nm

0.0 nm

-5 nm

R ≈ 0.3 nm

(b)

5.0 nm

0.0 nm

R ≈ 0.5 nm

Figure S15. (a) The AFM image of the PTIO film prior to the enzymatic degradation. (b) The AFM image of the PTIO film at the time of enzymatic degradation of ~ 90 min in the presence of SO_4^{2-} at an ionic strength of 0.72 M, where the ΔD has the maximum value (Figure S14).