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Electronic Supplementary Information

Fluorescein functionalized random amino acid copolymers in the biomimetic synthesis of CaCO_3

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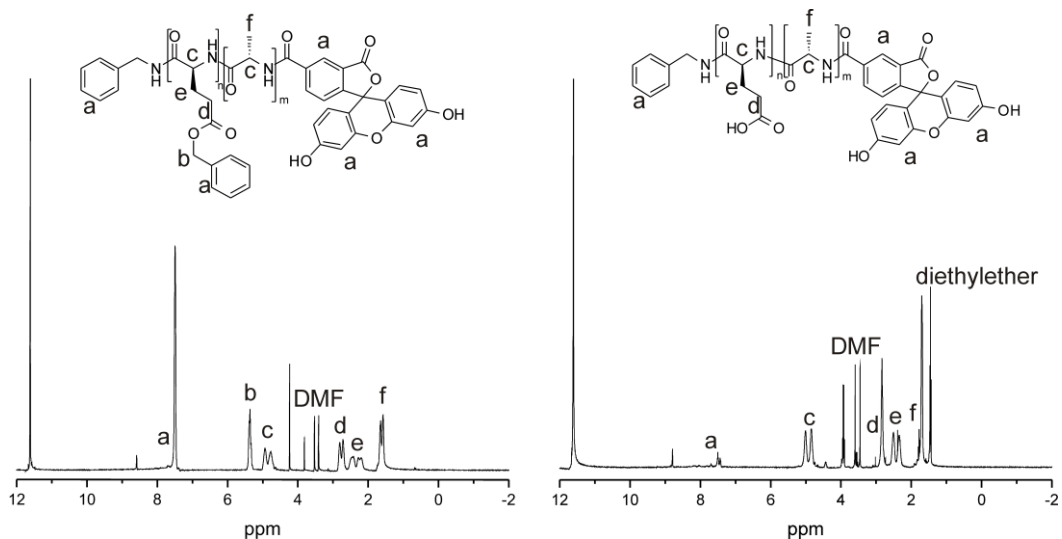
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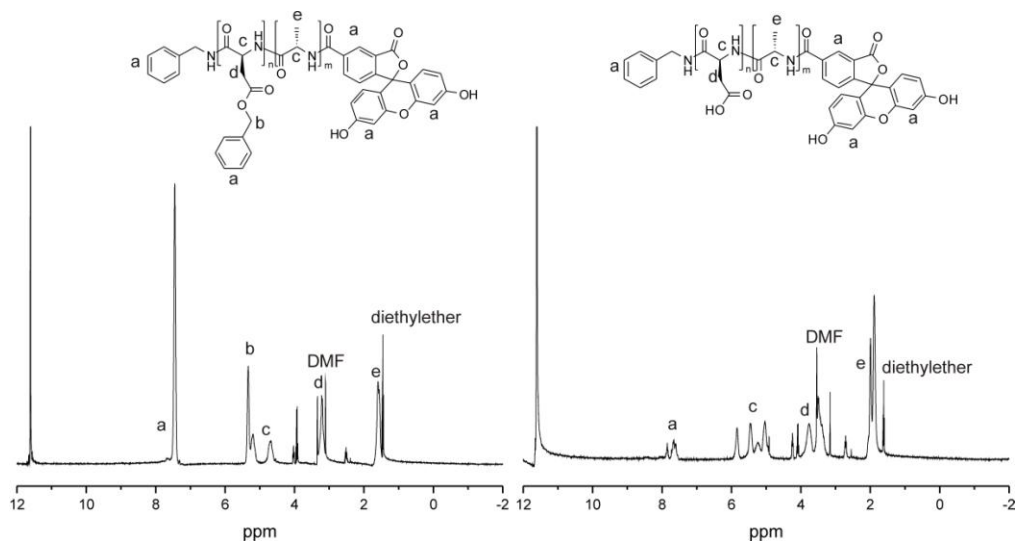
§These two authors contributed equally to this project

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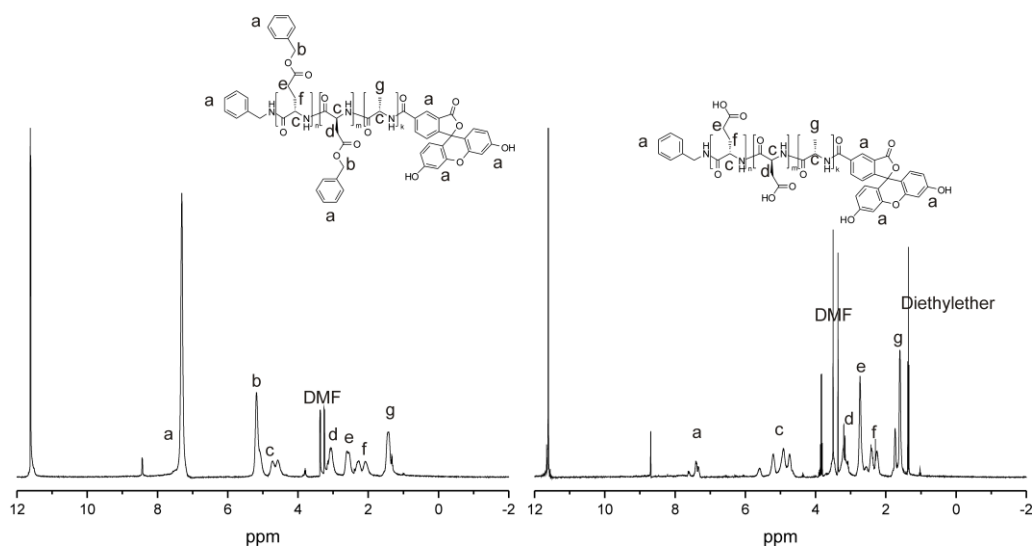
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(a)



(b)



(c)

Fig.S1 $^1\text{H-NMR}$ of deprotection of the fluorescein-labeled (a) P(BLG-co-Ala) (Entry 2, Table 1), (b) P(BLA-co-Ala) (Entry 4, Table 1) and (c) P(BLG-co-BLA-co-Ala) (Entry 6, Table 1).

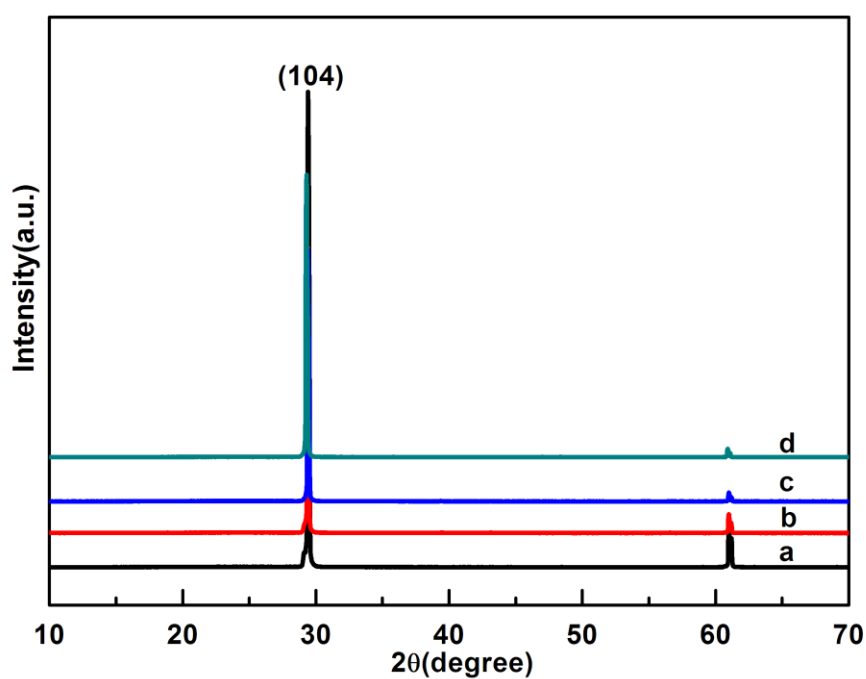


Fig.S2 XRD patterns of CaCO_3 crystals prepared in the absence of polymer (a); in the presence of (b) fluorescein labeled P(Glu-co-Ala); (c) fluorescein labeled P(Asp-co-Ala) and (d) fluorescein labeled P(Glu-co-Asp-co-Ala). [Copolymer] = 4.5×10^{-3} mM, $[\text{Ca}(\text{HCO}_3)_2] = 9$ mM.

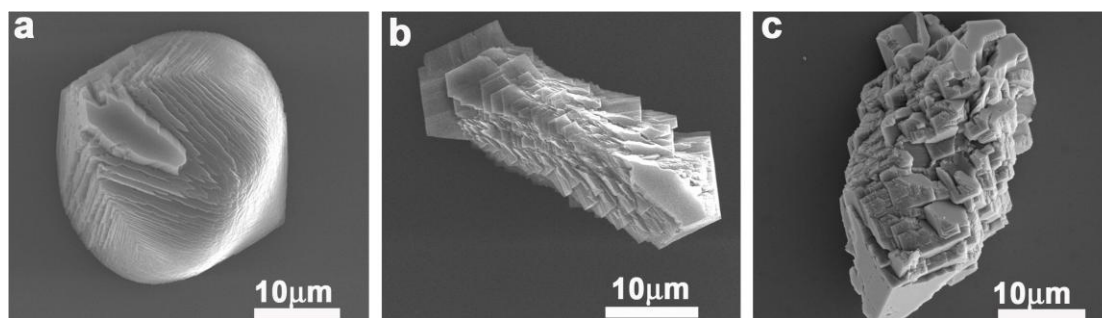


Fig.S3 SEM images of CaCO₃ crystals formed on glass substrates in supersaturated Ca(HCO₃)₂ solutions after 72 h mineralization in the presence of (a) P(Glu-co-Ala); (b) P(Asp-co-Ala), and (c) P(Glu-co-Asp-co-Ala) .[Copolymer] = 4.5×10⁻³ mM, [Ca(HCO₃)₂] = 9 mM.

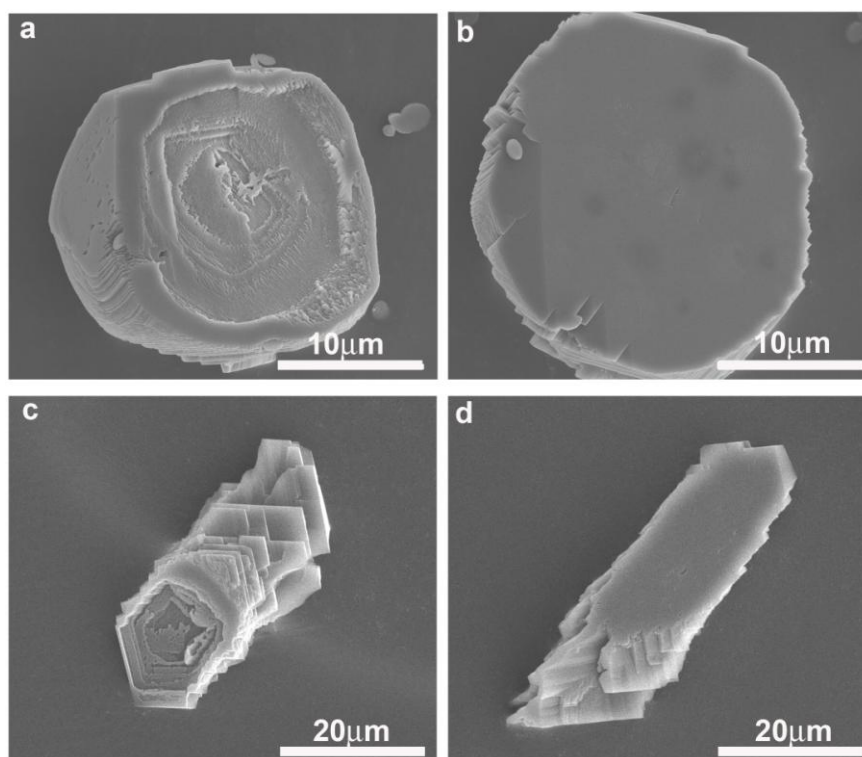


Fig.S4 SEM images of CaCO₃ crystals with exposed nucleated faces prepared in present of fluorescein labeled (a-b) P(Glu-co-Ala) and (c-d) P(Asp-co-Ala), [Copolymer] = 4.5×10^{-3} mM.

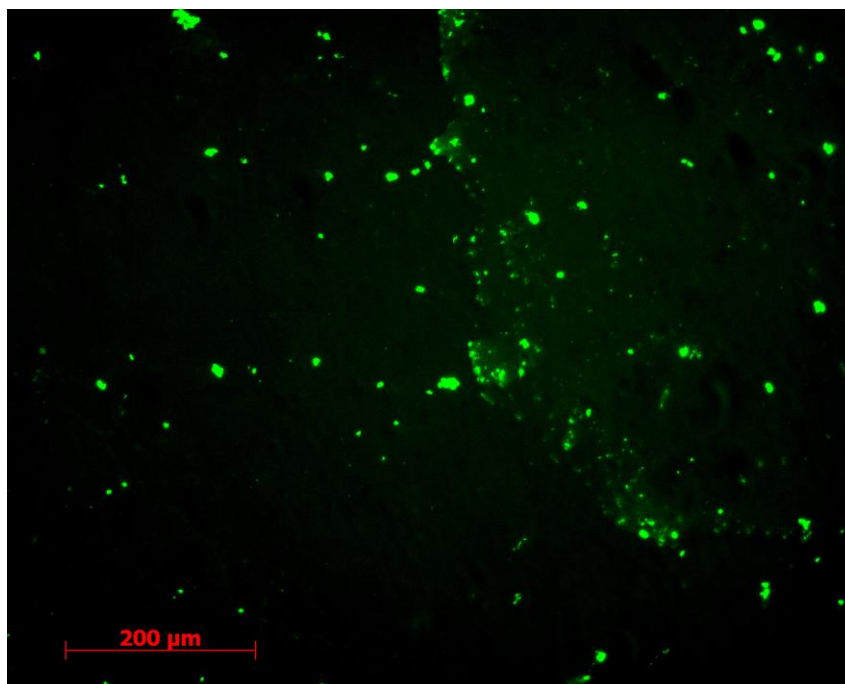


Fig.S5 Fluorescent microscopy image of fluorescein labeled copolymer aggregates physisorbed on glass substrates.

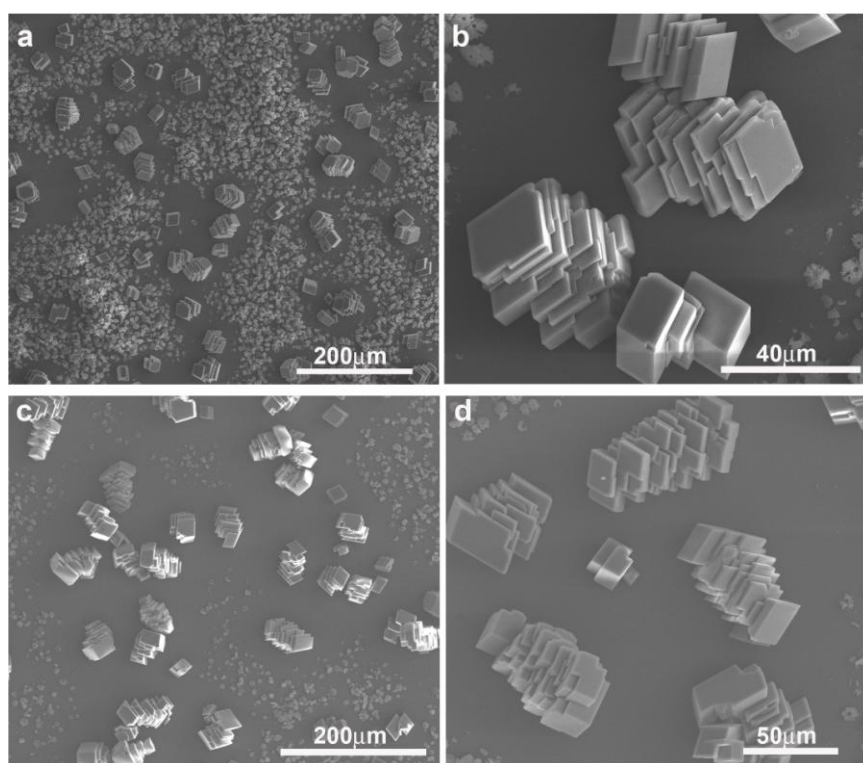


Fig.S6 SEM images of the **overgrown** CaCO_3 crystals prepared in the fresh supersaturated $\text{Ca}(\text{HCO}_3)_2$ solutions. Two CaCO_3 **samples** prepared in presence of (a, b) fluorescein labeled P(Glu-co-Ala) and (c,d) fluorescein labeled P(Asp-co-Ala) were used in this overgrowth experiment. $[\text{Ca}(\text{HCO}_3)_2] = 9 \text{ mM}$.

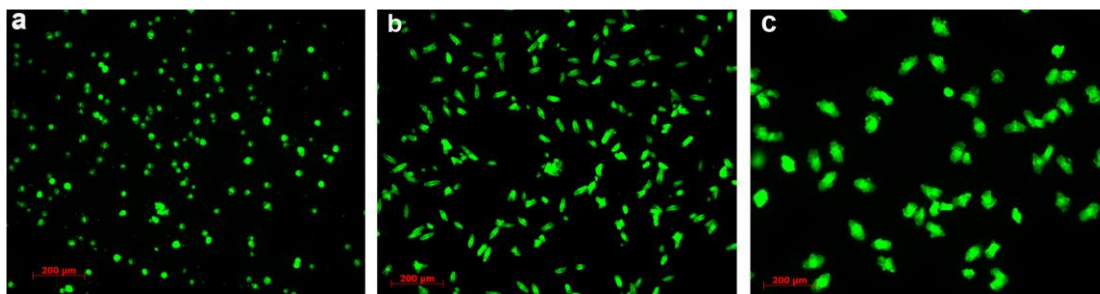


Fig.S7 Fluorescent microscopy images of CaCO_3 crystals prepared in presence of (a) fluorescein labeled P(Glu-co-Ala) and (b) fluorescein labeled P(Asp-co-Ala). $[\text{Copolymer}] = 4.5 \times 10^{-3} \text{ mM}$, $[\text{Ca}(\text{HCO}_3)_2] = 9 \text{ mM}$. (c) fluorescein labeled P (Glu-co-Asp-co-Ala). $[\text{Copolymer}] = 3.3 \times 10^{-3} \text{ mM}$, $[\text{Ca}(\text{HCO}_3)_2] = 9 \text{ mM}$.

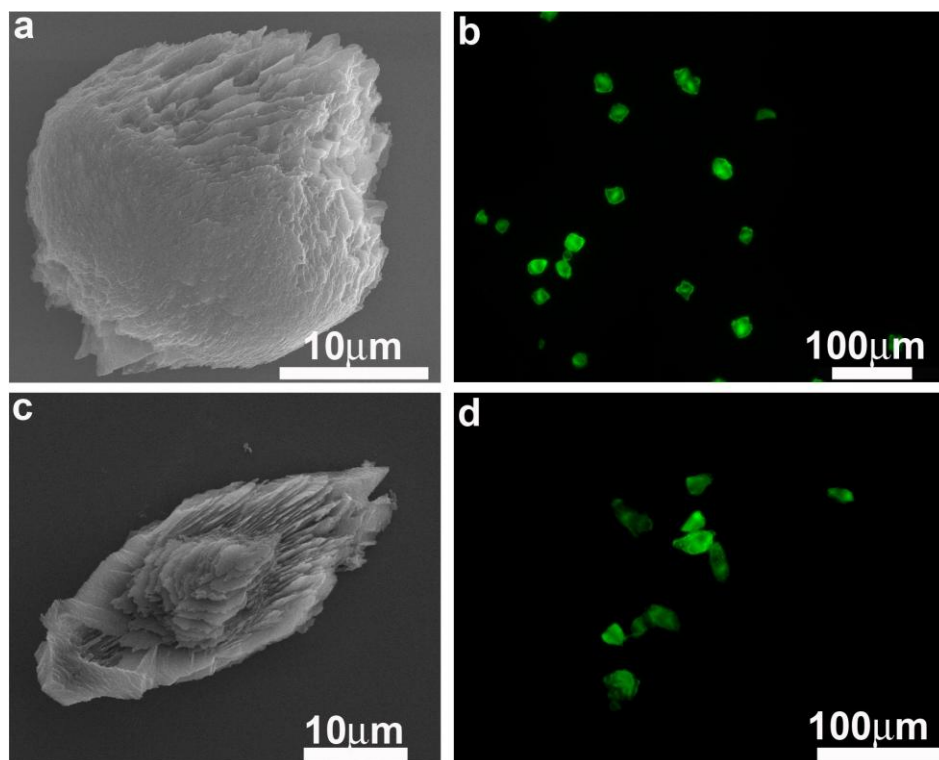


Fig.S8 SEM (a, c) and (b, d) fluorescence microscopy images of the CaCO₃ crystals prepared in present of fluorescein labeled (a,b) P(Glu-co-Ala) and (c,d) P(Asp-co-Ala) that were subsequently etched with 1.0 M acetic acid for 30 s.