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Electronic Supplementary Information

Fluorescein functionalized random amino acid copolymers in the biomimetic synthesis of CaCO₃

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**Fig.S1** $^1$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).

![H-NMR spectrum](image1.png)

**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, [Ca(HCO$_3$)$_2$] = 9 mM.
**Fig. S3** SEM images of CaCO$_3$ crystals formed on glass substrates in supersaturated Ca(HCO$_3$)$_2$ 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(HCO$_3$)$_2$] = 9 mM.
**Fig.S4** SEM images of CaCO$_3$ 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.

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**Fig.S5** Fluorescent microscopy image of fluorescein labeled copolymer aggregates physisorbed on glass substrates.
Fig. S6 SEM images of the overgrown CaCO₃ crystals prepared in the fresh supersaturated Ca(HCO₃)₂ solutions. Two CaCO₃ 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. [Ca (HCO₃)₂] = 9 mM.
Fig. S7 Fluorescent microscopy images of CaCO₃ crystals prepared in presence of (a) fluorescein labeled P(Glu-co-Ala) and (b) fluorescein labeled P(Asp-co-Ala).

[Copolymer] = 4.5×10⁻³ mM, [Ca(HCO₃)₂] = 9 mM. (c) fluorescein labeled P (Glu-co-Asp-co-Ala).[Copolymer] = 3.3×10⁻³ mM, [Ca(HCO₃)₂]=9 mM.
**Fig. S8** SEM (a, c) and (b, d) fluorescence microscopy images of the CaCO$_3$ 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.