Supporting Information:

Selective enzymatic degradation of self-assembled particles from amphiphilic block copolymers obtained by the combination of N-carboxyanhydrate (NCA) and nitroxide mediated polymerization

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Figure SI 1. MALDI-ToF-MS spectrum of P(BLG₄₀₀-co-Ala₄₀₀) at 5% conversion.



Figure SI 2. Gradient polymer elution chromatography (GPEC) of PBA, PBLG₃₀-*b*-P(BLG₁₅-co-Ala₁₅) (entry 6, Table 1) and PBLG₃₀-*b*-P(BLG₁₅-*co*-Ala₁₅)-*b*-PBA (entry 6, Table 2). The eluent was 100% toluene for the first 2 minutes and gradually changed to 20% DMF over 30 minutes.



Figure SI 3: GPEC measurement of P(BLG₃₀-*co*-Ala₃₀) (Entry 3, Table 1), P(BLG₃₀-*co*-Ala₃₀)-*b*-PBA (Entry 4, Table 2) and PBA. The eluent was 100% toluene for the first 2 minutes, then the eluent was changed to 15% DMF over 28 minutes.



Figure SI 4: GPEC measurement of $P(BLG_{50}$ -*co*-Ala₁₀) (Entry 2, Table 1), $P(BLG_{50}$ -*co*-Ala₁₀)-*b*-PBA (Entry 3, Table 2) and PBA. The eluent was 100% toluene for the first 2 minutes, then the eluent was changed to 20% DMF over 28 minutes.



Figure SI 5: GPEC measurement of PBLG₆₀ (Entry 10, Table 1), PBLG₆₀-*b*-PS (Entry 8, Table 2) and PS. The eluent was 100% toluene for the first 2 minutes. The eluent was changed to 20% DMF over 28 minutes.



Figure SI 6: Selective deprotection of PBLG₃₀-*b*-P(BLG₁₅-*co*-Ala₁₅)-*b*-PBA ¹H-NMR in d-TFA.





Figure SI 8: Cryo-TEM of PGlu₆₀-*b*-PS. The dark spots >50nm are ice crystals.



Figure SI 9: CMC determination for PGlu₆₀-*b*-PBA by SLS.



Figure SI 10. LC-MS of degradation of P(Glu-*co*-Ala)fluorescein with elastase. LC UV: λ =494 nm (c) and λ =280 nm (d) and MS for P(Glu-*co*-Ala)fluorescein corresponding to the retention time of 9 to 10 minutes (a) and the retention time of 15 to 16 minutes (b). A stands for units of L-alanine, E represents the units of L-glutamic acid and F is the fluorescein.



Figure SI 11: LC (UV: λ =494 nm) of degradation of P(Glu-*co*-Ala)fluorescein with elastase.



Figure SI 12: LC (UV: λ =280 nm) of degradation of P(Glu-*co*-Ala)fluorescein with elastase.



Figure SI 13: MS Data for 14.7-16.4 minutes elution time of P(Glu-*co*-Ala)fluorescein with elastase. E represents the units of L-glutamic acid and F is the fluorescein.



Figure SI 14: LC traces of fluorescein functionalized PGlu₄₀ at λ =490 nm.



Figure SI 15: Enzymatic degradation of $P(Glu_{30}-co-Ala_{30})-b-PS$ at 70 °C with Thermolysin. (a) $P(Glu_{30}-co-Ala_{30})-b-PS$ solution before addition of enzyme, $P(Glu_{30}-co-Ala_{30})-b-PS$ solution without the enzyme after 3 days at 70 °C (b) and (c) $P(Glu_{30}-co-Ala_{30})-b-PS$ solution with the enzyme thermolysin after 3 days at 70 °C.



Figure SI 16: Enzymatic degradation of P(Glu₃₀-*co*-Ala₃₀)-*b*-PS and P(Glu₃₀-*co*-Ala₃₀)-*b*-PBA mixed micelle solution (Entry 8, Table 7.3) Left: Blank, Right: with elastase.