Supporting Information

Tough and self-healing poly(L-glutamic acid) based composite hydrogel for tissue engineering

Weijun Zhang, Kunxi Zhang*, Shifeng Yan, Jie Wu and Jingbo Yin*

Department of Polymer Materials, Shanghai University, 99 Shangda Road, Shanghai 200444, P. R. China.

E-mail: zhangkunxi@shu.edu.cn; jbyin@oa.shu.edu.cn

* Corresponding author: Dr. Kunxi Zhang

E-mail: zhangkunxi@shu.edu.cn

* Corresponding author: Prof. Jingbo Yin

E-mail: jbyin@oa.shu.edu.cn
Figure S1. Characterization of PLGA-g-PCL. (a) $^1$H NMR spectra, (b) FTIR spectra.

Figure S2. PLGA-g-PCL hydrogels with different cross-linking degrees after dialysis in water. (a) Macromorphology. (b) Compression strength. Response #1.3
Figure S3. (a) G’ and Tanδ, (b) compressive stress-strain curve of the PLGA hydrogel and the PLGA-g-PCL hydrogel.

Figure S4. (a) Swelling kinetics, (b) porosity and average pore diameter of the PLGA based tough porous hydrogel skeleton.
**Figure S5.** In vivo degradation of the PLGA based tough porous hydrogel skeleton. The data was calculated according to the thickness of the remaining skeleton from H&E staining images.

**Figure S6.** FT-IR spectra of (a) (PLGA-EA)-g-FA and (b) CS-PO. $^1$H NMR spectra of (c) (PLGA-EA)-g-FA and (d) CS-PO.
Figure S7. (a) Hydroxylamine hydrochloride titration curve and differential curve of (PLGA−EA)-g-FA. (b) Polymer potentiometric titration curve and differential curve of CS−PO.

Figure S8. FT-IR spectra of (PLGA-EA)-g-FA/CS-PO mixture and self-healing hydrogel.
**Figure S9.** Gelation time of self-healing hydrogel with (a) different solid content and (b) different -CHO/-NH₂ molar ratio.

**Figure S10.** Rheological characterization of self-healing hydrogel with (a, c) different solid content and (b, d) different -CHO/-NH₂ molar ratio. The experiment was carried out under 1% strain and values in (c, d) represent $G'$ at $\omega = 1$ rad s$^{-1}$. 
Figure S11. Tensile test of the PLGA based self-healing hydrogel after different healing period.

Figure S12. Fluorescent images of Dio labelled ASCs in the PLGA based tough porous hydrogel skeleton.
**Figure S13.** Cell viability after culture for 1, 3, and 7 days in the PLGA based composite hydrogel.

**Figure S14.** Self-healing of the composite hydrogel after cell seeding. (a) Compressive stress-strain curves. (b) Compression strength at different self-healing period.

| Table S1. Characterization of PLGA-g-PCL. |
|-------------------------------|----------------|----------------|----------------|----------------|
| Polymer                        | Feed ratio (mol/mol) | DP<sup>a</sup> | $M_n$<sup>a</sup> | $M_a$<sup>b</sup> | PDI<sup>b</sup> |
| BA-PCL                         | BA/ε−CL (1 : 20)    | 21             | 2400           | 12300          | 1.10           |
| PLGA-g-PCL                     | PCL/COOH (1 : 10)   |                |                |                |                |
|                                | Grafting ratio<sup>c</sup>: 9.8 |                |                |                |                |

<sup>a</sup> was determined by $^1$H NMR. <sup>b</sup> was determined by GPC.