Copolymacrolactones Grafted with L-Glutamic Acid: Synthesis, Structure, and Nanocarrier Properties

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Figure S1. $^1$H NMR (a) and $^{13}$C NMR (b) of the P(Gl$_{13}$-r-PDL$_{87}$) copolyester registered in CDCl$_3$.

Figure S2. $^1$H NMR (CDCl$_3$) of the P(Gl$_{x}$-r-PDL$_{y}$) copolyesters series.

Figure S3. $^{13}$C NMR spectra of Gl and PGl highlighting the characteristic peaks of the different isomers used for quantification.

Figure S4. TGA traces (a) and derivative curves (b) of the P(Gl$_{x}$-r-PDL$_{y}$) copolyesters.

Figure S5. $^1$H NMR (CDCl$_3$) spectra of the [P(Gl-BAET)$_{13}$-r-PDL$_{87}$] (a), and [P(Gl-NH$_2$)$_{13}$-r-PDL$_{87}$] (b).

Figure S6. GPC curves of the P[(Gl$_{x}$-r-PDL$_{y}$)-g-(LGlu)$_z$] copolymers. Peaks observed at elution times longer than 25 min (framed area) are due to salts added to the running solvent.

Figure S7. $^1$H NMR (CDCl$_3$/TFA) spectra of the P[(Gl$_{48}$-r-PDL$_{52}$)-g-(BLG)$_2$] (a), and P[(Gl$_{48}$-r-PDL$_{52}$)-g-(LGA)$_2$] (b).

Figure S8. TGA traces (a, b) and derivative curves (a’, b’) of the P[(Gl$_{x}$-r-PDL$_{y}$)-g-(BLG)$_z$] and P[(Gl$_{x}$-r-PDL$_{y}$)-g-(LGA)$_z$] copolymers.

Figure S9. 1,800-1,500 cm$^{-1}$ region of FTIR spectra of P[(Gl$_{13}$-r-PDL$_{87}$)-g-(BLG)$_{10}$] (a) and P[(Gl$_{48}$-r-PDL$_{52}$)-g-(BLG)$_2$] (b) at different temperatures over the 20-200 ºC range.

Figure S10. Evolution of the WAXS (a) and SAXS (b) profiles recorded from P[(Gl$_{48}$-r-PDL$_{52}$)-g-(BLG)$_2$] copolymer at heating over the 10-200 ºC range.

Figure S11. Evolution of the WAXS (a) and SAXS (b) profiles recorded from P[(Gl$_{48}$-r-PDL$_{52}$)-g-(LGA)$_2$] copolymer at heating over the 0-200 ºC range.

Figure S12. SEM images of nanoparticles made of P[(Gl$_{13}$-r-PDL$_{87}$)-g-(BLG)$_{10}$].
**Figure S13.** DLS profiles (a) and plot used for determining the critical concentration (b) of micelles made of P[(Gl13-r-PDL87)-g-(LGA)10].

**Figure S14.** Chemical structure of DOX·HCl.
Figure S1. $^1$H NMR (a) and $^{13}$C NMR (b) of the P(Gl$_{13}$-r-PDL$_{87}$) copolyester registered in CDCl$_3$.

Figure S2. $^1$H NMR (CDCl$_3$) of the P(Gl$_{r}$-PDL$_{y}$) copolyesters series.
| Sample | % mol-mass isomers          | oxapentadecen-12-one | oxapentadecen-13-one |
|--------|----------------------------|----------------------|----------------------|
|        | E    | Z    | E    | Z    | E    | Z    |
| Gl     | 44.3 | 15.7 | 33.6 | 6.3  | 33.6 | 6.3  |
| PGI    | 45.6 | 13.0 | 35.1 | 6.3  | 35.1 | 6.3  |

**Figure S3.** $^{13}$C NMR (CDCl$_3$) spectra of Gl and PGI highlighting the characteristic peaks of the different isomers used for their quantification.
Figure S4. TGA traces (a) and derivative curves (b) of the P(Gl-r-PDL) copolyesters.
Figure S5. $^1$H NMR (CDCl$_3$) spectra of the P[(Gl-BAET)$_{13}$-$r$-PDL$_{87}$] (a), and P[(Gl-NH$_2$)$_{13}$-$r$-PDL$_{87}$] (b).
Figure S6. GPC curves of the P[(Gl_{13-r-PDL_{87}})-g-(BLG)_{10}] and P[(Gl_{48-r-PDL_{52}})-g-(BLG)_{2}] copolymers. Peaks observed at elution times longer than 25 min (framed area) are due to the sodium trifluoroacetate salts added to the running solvent.
Figure S7. $^1$H NMR (CDCl$_3$/TFA) spectra of the P[(Gl$_{48}$-r-PDL$_{52}$)-γ-(BLG)$_2$] (a), and P[(Gl$_{48}$-r-PDL$_{52}$)-γ-(LGA)$_2$] (b).
Figure S8. TGA traces (a, b) and derivative curves (a’, b’) of the P[(Gl$_{13}$-r-PDL$_{87}$)-g-(BLG)$_{10}$] and P[(Gl$_{48}$-r-PDL$_{52}$)-g-(LGA)$_{2}$] copolymers.

Figure S9. 1,800-1,500 cm$^{-1}$ region of FTIR spectra of P[(Gl$_{13}$-r-PDL$_{87}$)-g-(BLG)$_{10}$] (a) and P[(Gl$_{48}$-r-PDL$_{52}$)-g-(LGA)$_{2}$] (b) at different temperatures over the 20-200 ºC range.
Figure S10. Evolution of the WAXS (a) and SAXS (b) profiles recorded from P[(Gla-r-PDL52)-g-(BLG)₃] copolymer at heating over the 0-200 °C range.

Figure S11. Evolution of the WAXS (a) and SAXS (b) profiles recorded from P[(Gla-r-PDL52)-g-(LGA)₃] copolymer at heating over the 0-200 °C range.
**Figure S12.** SEM images of nanoparticles made of P[(Gl13-r-PDL87)-g-(BLG)10].

**Figure S13.** DLS profiles (a) and plot used for determining the critical concentration (b) of micelles made of P[(Gl13-r-PDL87)-g-(LGA)10].

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