

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

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Figure S1. ^1H NMR (a) and ^{13}C NMR (b) of the $\text{P}(\text{Gl}_{13-r}\text{-PDL}_{87})$ copolyester registered in CDCl_3 .

Figure S2. ^1H NMR (CDCl_3) of the $\text{P}(\text{Gl}_x\text{-PDL}_y)$ copolyesters series.

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

Figure S4. TGA traces (a) and derivative curves (b) of the $\text{P}(\text{Gl}_x\text{-PDL}_y)$ copolyesters.

Figure S5. ^1H NMR (CDCl_3) spectra of the $\text{P}[(\text{Gl}\text{-BAET})_{13-r}\text{-PDL}_{87}]$ (a), and $\text{P}[(\text{Gl}\text{-NH}_2)_{13-r}\text{-PDL}_{87}]$ (b).

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

Figure S7. ^1H NMR (CDCl_3/TFA) spectra of the $\text{P}[(\text{Gl}_{48-r}\text{-PDL}_{52})\text{-g}\text{-}(\text{BLG})_2]$ (a), and $\text{P}[(\text{Gl}_{48-r}\text{-PDL}_{52})\text{-g}\text{-}(\text{LGA})_2]$ (b).

Figure S8. TGA traces (a, b) and derivative curves (a', b') of the $\text{P}[(\text{Gl}_x\text{-PDL}_y)\text{-g}\text{-}(\text{BLG})_z]$ and $\text{P}[(\text{Gl}_x\text{-PDL}_y)\text{-g}\text{-}(\text{LGA})_z]$ copolymers.

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

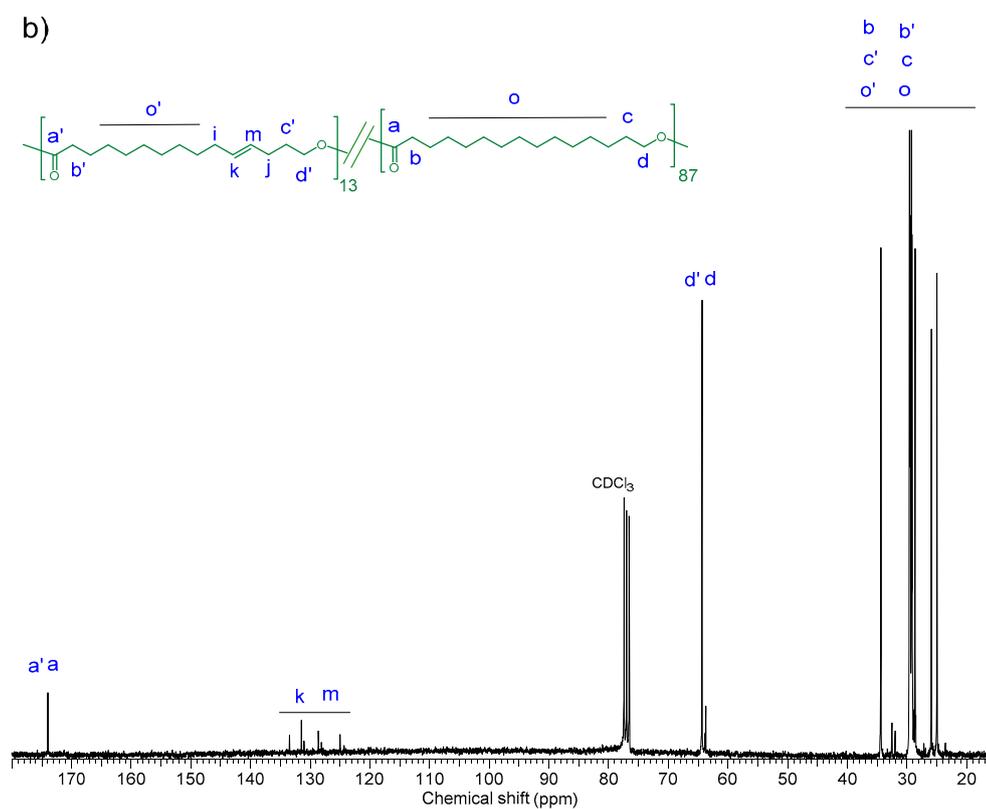
Figure S10. Evolution of the WAXS (a) and SAXS (b) profiles recorded from $\text{P}[(\text{Gl}_{48-r}\text{-PDL}_{52})\text{-g}\text{-}(\text{BLG})_2]$ copolymer at heating over the 10-200 $^\circ\text{C}$ range.

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

Figure S12. SEM images of nanoparticles made of $\text{P}[(\text{Gl}_{13-r}\text{-PDL}_{87})\text{-g}\text{-}(\text{BLG})_{10}]$.

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.



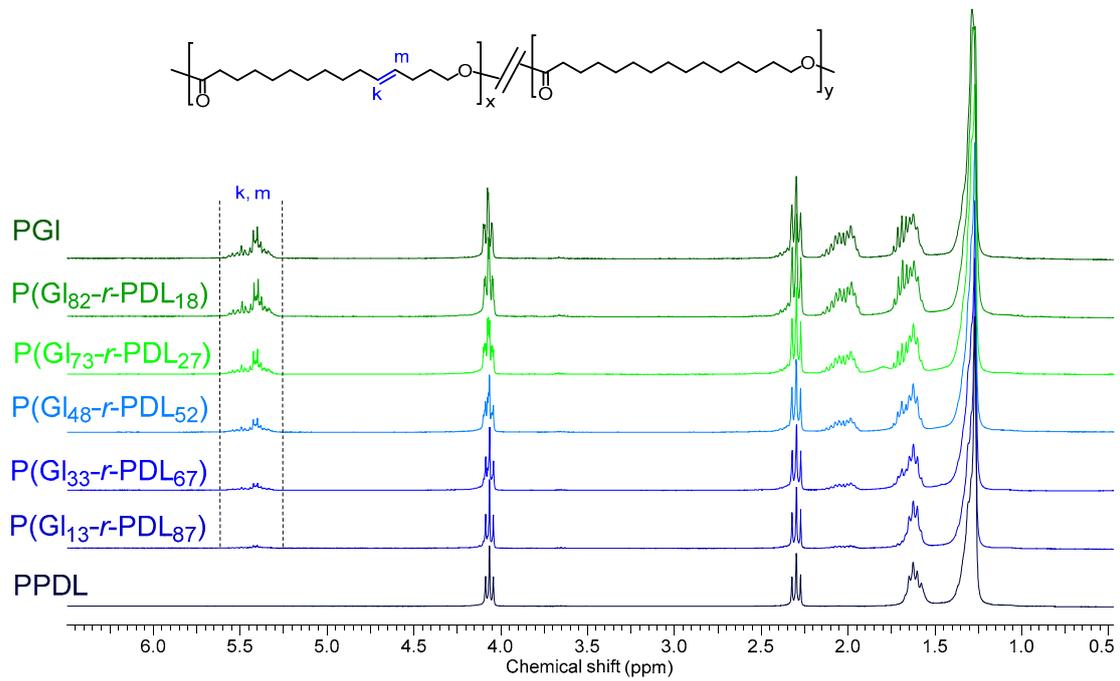
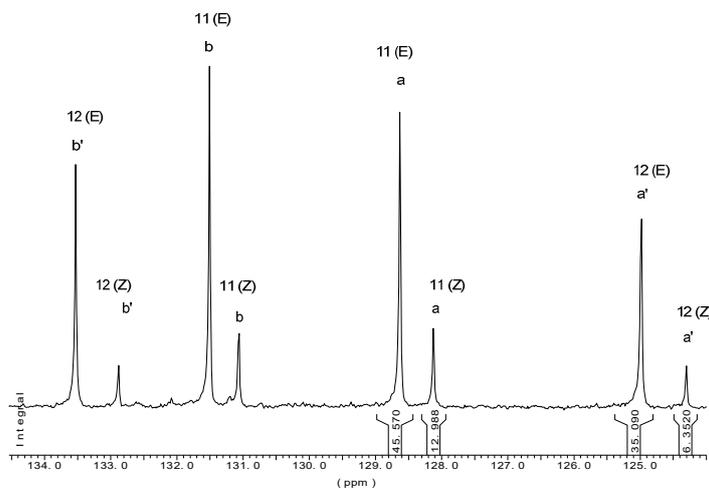
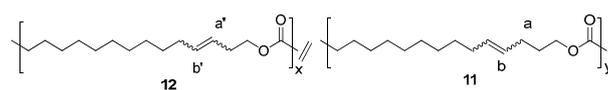
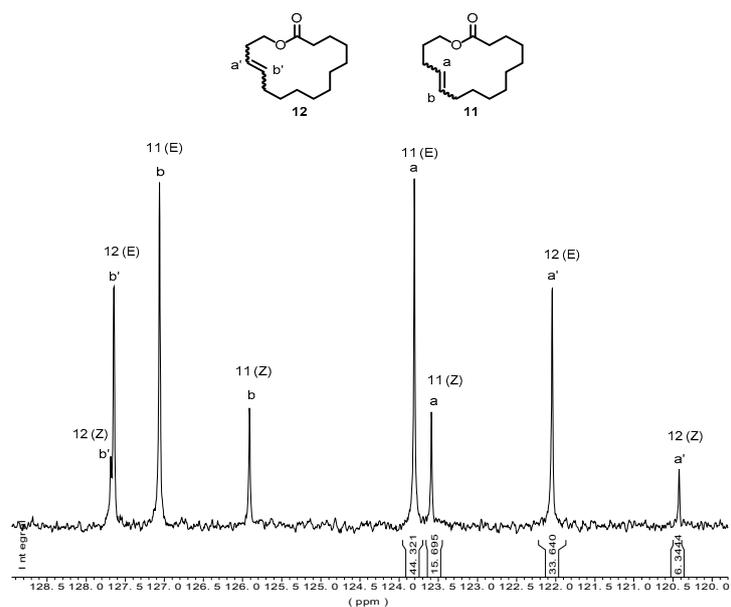


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Figure S2. ¹H NMR (CDCl₃) of the P(Gl_x-r-PDL_y) copolyesters series.



| Sample | % mol-mass isomers | | | |
|--------|----------------------|------|----------------------|-----|
| | oxapentadecen-12-one | | oxapentadecen-13-one | |
| | E | Z | E | Z |
| GI | 44.3 | 15.7 | 33.6 | 6.3 |
| PGI | 45.6 | 13.0 | 35.1 | 6.3 |

Figure S3. ^{13}C NMR (CDCl_3) spectra of GI and PGI highlighting the characteristic peaks of the different isomers used for their quantification.

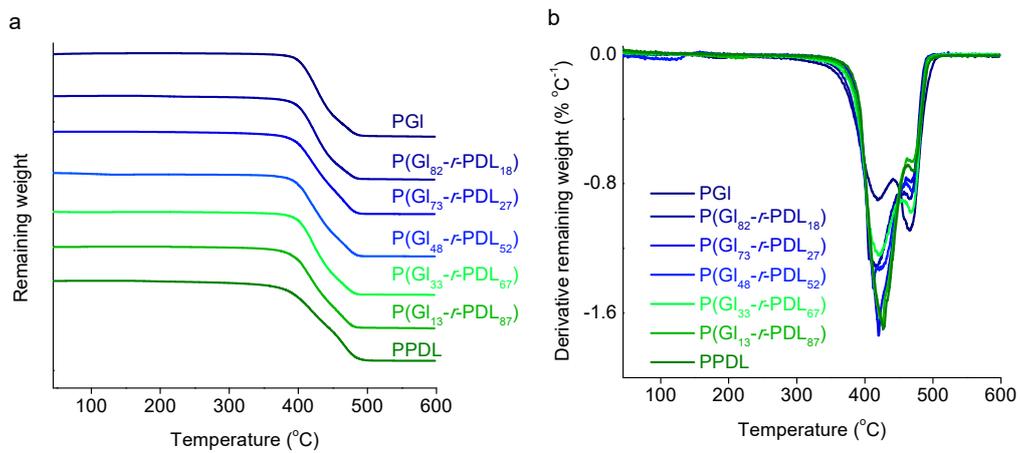


Figure S4. TGA traces (a) and derivative curves (b) of the P(GI_k-r-PDL_y) copolyesters.

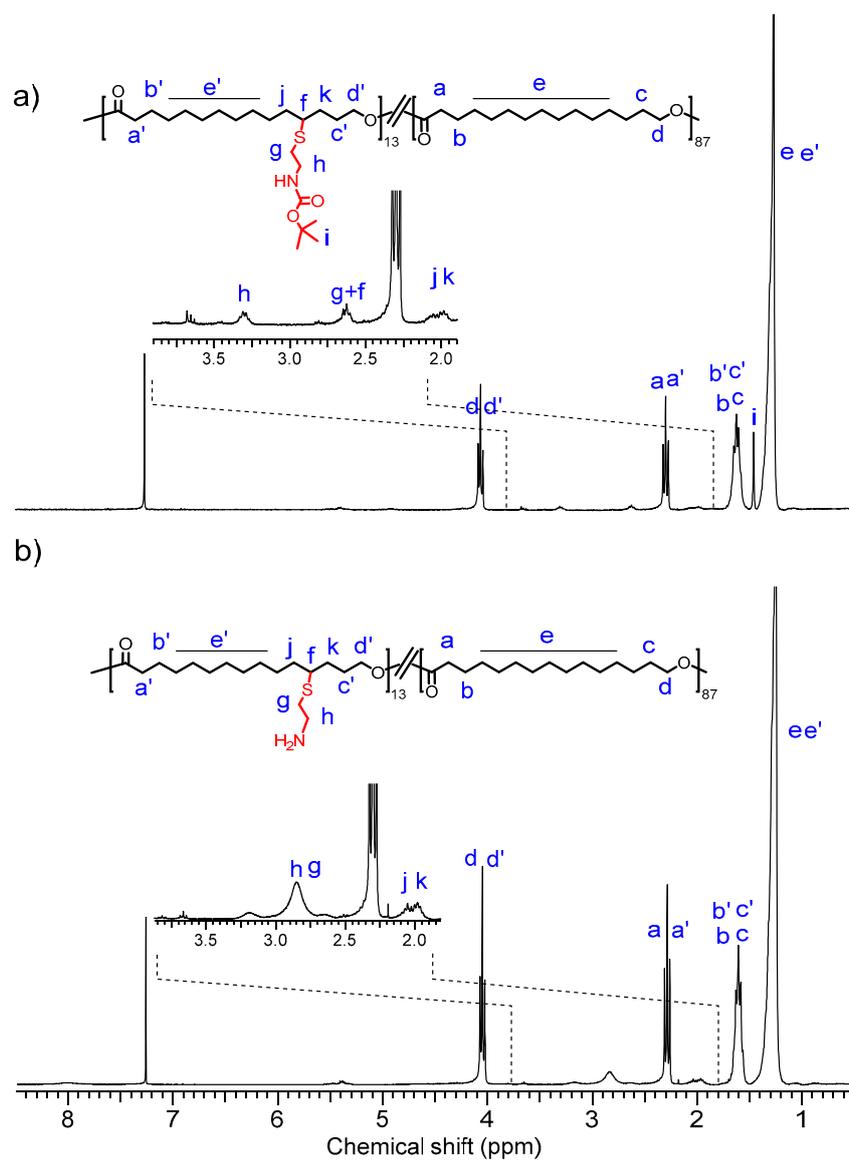


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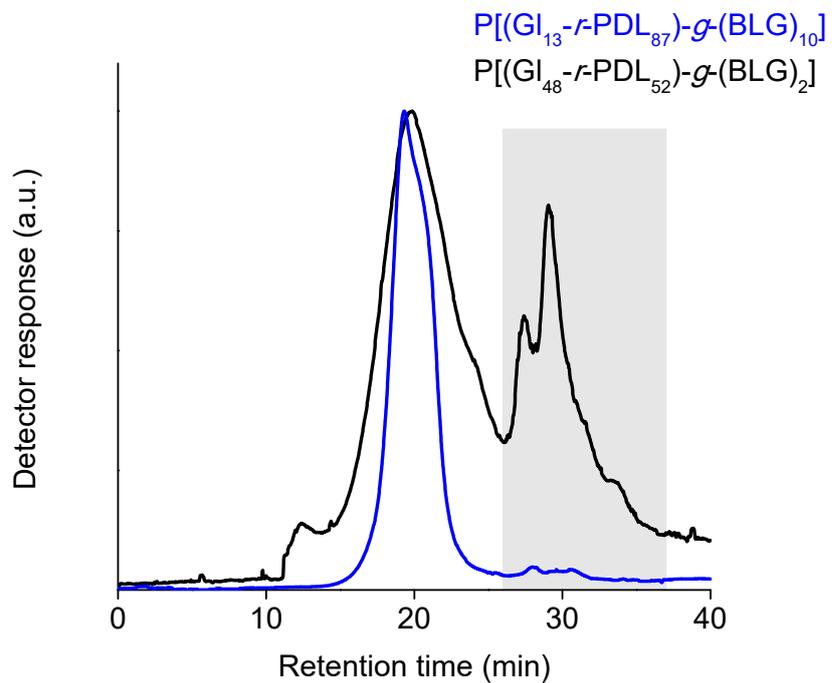


Figure S6. GPC curves of the $P[(GI_x-r-PDL_y)-g-(LGlu)_z]$ copolymers. Peaks observed at elution times longer than 25 min (framed area) are due to the sodium trifluoroacetate salts added to the running solvent.

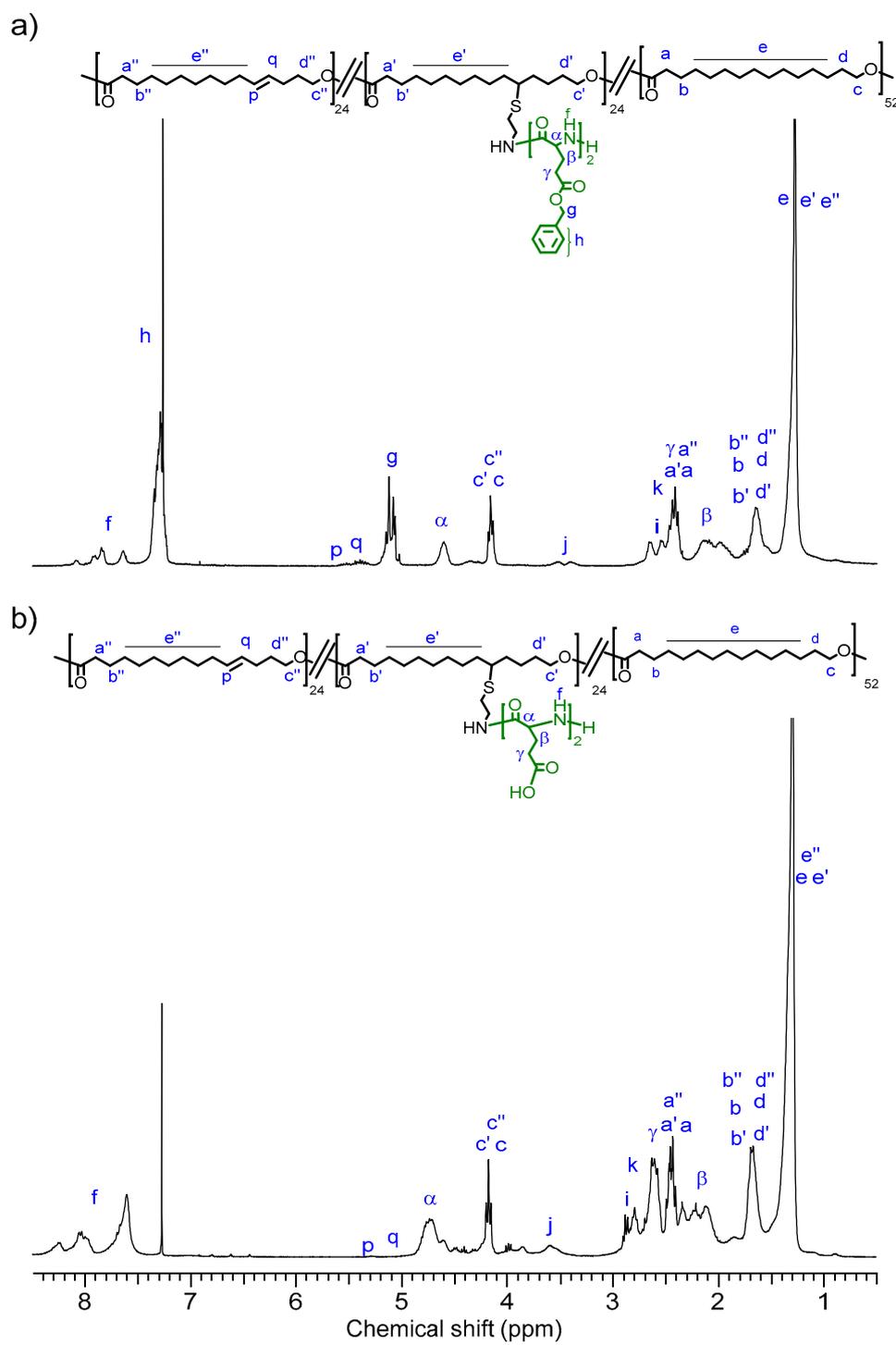


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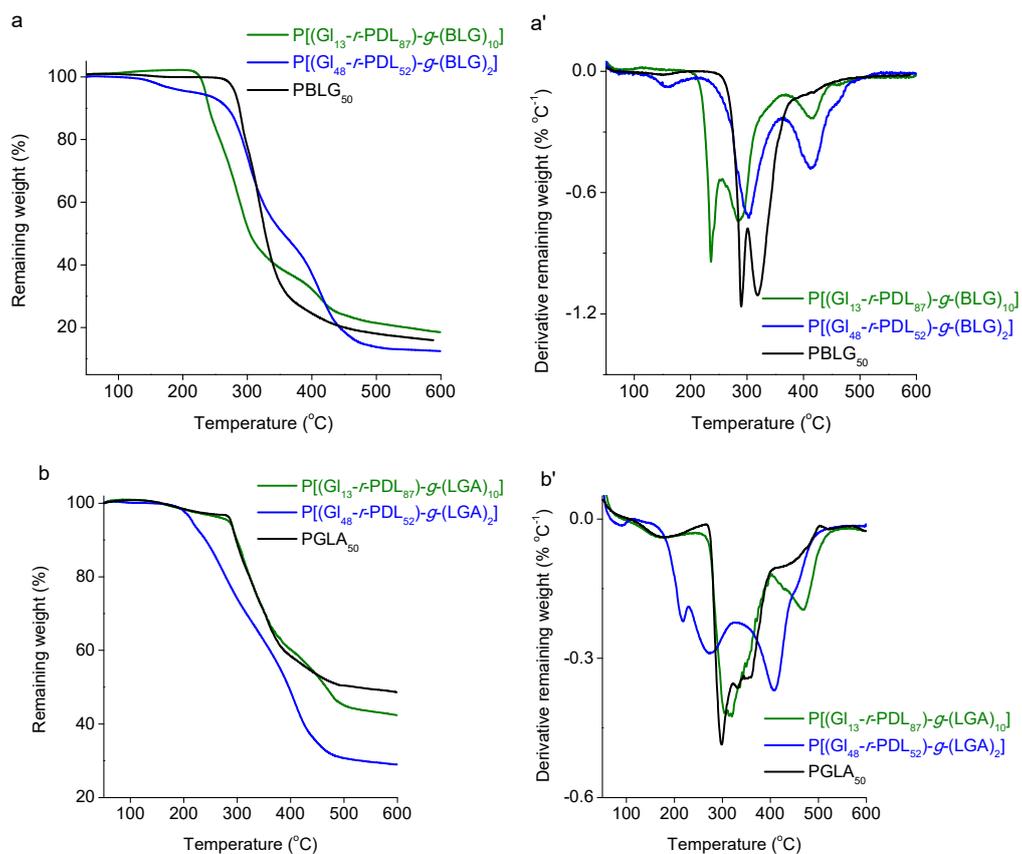


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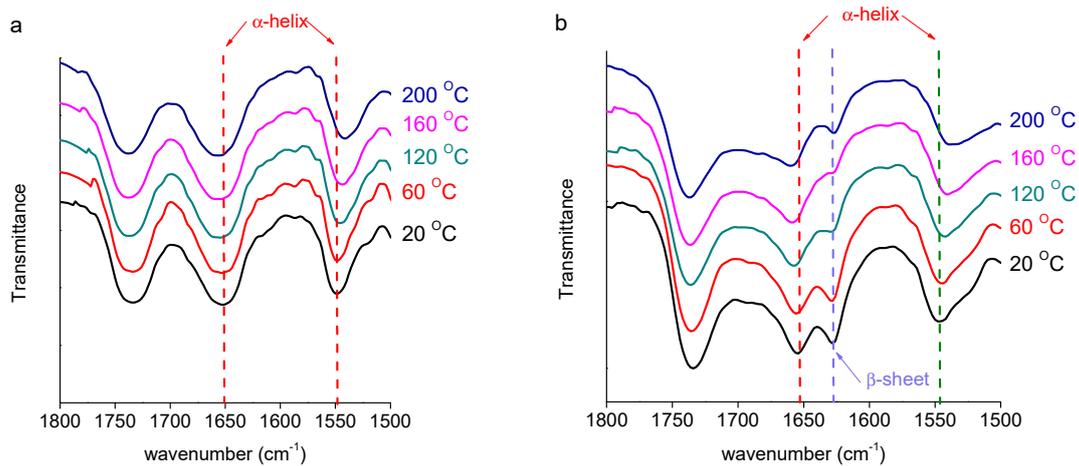


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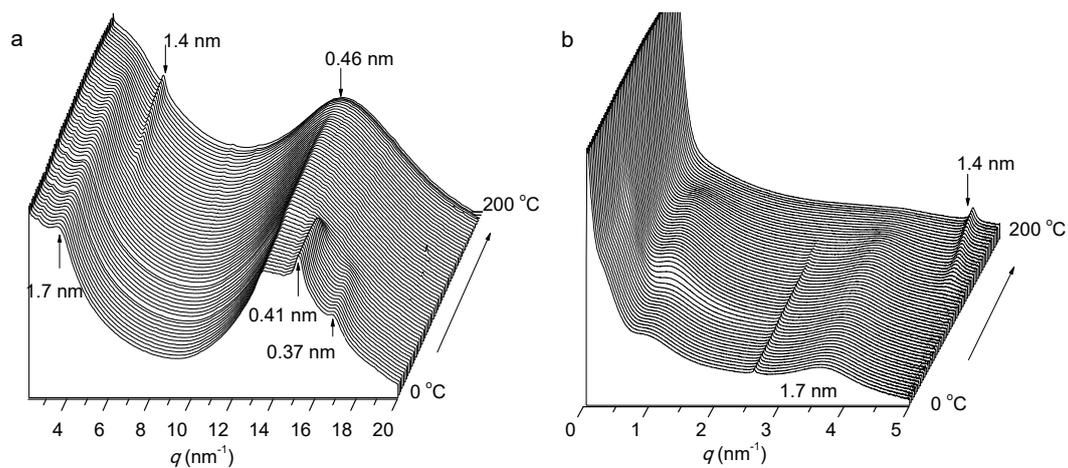


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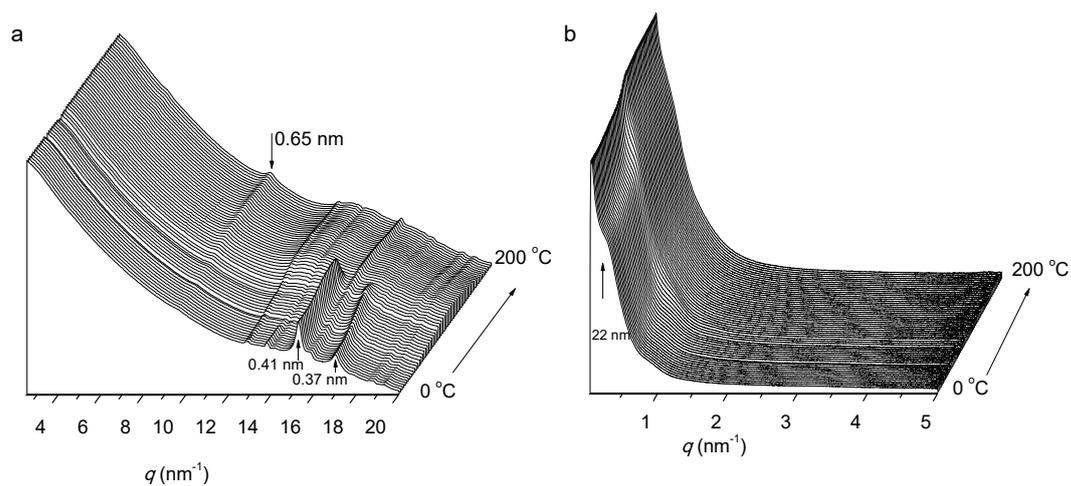


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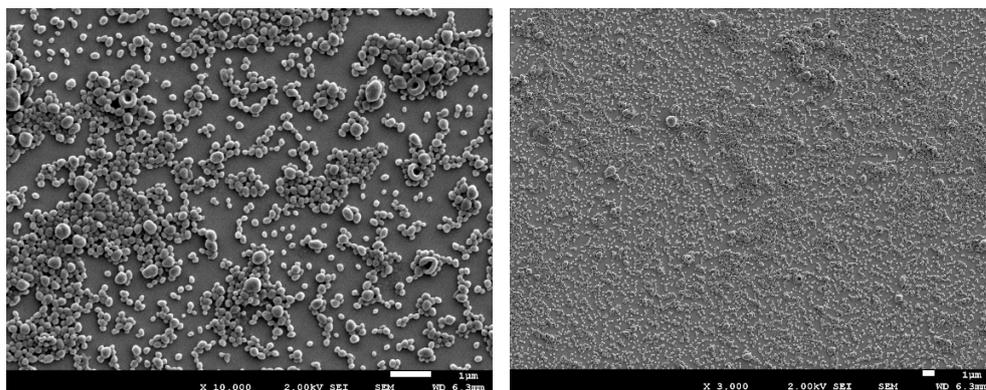


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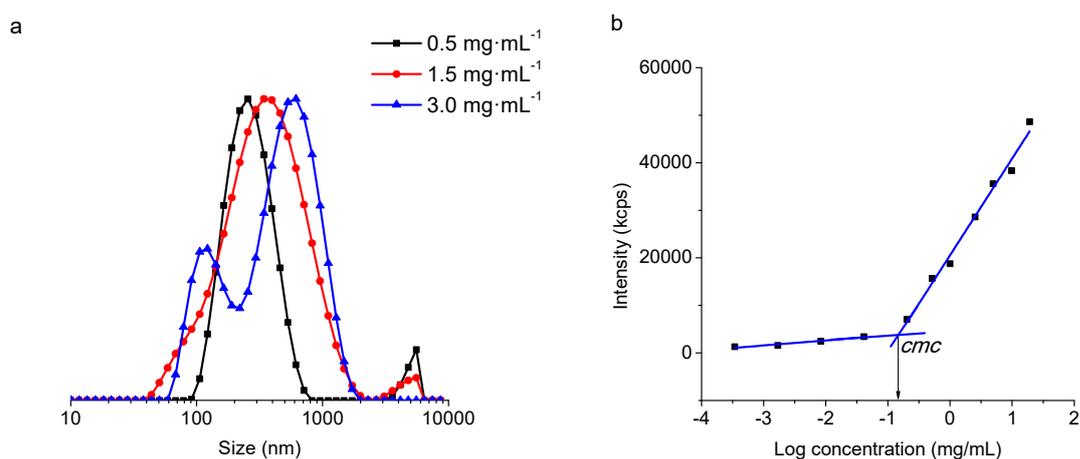


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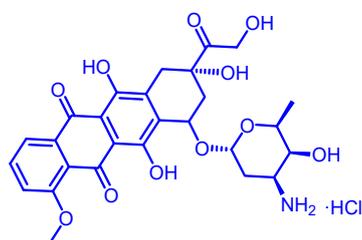


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