Appendix I

Figure 1: $^1$H NMR of ε-carbobenzoxy-$a$-carboxyl-L-lysine anhydride

Figure 2: $^{13}$C NMR of ε-carbobenzoxy-$a$-carboxyl-L-lysine anhydride
Figure 3: $^{13}$C DEPT NMR of $\varepsilon$-carbobenzoxy-$\alpha$-carboxyl-L-lysine anhydride

Figure 4: $^{13}$C NMR of L-benzylglutamate-$\alpha$-carboxyl anhydride
Figure 5: $^{13}$C DEPT NMR of L-benzylglutamate-$\alpha$-carboxyl anhydride

Figure 6: $^1$H NMR of phthalozl-L-glutamic anhydride
Figure 7: $^{13}$C NMR of phthalozl-L-glutamic anhydride

Figure 8: $^{13}$C DEPT NMR of phthalozl-L-glutamic anhydride
Figure 9: $^1$H NMR of phthaoyl-para methoxybenzyl-L-glutamate

Figure 10: $^{13}$C NMR of phthaoyl-para methoxybenzyl-L-glutamate
Figure 11: $^{13}$C DEPT NMR of phthaloxy-para methoxybenzyl-L-glutamate

Figure 12: $^1$H NMR of para-methoxybenzyl-L-glutamate
Appendix I

Figure 13: $^{13}$C NMR of para-methoxybenzyl-L-glutamate

Figure 14: $^{13}$C DEPT NMR of para-methoxybenzyl-L-glutamate
Figure 15: $^1$H NMR of $p$-methoxybenzyl-L-glutamate NCA

Figure 16: $^{13}$C NMR of $p$-methoxybenzyl-L-glutamate NCA
Figure 17: $^{13}$C DEPT NMR of p-methoxybenzyl-L-glutamate NCA

Figure 18: $^1$H NMR of poly-L-glutamic acid after D$_2$O exchange
Figure 19: $^1$H NMR of tricarbobenzoxylated L-arginine

Figure 20: $^{13}$C NMR of tricarbobenzoxylated L-arginine
Figure 21: $^{13}$C DEPT NMR of tricarbobenzyoxylated L-arginine

Figure 22: $^1$H NMR of di-carbobenzoxy-$\alpha$-carboxyl-L-arginine
Figure 23: $^{13}$C NMR of di-carbobenzoxy-$\alpha$-carboxyl-L-arginine

Figure 24: $^{13}$C DEPT NMR of di-carbobenzoxy-$\alpha$-carboxyl-L-arginine
Appendix II

Crude calculation for freezing of the dispersion, when a vial containing it is dipped into liquid nitrogen:

Parameters: Thermal conductivity, \( k = 0.58 \) W/mK; density, \( \rho = 1000 \) kg.m\(^{-3}\); specific heat, \( C_p = 4187 \) J/kgK. \( k/\rho C_p = 1.38524 \times 10^7 \) m\(^2\)s\(^{-1}\)

Assumptions: We assume that the vial wall temperature is 77 K on plunging into liquid nitrogen and that the freezing front propagates from the wall, and calculate the temperature in the dispersion. For a location in the center of the sample, we assume that the heat removal is primarily by conduction and approximate this as a 1D heat transfer problem, with a sample of 4 mm thickness with walls held at 77 K. Under these assumptions, and assuming no phase change, the temperature in a point 2 mm (thickness \( T \)) from the top/bottom of the sample is given by above cartoon. This crude calculation is used to get a rough estimate of the time for the sample to freeze, (viz. for the temperature to get to 273 K).

\[
\tau = \frac{T^2}{k/\rho C_p} \approx 28.87 \text{ s. Temperature} = 77 + (300-77)x10^{-\frac{\text{time}(s)}{\tau}} \text{ K}
\]

Figure 4.1: Time dependent temperature profile at a point in the center of the sample.

For a location within the sample close to the side walls, the assumption of 1D heat transfer is clearly wrong. It is easy to see that for a point in the sample close to the side walls, but distant from the top/bottom, the conductive heat flux is primarily from the side walls. Thus, it is easy to imagine that the macroporous morphology obtained will be rotated through 90°, as observed in Figure S5.

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Figure 1: SEM of silica-PLGA scaffold.

Figure 2: $^1$H NMR of azidopropyl triethoxysilane
Figure 3: $^{13}$C NMR of azidopropyl triethoxysilane

Figure 4: $^{13}$C DEPT NMR of azidopropyl triethoxysilane
Figure 1: 1H NMR of azidopropyl trimethoxy silane