Electronic Supplementary Information

Fourier Transform Infrared spectroscopy (FTIR)

Fourier transform infrared spectra were recorded in the absorbance mode between 600 and 4000 cm^{-1} on a Perkin Elmer spectrometer. The samples were thoroughly dried by centrifugation under vacuum and heating. Several measurements were carried out and compared for reproducibility.

All experiments were carried out at room temperature, and since the complexation between the polymer and the cyclodextrins is a kinetic process, sufficient time was allowed before each measurement to ensure that complexation had taken place.

FTIR was used in addition to SANS and WAXS in order to detect the formation or otherwise of an inclusion complex and identify differences in behaviour between hep2,6-βCD and hep2,3,6-βCD. He-βCD and hp-βCD were not used in this section since their structure is not as well defined and their IR signal not 'neat' enough to be able to monitor possible changes occurring upon complexation.

Samples were made in D_2O and sufficient time was allowed before drying in order to ensure full H-D exchange of the OH group of hep2,6-βCD. This exchange was made in order to clearly identify the band corresponding to the C-O-D stretching mode. Monitoring any changes in this specific region of the molecule is highly important as it is believed to be key to the complexation mechanism with F127. The comparative spectra in D_2O and H_2O, reproduced in **Fig. 1**, show the presence of an extra peak for the cyclodextrin dissolved in D_2O as expected. The FTIR spectra of hep2,3,6-βCD, both in D_2O and H_2O, are obviously identical (not shown here).

Fig. 2a and b show the FTIR spectra of solutions of 5 wt% hep2,6-βCD and hep2,3,6-βCD, respectively, with increasing amounts of F127 (1 to 9 wt%). With 1 wt% F127, the PO/ βCD ratio is ca 1.4, i.e. above the ratio for full complexation and the IR spectrum corresponds quite closely to that obtained from pure cyclodextrin (both for hep2,6-βCD and hep2,3,6-βCD). Upon addition of increasing amounts of polymer, the signal shifts slightly to show the characteristic bands of F127. For instance, the hep2,6-βCD band at 965 cm^{-1}, visible in the sample with 1 wt% polymer, gradually shifts to 960 cm^{-1} (characteristic peak of F127). This is also particularly clear in the 1200-1500 cm^{-1} region (inset of **Fig. 2a**): with increasing amounts of polymer in the mixture, characteristic bands at 1241, 1279, 1342 cm^{-1}, absent from the

βCD signal, become stronger. The behaviour observed is very similar for both βCD derivatives. Overall, when gradually adding polymer to βCD, the IR spectra change smoothly from showing characteristic bands of βCD to revealing bands characteristic of the polymer. FTIR does not enable us to establish a clear difference between the complexing behaviour of hep2,6-βCD and hep2,3,6-βCD with Pluronics, despite the very different effect they had on the Pluronic micelles. Although FTIR measurements have been used by other groups to confirm the formation of host-guest interactions between α-cyclodextrin and PEO [1-3], our measurements do show major shifts in the spectra that could point to a different type of interaction between the two βCD derivatives. The data suggest that some form of interaction takes place between the Pluronic and all βCDs, but this interaction cannot be quantified.

References

[1] Rusa, C. C.; Fox, J.; Tonelli, A. E., *Macromolecules*, 2003, **36**, 2742-2747

[2] Rusa, C. C.; Luca, C.; Tonelli, A. E., *Macromolecules*, 2001, **33**, 1318-1322

[3] Rusa, C. C. & Tonelli, A. E., *Macromolecules*, 2000, **33**, 1813-1818

Figures

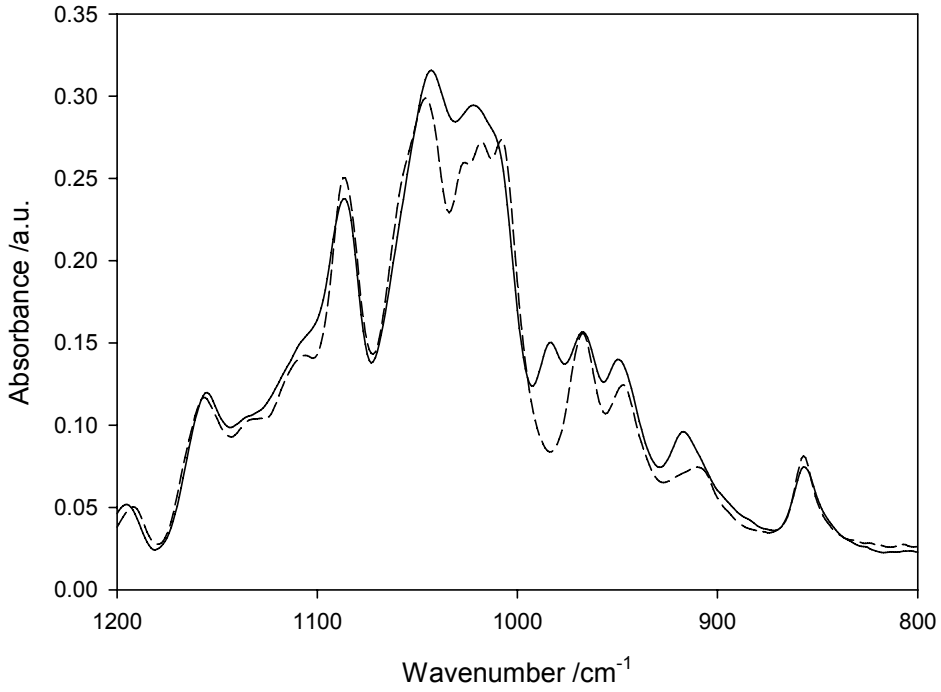

Fig. 1. Compared FTIR spectra of hep2,6-βCD in D_2O (full line) and H_2O (dashed line).

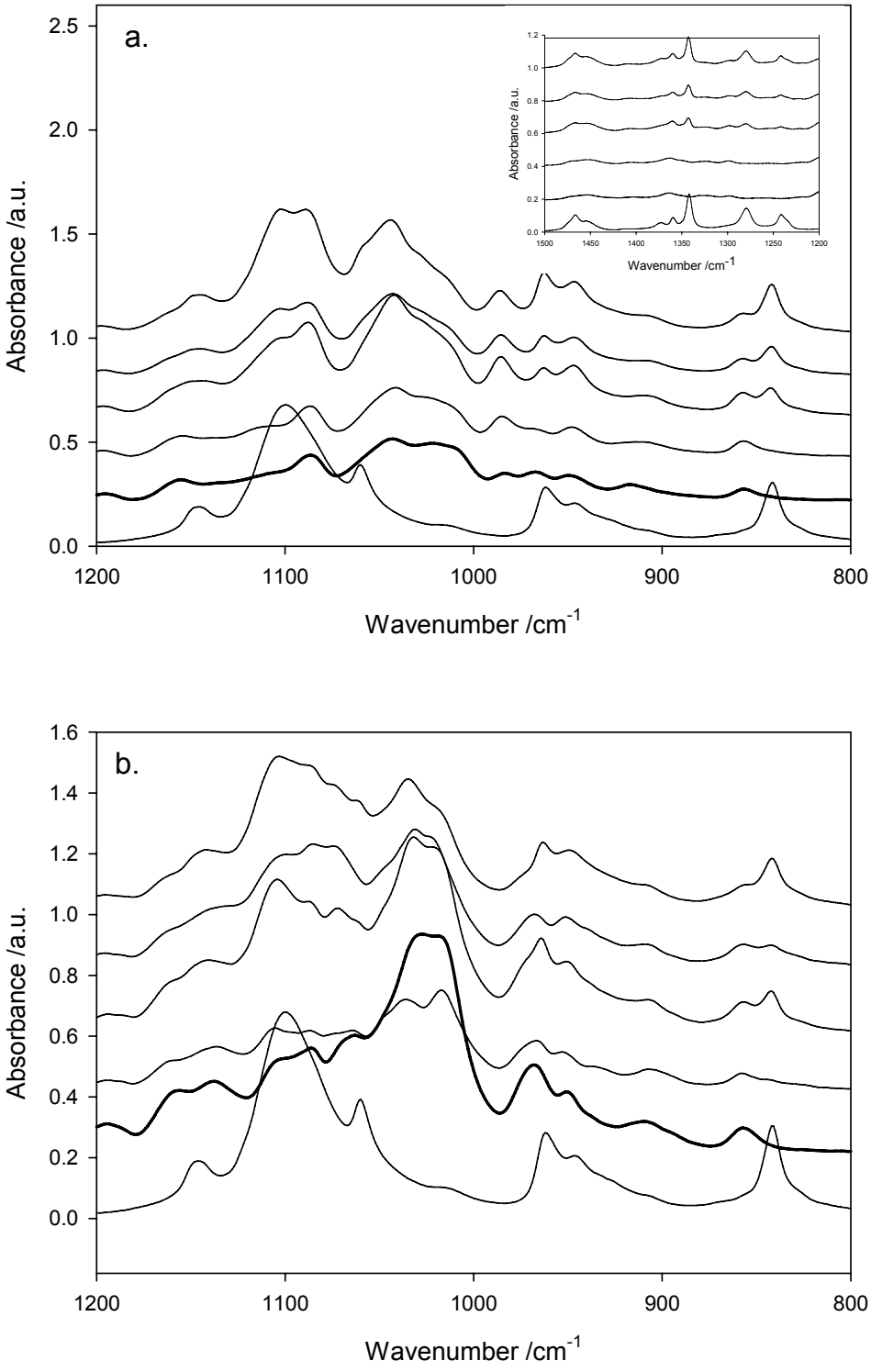

Fig. 2 a) FTIR spectra of solutions of F127 (bottom) and hep2,6-βCD (thick line) with increasing concentrations of F127, corresponding to PO/βCD ratios of: 1.4 (), 4.1 (), 6.9 (), 9.6 () and 12.4 (). Each curve has been shifted by 0.2 with respect to the previous. Inset: close up on the 1200 to 1500 cm^{-1} region. b) FTIR spectra of F127 (bottom) and hep2,3,6-βCD (thick line) with increasing concentrations of F127, corresponding to PO/ βCD ratios of: 1.5, 4.4, 7.4, 10.3 and 13.3 (all curves shifted).

Wide Angle X-ray Scattering (WAXS)

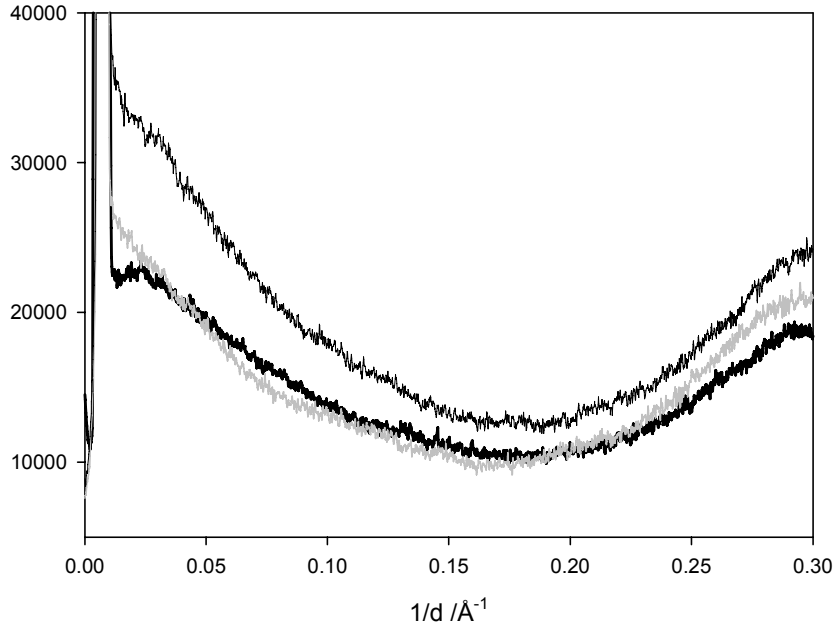

Fig. 3. WAXS signal from solutions of F127 (thick black line), hep2,6-βCD (grey line) and hep2,3,6-βCD (thin black line).