Porphyrin Cored Hyperbranched Polymers

1.0 Determining the extent and distribution of the porphyrin core.

To assess the porphyrins distribution across the polymer's molecular weight range (i.e. to determine if the porphyrins are concentrated at the high/low molecular weight ends or are evenly distributed), the bulk polymer was fractionated using preparative GPC (see section 1.2). After fractionation the level of core incorporation was assessed for each fraction using the methods described within the paper; the results from this analysis are shown in Table 1. A similar level of incorporation to that obtained from the bulk polymer was observed for **all** fractions (59% +/- 3%). These results clearly indicate that the porphyrin core is evenly distributed across the complete molecular weight distribution of the hyperbranched polymer. More information regarding the level of core incorporation was obtained from the electrospray mass spectra of the most narrowly dispersed sample. This showed a Gaussian shaped series of peaks all separated by 178D (the repeat unit). Further analysis revealed that each peak corresponded to an individual polymer molecule possessing a single porphyrin core plus *n*-monomer units, Figure 1. Peaks corresponding to polymeric products without porphyrin core were *not* detected. This tells us that for this fraction the level of core incorporation was very high (i.e. approaching 100%). Taking the information provided from this sample, alongside the fractionation and distribution results described above and in the paper, we can conclude that almost every polymer molecule contains a porphyrin core (i.e. a level of incorporation approaching 100%). For more information regarding core incorporation see: (a) J. Alston, Y. Ge, P. J. Gittins, L. J. Twyman, *Macromolecules*, 2004, *37*. 7428. (b) P. J. Gittins, L. J. Twyman, *J. Am. Chem. Soc.* 2005, *127*, 1646.

Table 1: Bulk and core M_n values for fractions of the HBP

M_n Bulk (GPC)	M_n Core (UV)	M_n Ratio (Bulk : Core)
3500	6000	0.58
5500	9300	0.59
12500	20000	0.62
24500	43500	0.56

1.1 Fractionation using preparative GPC.

Fractionation was carried out using columns packed Biobead SX-1 beads (Biorad). These were swelled overnight in THF, and then loaded onto a standard glass chromatography column (approx. 3cm diameter by 20cm long), with a small amount of sand used to stop the beads from floating. The solvent was then changed to dichloromethane by flushing the column under gravity. 500mg of the (free base) porphyrin cored polymer was then loaded onto the column using the minimum amount of CH_2Cl_2 and with the solvent flow controlled by gravity. 1ml fractions were collected, monitored using analytical GPC, and combined accordingly.

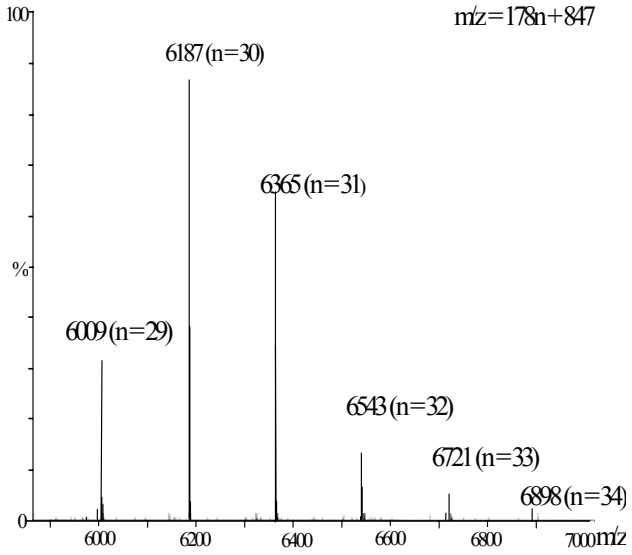

Figure 1: The ESMS of a fraction sample of the HBP **3**.