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Synthesis of Porphyrin Cored Hyperbranched Polymers

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Reversible transesterification has been used to synthesize a porphyrin cored hyperbranched polymer. Fractionation, followed by UV and mass spectroscopic analysis, revealed that the porphyrin cored had been incorporated across the complete molecular weight range of the polymer and with a high degree of incorporation (approaching 100%). These fractionated samples therefore represent simple/crude analogues of porphyrin cored dendrimers.

Keywords: Hyperbranched polymers; Core; Dendritic; Porphyrin

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INTRODUCTION

Recent attempts to mimic the function of porphyrin containing biological molecules embed active porphyrin units within the globular structure of a perfectly branched dendrimer [1,2]. These systems perfectly mimic both the shape/size and functionality of various porphyrin containing proteins, and currently represent the "state of the art" with respect to biomimetic design [3,4]. Despite their success and potential, the synthesis of core functionalized dendrimers is expensive, time consuming and arguably limited to small scale laboratory samples. In an effort to overcome these problems, simpler, less perfect macromolecules known as hyperbranched polymers (HBPs) were developed [5,6]. Despite high poly-dispersities and structural imperfections, HBPs retain almost identical physical properties to their perfectly branched mono-dispersed dendrimer counterparts. Nevertheless, hyperbranched polymers do differ from dendrimers in one important respect. Although it is relatively easy to incorporate an exotic or functional core within each and every dendrimer molecule, it remains a significant challenge to incorporate a functional/exotic core across the complete molecular weight range of a hyperbranched polymer (particularly with a high level of integration) [7]. An even distribution of a functional core across the full molecular weight range is an essential requirement for many applications where it is imperative to know the effect of molecular weight on a particular core property. In this paper we describe the first synthesis of an exotically cored hyperbranched polymer. Specifically, we describe the synthesis of a porphyrin cored hyperbranched polymer whose core unit has been evenly incorporated across all molecular weights, with an almost 100% level of incorporation.

RESULTS AND DISCUSSION

Based on our previous work, we proposed that a suitably functionalized porphyrin core could be incorporated across the complete molecular weight range of a hyperbranched polymer if reversible/equilibrium chemistry was applied [8,9]. The synthetic procedure is shown in Scheme 1 and is based on a method previously described by Voit *et al*. [10] Specifically, the synthesis involves the reversible transesterification polymerization of an excess of the branching monomer 3–5 diacetoxybenzoic acid **1**, in the presence of the tetra-acetate porphyrin core unit **2** (7.0 mole %). GPC analysis of the product **3** in THF gave an Mn of 5100 Da (relative to linear polystyrene standards) and a polydispersity of 2.11. The degree of branching was calculated from ^{1}H NMR to be 49% [10]. ^{1}H NMR spectroscopy further confirmed the porphyrins incorporation, showing a distinct (new) resonance from the porphyrins aromatic protons at 8.22 ppm. When the same NMR sample was "doped" with

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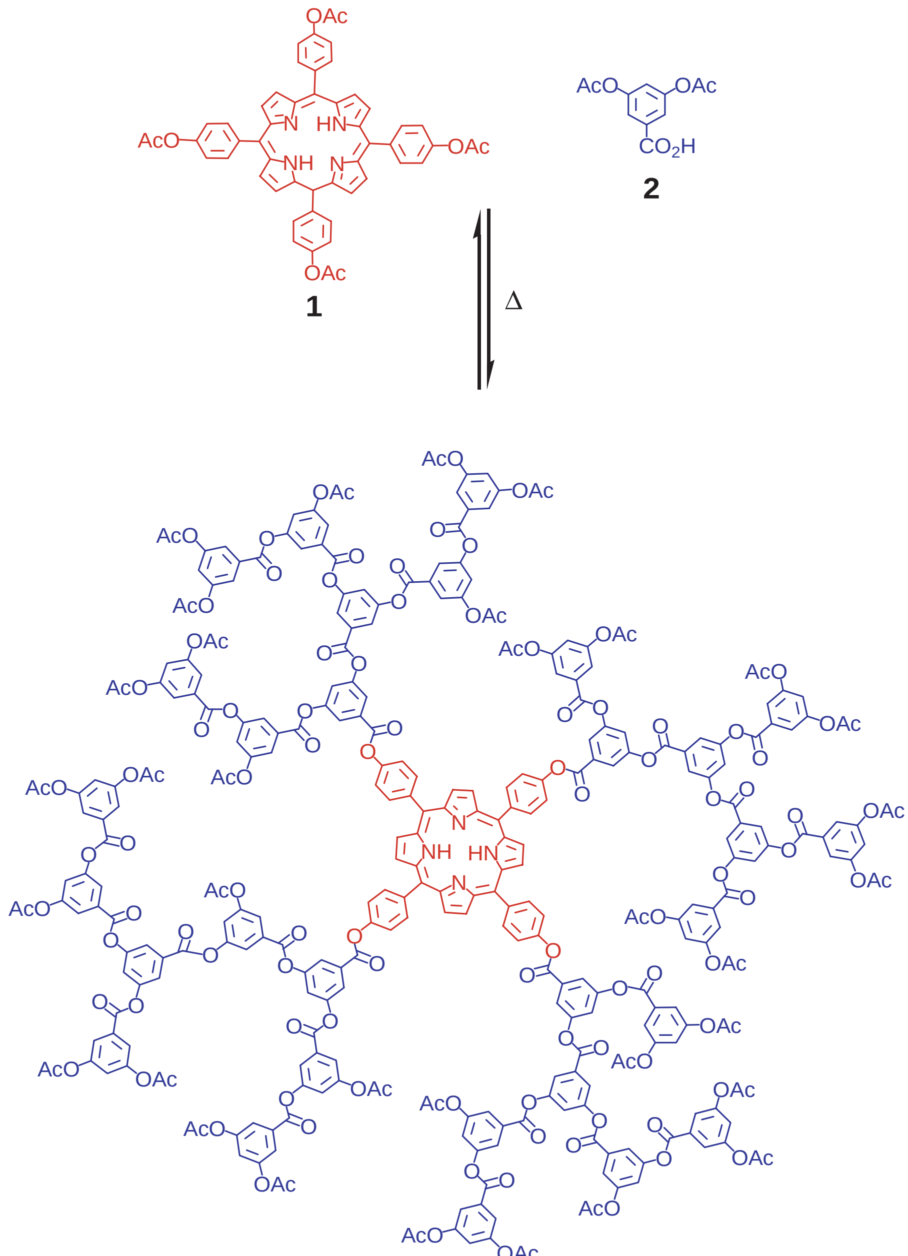

SCHEME 1 Synthesis and idealized representation of a porphyrin cored HBP.

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the tetra-acetate porphyrin core unit **2**, an additional peak could be seen at a slightly lower chemical shift (8.20 ppm), confirming covalent attachment of the porphyrin core within the hyperbranched polymer. Control over molecular weight could be achieved by varying the amount of porphyrin core added to the reaction mix (i.e. when less or more porphyrin was used higher or lower molecular weight polymers were obtained respectively). When the same polymerization was carried out in the absence of any core, an Mn value of 150,000 Da and a polydispersity greater than 6.0 was obtained. These experiments clearly show that the porphyrin core (and the reversible conditions adopted), are having an effect on the polymerization and helping to control the molecular weight and polydispersity.

The extent of core incorporation can be assessed by comparing the Mn values obtained from a bulk property (GPC) with those calculated using an independent property (only) associated with the core unit [8,9]. Quantitatively comparing the porphyrins *p*-substituted phenyl doublet at 8.22 ppm with the polymers terminal acetoxy peak at 2.21 ppm (from the polymer's ^{1}H NMR spectrum), enabled us to calculate an Mn value of 8150 Da. A similar value of Mn was obtained from UV (i.e. molecular weight determined from the *porphyrin* concentration of a known *mass* of polymer). Although at first the discrepancy between the core (NMR/UV) and bulk (GPC) values for Mn suggested that the level of incorporation was less than 100% (~60%), it should be noted that GPC calibrated against linear polystyrene is well known to underestimate the molecular weights of dendritic molecules [11]. Taking these deviations into account, we can be sure that the level of core incorporation is much higher than the 60% indicated from these two Mn ratios. Although these results tell us that porphyrin cored hyperbranched polymers have been synthesized, it is possible that the porphyrin cores are concentrated in one particular molecular weight fraction (i.e. the low or high molecular weight fractions). If this were the case, any assessment of core property related to polymer size would be speculative and difficult. The bulk polymer was therefore fractionated (using preparative GPC) [12] and the level of core incorporation assessed for each fraction using the methods described above. Four fractions were collected and their Mn values determined using UV (core) and bulk (GPC) methods; the results from this analysis are shown in Table I. When comparing the ratio of Mn for each of the fractionated samples (from bulk and core), a similar level of incorporation to that obtained from the bulk polymer was observed (60 ± 3%). These results clearly indicate that the porphyrin core is evenly distributed across the complete molecular weight distribution of the hyperbranched polymer. Furthermore, when considering the errors involved in estimating molecular weights from GPC calibrated with linear standards, we can conclude that the porphyrin cores have been incorporated across all molecular weights, with a level of incorporation higher than the 60% indicated from chromatography and spectroscopy.

As with our previously reported work [8], more information regarding the level of core incorporation can be obtained using electrospray mass spectrometry. For the bulk polymer, a series of peaks with decreasing intensity were observed (as is typical for a polydisperse system). Analysis of the spectra revealed that each peak was separated by a single monomer unit (178 Da). The mass spectra of the most narrowly dispersed fractionated samples [13] showed a Gaussian shaped series of peaks all separated by 178 D (the average monomer unit).

TABLE I Bulk and core Mn values for fractions of the HBP.

Mn Bulk (GPC)	Mn Core (UV)	Mn Ratio (Bulk:Core)
3150	5050	0.62
5500	9850	0.57
11,200	18,250	0.61
15,050	26,500	0.57

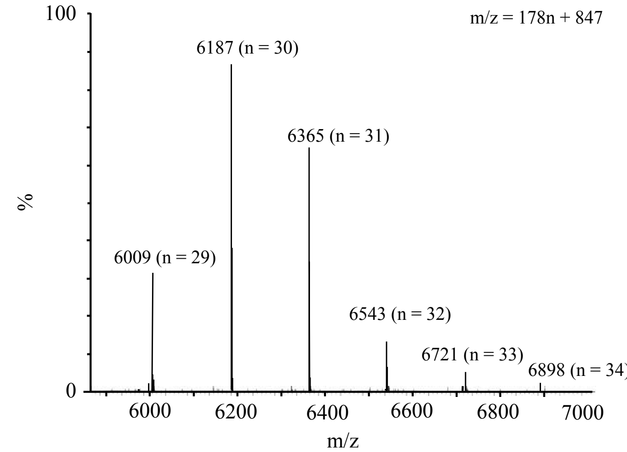

FIGURE 1 The ESMS of a fraction sample of the HBP 3.

Further analysis revealed that each peak corresponded to an individual polymer molecule possessing a single porphyrin core plus *n*-monomer units, Fig. 1. Peaks corresponding to polymeric products without porphyrin core were *not* detected. This tells us that the level of core incorporation is very high for these fractions. When considering this information alongside the fractionation results described above (which showed that the porphyrin core was incorporated evenly across the complete molecular weight range), we can conclude that each and every polymer molecule possess a porphyrin core (i.e. a level of core incorporation approaching 100% has been achieved for the bulk polymer). Therefore, we have achieved our desired aim of incorporating core units evenly throughout the polymeric mix, which in turn allows us to study various properties with respect to the polymers molecular weight, in effect allowing us to treat the various (narrowly dispersed) fractions as pseudo dendrimers.

CONCLUSIONS

When considering all of the spectral and fractionation data together, we can conclude that porphyrin cores have been incorporated evenly, and with a very high level of integration, across the complete molecular weight range of the HBP. These polymers, along with their fractionated samples, can be considered as "pseudo" dendrimers and any effects relative to molecular weight (size) can be measured with a relatively high degree of confidence. Overall the methodology described is generic and should allow for a variety of functional cores to be incorporated within these and similar ester based hyperbranched polymers. Work is progressing in our laboratory to establish whether or not these simple porphyrin containing polymers have the same core

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isolation and surface properties of their (much more complicated) dendrimer analogues.

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References

[1] Dandliker, P. J.; Diederich, F.; Zingg, A.; Gisselbrecht, J. P.; Gross, M.; Louati, A.; Sanford, E. *Helv. Chim. Acta.* **1997**, *80*, 1773.
[2] Weyermann, P.; Diederich, F. *J. Chem. Soc., Perkin Trans. 1*. **2000**, *24*, 4231.
[3] Weyermann, P.; Gisselbrecht, J. P.; Boudon, C.; Diederich, F.; Gross, M. *Angew. Chem.* **1999**, *111*, 3400 (Angew. Chem., Int. Ed. **1999**, *38*, 3215).
[4] Collman, J. P.; Fu, L.; Zingg, A.; Diederich, F. *Chem. Commun.* **1997**, *2*, 193.
[5] Newlome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Synthesis and Applications*; VCH: Weinheim, 2001; pp 331–381.
[6] Yates, C. R.; Hayes, W. *Eur. Polym. J.* **2004**, *40*(7), 1257.
[7] Hecht, S.; Vladimirov, N.; Fréchet, J. M. J. *J. Chem. Soc.* **2001**, *123*, 18.
[8] Gittins, P. J.; Alston, J.; Ge, Y.; Twyman, L. J. *Macromolecules* **2004**, *27*(6), 1611.
[9] Gittins, P. J.; Twyman, L. J. *J. Am. Chem. Soc.* **2005**, *127*(6), 1646.
[10] Turner, S. R.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1993**, *26*, 4617.
[11] Twyman, L. J.; Beezer, A. E.; Mitchel, J. C. As GPC often underestimates the molecular weights of globular polymers it is not necessary for (or expected that) the molecular weights obtained from these two methods to be identical (i.e. core analysis and GPC)*Chem. Soc. Perkin 1*. **1994**, *4*, 407, and references therein.
[12] Preparative GPC was carried out using a glass column packed with Bio-Beads S-X1 beads (Bio-Rad Laboratories). The beads were pre-swollen overnight with THF and the slurry packed into a column (20 mm diameter, 600 mm column height/300 mm packed height). The THF was exchanged for eluent by passing 10 column lengths of CH2Cl2 through the column, 500 mg of crude polymer was then added to the column bed and the column eluted under gravity.
[13] Good mass spectra for the larger fractions were more difficult to obtain and the ESMS spectra recorded were similar to the original bulk polymer. That is, a series of peaks of decreasing intensity each separated by a single monomer unit (178 Da). However, because the fractionation and UV experiments had previously shown that the core was evenly distributed across *all* fractions, a good mass spectrum from just one fraction, is all that's required to determine the overall level of incorporation

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