Total Core Functionalization of a Hyperbranched Polymer

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Introduction. In recent years the synthesis of tailored hyperbranched polymers (HBP) has generated increasing interest,[1] and such molecules are often put forward as realistic alternatives to dendrimers for the production of performance materials. Although peripheral functionalization has received the most attention,[2] a significant body of research concerns the use of core molecules. Core molecules have been demonstrated to affect a degree of control over molecular weight, polydispersity, and in some cases average degree of branching.[3] One particular characteristic of dendrimers difficult to replicate with hyperbranched polymers is the inclusion of a specific core molecule in each and *every* polymer molecule. This is vital for applications such as catalysis, where it is imperative to know the effect that the molecular weight has on the rate and selectivity of a particular catalyst.[6] One-pot methods have consistently shown to be unproductive in this regard.[4] Stepwise or slow monomer addition to a core molecule is the only previously reported methodology for the production of hyperbranched polymers with a high core loading.[5] If hyperbranched polymers are to compete with dendrimers in applications requiring core isolation, it is important that methods ensuring the complete incorporation of core molecules across all molecular weights are developed. In a conventional one-pot hyperbranched polymer synthesis an even distribution of core molecule cannot be guaranteed when kinetic influences dominate. Unless reactivity ratios are finely balanced, the distribution of core molecule will be biased toward inclusion in the high or low molecular weight portion of the polymer. In contrast, a reversible reaction (dominated by thermodynamics) will result in a statistical distribution of core units, providing the reaction conditions are such that equilibrium lies in favor of the products. We therefore decided to investigate a polyestherification ($K \sim 1.0$) with a view to controlling the extent and distribution of core incorporation within a hyperbranched polymer. This communication describes the first specific example of a core molecule being *fully* incorporated into a hyperbranched polymer using a one-pot synthesis. As such, this methodology represents a proof of principle which can be exploited toward a number of specific applications requiring total core incorporation.

Results and Discussion. We chose the polycondensation of 3,5-diacetoxybenzoic acid as a model system (Scheme 1). This reaction proceeds via a reversible transesterification mechanism, and the equilibrium can be shifted to produce higher molecular weight polymers by removal of the acetic acid byproduct. On choosing the core molecule, it was postulated that the activated ester *p*-nitrophenyl acetate would be biased toward inclusion, while maintaining the required reversibility. *p*-Nitrophenyl acetate can also be monitored with relative ease using ^{1}H NMR spectrometry and UV spectrophotometry. First, the β aromatic protons of the *p*-nitrophenyl acetate resonate at around 8.3 ppm, corresponding to a "window" in the NMR spectrum of the polymer. Second, upon hydrolysis of a polymer containing a *p*-nitrophenyl ester, *p*-nitrophenolate is liberated, producing an intense absorption at 420 nm (in aqueous NaOH). This provides two independent methods for monitoring the incorporation of the core unit, which in turn can be used to quantifiy the extent and distribution of core molecule.

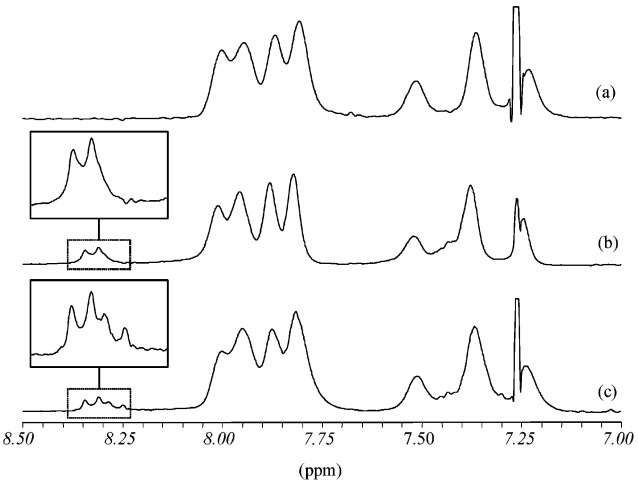

Figure 1. Spectra for the polymer without core (a), polymer with core (b), and polymer with core doped with free *p*-nitrophenyl acetate (c).

The polymer synthesis was adapted from a procedure previously published by Turner et al.[7] The monomer/core mixture (5:1 mole ratio) was heated with an equal mass of diphenyl ether at 225 °C for 45 min in a nitrogen atmosphere. The temperature was then lowered to 180 °C, and acetic acid was removed under vacuum for 2 h. The resulting polymer was precipitated from THF into methanol and washed repeatedly to remove all traces of "free" unreacted *p*-nitrophenyl acetate. The ^{1}H NMR spectrum confirmed this showing a distinct resonance attributed to the *p*-nitrophenyl ester aromatic β protons at 8.32 ppm. To distinguish this peak from free or encapsulated *p*-nitrophenyl acetate, the same NMR sample was doped with *p*-nitrophenyl acetate. An additional (new) peak, corresponding to free *p*-nitrophenyl acetate, could now be seen at a slightly lower chemical shift (8.27 ppm), therefore confirming the physical incorporation of core within the hyperbranched polymer (Figure 1). GPC analysis calibrated against polystyrene standards gave an M_n value of 4100 Da and a polydispersity of 1.92 in THF. The core molecule is seen to be limiting the molecular weight and polydispersity, with polymers of similar molecular weights being achieved consistently over a number of reactions irrespective of reaction time. This confirms the involvement of the core molecule in the polymerization. (Polymerizations conducted in the absence of core molecule were of high molecular weight, ~150 000, and high polydispersity,

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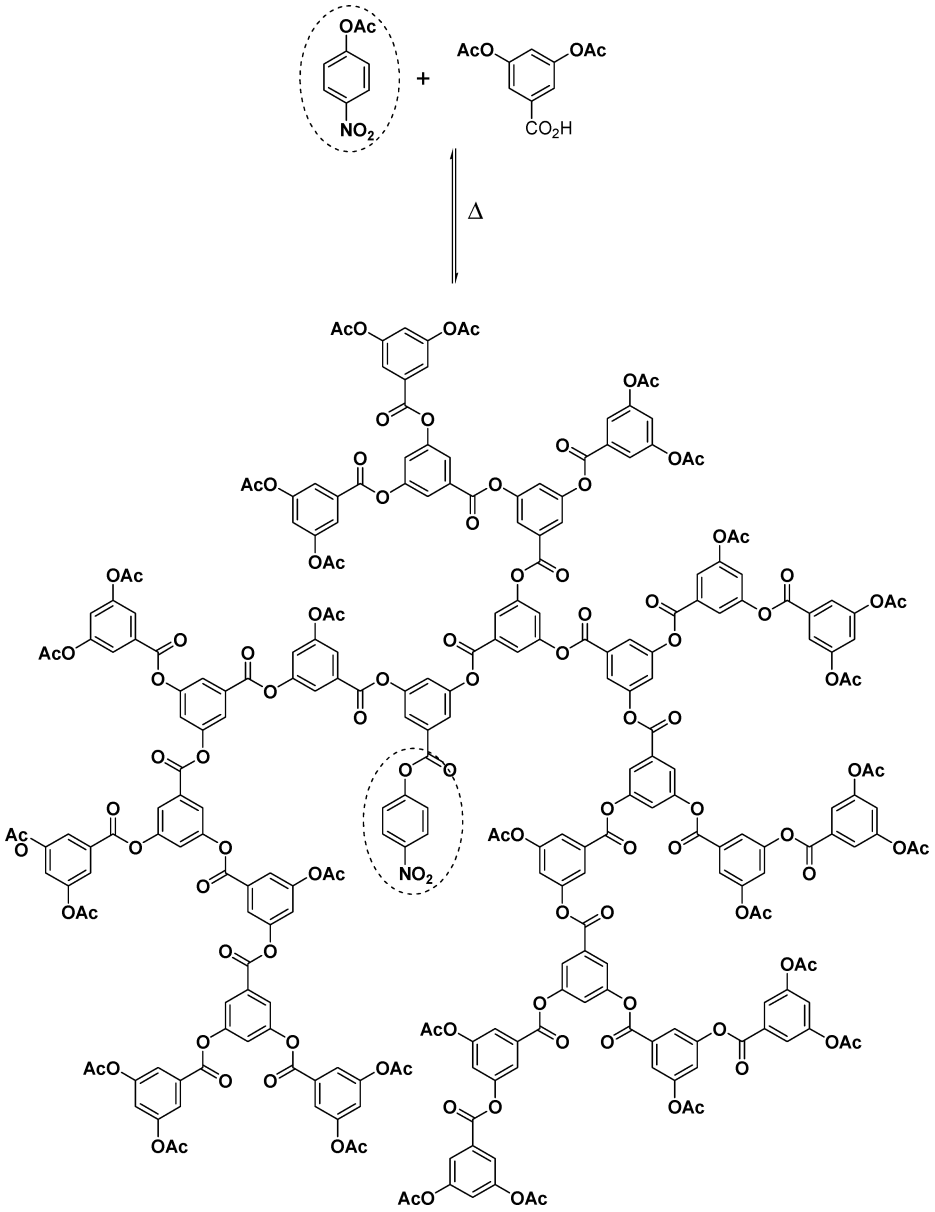
Scheme 1



3−6.) The degree of branching was calculated from ^{1}H NMR to be 50%.[7]

GPC estimates molecular weight from the polymers bulk properties and is independent of core functionality. In an effort determine the level of core incorporation, M_n was calculated from the core functionality itself using ^{1}H NMR. An M_n of 6950 Da was calculated by "core group analysis"[8] using the ^{1}H NMR peak at 1.30 ppm from the acetoxy terminal functionalities (not shown), which was quantitatively compared to the *p*-nitrophenyl ester doublet at 8.32 ppm (Figure 1). This value for M_n is significantly larger than the value from GPC. It is however important to remember that a "core analysis" calculation assumes that every polymer molecule contains a core, and until this was verified, M_n from NMR can only be treated as a maximum possible value (M_n^{max}). Although at first the discrepancy between NMR and GPC values for M_n indicates less than 100% incorporation (∼60%). It is well established that GPC calibrated against linear polystyrene underestimates molecular weight values for dendritic molecules. GPC was thus considered as providing minimum values for both the M_n (M_n^{min}) and the average level of incorporation. Without further investigation it was impossible to determine conclusively the level of incorporation.

To gain a more accurate value for the molecular weight, mass spectrometry was employed. Because of the polydisperse nature of the product and problems with disproportionate ionization of higher molecular weight polymers, these data proved questionable. To overcome these problems, the tail end of an analytical GPC sample was collected. This was analyzed by electrospray ionization mass spectrometry and produced a series of peaks (with a Gaussian distribution) that could be easily assigned (Figure 2). No evidence for cyclization or nonincorporation could be seen, and all peaks could be assigned to polymers containing one core molecule and *n* monomer repeat units (Figure 2). This is direct evidence of 100% incorporation; however, this only holds for this molecular weight fraction. If the core molecule was distributed unevenly across the molecular weight range, higher molecular weight polymers may in fact contain less than one core per polymer.

Although mass spectrometry provided direct evidence for 100% core incorporation, it was only true for the low molecular weight fractions. (Mass spectrometry on the

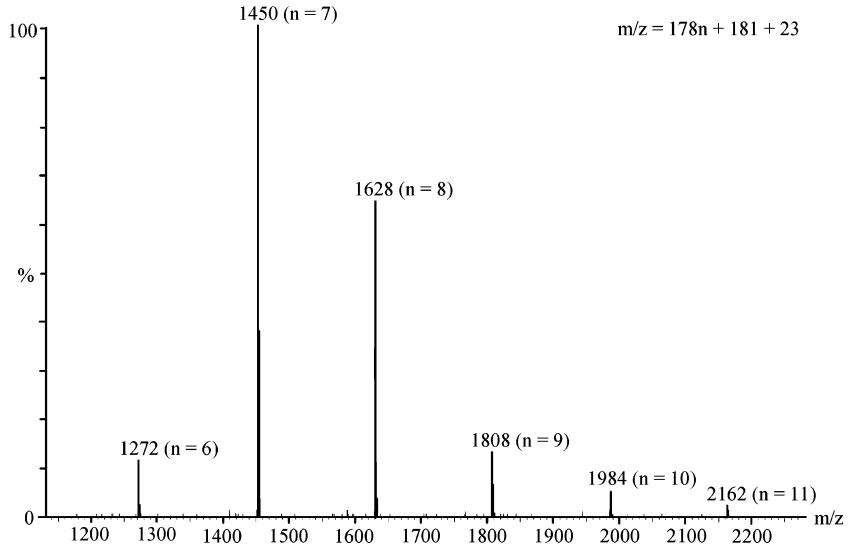


Figure 2. Electrospray mass spectrum of fractionated hyperbranched polyester. *m/z* for *each* peak corresponds to a polymer containing a single core unit (mass = 181) and *n* monomer units (mass = 178*n*) plus sodium (mass = 23). Peaks corresponding to cyclized polymer and polymers without core are *not* observed.

Table 1. GPC and UV Data Showing that the Core Molecule Is Distributed Evenly across All Molecular Weights

M_n by GPC	M_n by UV	$M_{n(GPC)}/M_{n(UV)}$
5204	8892	0.59
4452	7182	0.62
3737	6602	0.57
2671	4401	0.61

high molecular weight fractions was inconclusive; see above.) To prove 100% incorporation across all molecular weights, the polymer needs to be fractionated into a series of differently sized molecules and the level of core incorporation determined for each. We therefore fractionated the polymer using GPC and measured the extent of core incorporation by comparing the polymer's molecular weight, M_n^{min} (determined using the polymers bulk property, i.e., GPC), with the molecular weight obtained from a core group analysis, M_n^{max}. If the ratio of these two molecular weights is consistent across all fractions, then an even distribution could be demonstrated.[9] Furthermore, having previously proven 100% incorporation for the low molecular weight fractions (via mass spectrometry), we then would be able to conclude that the bulk polymer sample must also have possessed a core incorporation of 100% (i.e., the core is evenly distributed). The samples obtained after fractionation were too small to be accurately analyzed using ^{1}H NMR. Therefore, each polymer fraction was exhaustively hydrolyzed,[10] and UV spectrophotometry was used to calculate the concentration of *p*-nitrophenolate liberated from a known mass of polymer (λ_{max} 420 nm). This concentration was used to calculate an M_n^{max}, and the data combined with the M_n^{min} value obtained from GPC and a percentage core incorporation for each fraction were then calculated; the results from these experiments are shown in Table 1.[11] Within error, all polymer fractions possess identical levels of incorporation; this conclusively proves that the core molecules are evenly distributed across all molecular weights. Furthermore, when these results are considered in conjunction with the mass spectrometry data described above (for the low molecular weight fractions), they provide substantial evidence for the complete incorporation (100%) of a specific core molecule within all molecular weight fractions of the hyperbranched polyesters prepared.

Conclusions. The results described in this communication describe a new methodology for the incorporation of a specific core molecule within a hyperbranched polymer, across all molecular weight fractions. The procedure works because of the reversible nature of the polymerization and reactivity of the core molecule chosen. This methodology will ultimately enable more exotic cores to be incorporated and allow for a more accurate comparison of specific properties with respect to molecular weight (e.g., as in the regioselective control observed in dendrimer-based catalytic reactions[6]). Overall, these results represent a significant step forward in the controlled synthesis of hyperbranched polymers. Work to further understand and exploit these results is currently in progress within our laboratory.

Acknowledgment. The authors thank the EPSRC for providing studentships (P.J.G. and Y.G.).

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(8) For an AB_2 polymer, the number of B functional groups is equal to the total number of monomer residues in the polymer.
(9) 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). Twyman, L. J.; Beezer, A. E.; Mitchel, J. C. *J. Chem. Soc., Perkin Trans. 1* **1994**, *4*, 407 and references therein.
(10) Hydrolysis was carried out on a known mass of polymer using a 0.1 M aqueous solution of NaOH. Reactions were monitored every 10 min by UV (λ_{max} 420 nm) until the absorbance remained constant.
(11) Higher molecular weight samples became increasingly more difficult to analyze using UV; the large amount of hydrolyzed monomers interfered with the phenolate peak, making concentration values difficult to calculate.

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