The One-Step Synthesis of a Dendronized (HBP) Polymer

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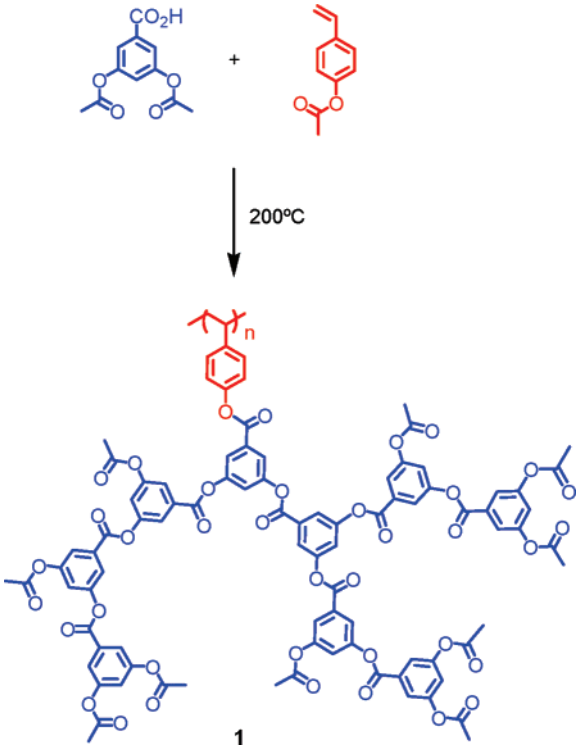
Introduction. Dendronized polymers can be defined as linear polymers with pendant dendritic units.[1] To date, most examples involve the use of perfect dendrons as the dendritic unit. The presence of these pendant dendrons effectively shields or insulates the linear polymeric backbone. This is particularly useful for electronic and photonic applications to prevent unwanted quenching via chain interactions.[2] Other potential applications include light-harvesting macromolecules,[3] solubility and processability aids,[4] and catalysts.[5] Although dendrons are the dominant protagonist in this field, there has been limited work on the use of hyperbranched polymers (HBPs). In order to distinguish these systems from their more perfect dendron counterparts, we refer to them as dendronized (HBP) polymers or DHPs. The limited number of reports using HBPs is surprising when considering that the specific properties of a "perfect" dendrimer are not necessarily important for their particular and intended applications. This is particularly relevant when you take into account the random synthesis of the linear polymer backbone. To date, the limited number of DHPs synthesized has been achieved using one of two approaches:[6,7] (i) a grafting from approach or (ii) the macromonomer approach. Although these methods are an improvement over the long-winded dendron approach, they still involve at least two synthetic steps. In this communication we describe an alternative and simple method that utilizes just one step for the synthesis of a dendronized (HBP) polymers. Specifically, we report the synthesis of a dendronized (HBP) polymer based on a polystyrene backbone with hyperbranched polyester pendant groups.

Results and Discussion. Our approach is shown in Scheme 1 and involves the linear cationic polymerization of 4-acetoxystyrene in combination with the hyperbranched polymerization of 3,5-diacetoxybenzoic acid,[8] a reversible transesterification process.[9] We proposed that both monomers could be polymerized under thermal conditions. On the basis of our previous work involving core controlled polymerizations,[10] we postulated that the acetoxy groups on the styrene would act as core/focal points from which to grow or initiate the hyperbranched polymer units. We therefore set about copolymerizing these monomers by heating them under vacuum (required to remove the acetic acid byproduct and drive the equilibrium/polymerization forward).[11] Specifically, 3,5-diacetoxybenzoic acid (5 mol equiv) and 4-acetoxystyrene (1 mol equiv) were heated to 220 °C at 2 mmHg for 3 h. Upon cooling, the product was dissolved in the minimum of THF and precipitated into a large excess of MeOH.[12] This precipitation procedure was repeated three times to give the final product as a white solid in 68% yield (based on mass recovery). The ^{13}C spectra of the product showed all of the expected peaks from the hyperbranched and linear polymeric units. Furthermore, the ^{1}H NMR spectrum of the product **1**, which is shown in Figure 1, was consistent with the representative structure shown in Scheme 1. A series of broad peaks between 6.55 and 8.00 ppm were assigned to the various aromatic protons from the two individual subunits (i.e., the linear and hyperbranched components). The aromatic signals from the hyperbranched polyester occur as a series of broad peaks between 7.2 and 8.0 ppm, while those from the linear unit occur at 6.55 and 6.84 ppm. Broad peaks at 1.40 and 1.76 ppm were assigned to the linear polymer's methylene and methine protons, respectively. The large peak at 2.25 ppm corresponds to the resonance from the terminal acetate groups on the hyperbranched unit. The number of hyperbranched units per monomer was calculated by integrating the aromatic regions of the HBP and poly(4-acetoxystyrene) (PAS) regions in the ^{1}H NMR. At this point it should be noted that any calculation based on integration ratios is oversimplified, as it assumes that every monomer along the linear block is functionalized with a small and identical hyperbranched unit. It is more probable that due to steric requirements the frequency of the hyperbranched units will be much lower than the 1:1 ratio used in the calculation and that the hyperbranched units probably possess more branched monomers than that calculated from NMR. Nevertheless, this calculation indicated that on average each monomer in the linear poly(acetoxystyrene) block possessed a hyperbranched oligomer with six monomer units. This 6:1 ratio compares favorably to the 5:1 ratio of starting materials, and the small difference in ratios can be accounted for by the loss of small oligomers during the purification process. However, ^{1}H NMR cannot be used to conclusively discriminate[12] between a blend and a dendronized polymer, and other methods must therefore be used. The GPC chromatogram of the dendronized (HBP) polymer 1 indicated

Scheme 1. One-Step Synthesis of Dendronized (HBP) 1



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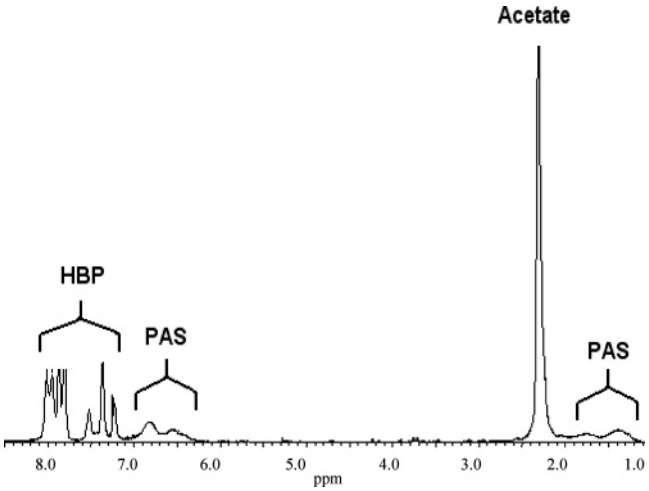

Figure 1. ^{1}H NMR spectra of dendronized (HBP) **1**.

an M_n of around 12 000 g mol^{-1} and a polydispersity of 2.5. For polymerizations involving AB_2-type monomers (such as 3,5-diacetoxybenzoic acid), a value of 2.5 represents a relatively narrow polydispersity and is typical of a core controlled procedure.[10] In comparison, the homopolymerization of 3,5-diacetoxybenzoic acid (performed under identical conditions to those described above) produced a polymer with an M_n of 150 000 g mol^{-1} and an extremely broad polydispersity (∼6). Therefore, if our synthesis had generated a mixture of branched and linear polymers (i.e., produced hyperbranched polyaromatic ester and linear poly(acetoxystyrene) as independent polymers), then we would have expected to observe a very broad polydispersity (and a probable bimodal distribution). The fact that we observe a relatively narrow polydispersity suggests that a dendronized (HBP) polymer has indeed been synthesized. That is, the acetate groups from 4-acetoxystyrene, or poly(acetoxystyrene), act as core units/focal points from which the hyperbranched polyester groups grow. This polymerization process eventually produces the dendronized (HBP) polymer **1** represented in Scheme 1. Further evidence against a simple blend would come from the thermal analysis of polymer **1** and a blend of its constituent parts (simple poly(acetoxystyrene) **2** and a simple hyperbranched poly(aryl ester) **3**). The individual linear and branched polymers[9] were prepared according to known procedures.[13] The simple HBP **3** was initially obtained as a high molecular weight polydisperse sample. In order to obtain a lower molecular weight/low polydisperse sample, it was first necessary to fractionate hyperbranched poly(aryl ester) **3** using a preparative GPC column.[14] After synthesis and purification linear poly(acetoxystyrene) **2** and hyperbranched poly(aryl ester) **3** were obtained with M_n values (and polydispersities) of 8000 (1.90) and 7000 (2.20), respectively.

The polymers were initially analyzed using DSC. The temperature at which maximum peak output occurs was recorded for all samples and is shown in Table 1. The linear poly(acetoxystyrene) **2** shows peak maxima at 125 °C (no significant peaks were observed for the HBP **3**). Analysis of a 1:5 monomer/monomer blend of the linear and hyperbranched units produced a DSC trace which was very similar to the linear poly(acetoxystyrene) **2** (monomer ratios selected to match those of HBP product **1**), with a strong peak at 127 °C. The DSC traces of our dendronized (HBP) polymer **1** and a blend of linear polymer **2** and branched polymer **3** are shown in Figure 2. The dendronized (HBP) polymer therefore has a DSC trace that is very different to the blend or either of its constituent parts. A similar analysis using TGA was also undertaken. Over the temperature range studied (100−700 °C), only the linear poly(acetoxystryrene) completely degraded. Therefore, the temperature at which 50% degradation occurred was selected with respect to analysis; the results are shown in Table 1. As with the DSC data above, the TGA data of the dendronized (HBP) polymer **1** is different than that observed for its constituent parts or its blend. It is also interesting to note that the DHP product **1** did not decompose over the temperature range studied. At 500 °C poly(acetoxystryrene) had completely decomposed, while the DHP product **1** had only degraded by 50%. That is, the dendronized component of DHP product **1** appears to provide some thermal protection to the linear polystyrene backbone.

Table 1. Thermal, Viscosity, and Solubility Data for Dendronized (HBP) 1 and Its Constituent Parts

	HBP (**3**)	PAS (**2**)	HBP/PAS blend (**2** + **3**)[a]	product (**1**)
max^m peak output/°C (DSC)	/	125	127	142
50% degradation occurs at/°C (TGA)	540	410	465	500
specific viscosity (×10^2 cm/g/30 °**C**)	0.11	0.30	0.13	0.23
solubility in $CHCl_3$	poor	excellent	partial	poor

[a] Blend produced such that a 1:6 linear monomer/branched monomer ratio was maintained.

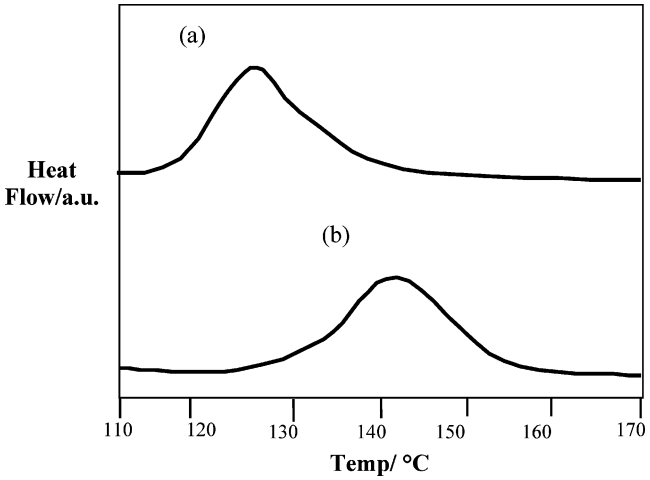

Figure 2. DSC traces for (a) the blend of poly(acetoxystyrene) **2** and (b) the dendronized HBP **1**.

Simple rheological studies also provide evidence for structure **1** and against a blend. The data obtained from specific viscosity measurements are shown in Table 1. Specific viscosities (η_{sp} × 10^2 cm/g) of the PAS **2** and HBP **3** were recorded as 0.30 and 0.11, respectively, while that of the blend was found to be 0.13, which is very close to that of HBP **3**. This was expected, as it is well-known that a significant reduction in specific viscosity can be achieved by adding very small amounts of HBP or dendrimer to a linear polymer.[15] The viscosity of the DHP product **1** was found to be 0.23 (η_{sp} × 10^2 cm/g), which is very different than that recorded for the blend and as such offers some support to the DHP structure **1** shown in Scheme 1. However, it could be argued that the specific viscosity is reasonably close to that recorded for the linear PAS **2**. The reason for this is twofold: First, the molecular weight of the DHP product **1** is slightly higher than that of the HBP **3** or linear PAS **2** used in the blend (which have M_n values of 12 000, 8000, and 7000, respectively), and as such we would expect DHP **1** to have a higher specific viscosity. Furthermore, as the structure of DHP **1** is essentially a linear polymer made up of

a macromonomer possessing very small branched units, we should probably expect the product to have much more linear character, and therefore a higher specific viscosity, than an equivalent blend of linear PAS **2** and HBP **3**. As a final test, a simple solubility experiment was performed, the results of which are shown in Table 1. The linear PAS **2** is readily and completely soluble in $CHCl_3$, while the DHP product **1** and HBP **3** were only sparingly soluble (a large portion of the mass could be recovered after filtration). Under the same conditions, a 1:6 blend of PAS **2** and HBP **3** was only partially soluble. The sample was filtered and the filtrate analyzed by NMR; the resulting spectra showed that proportion of HBP was greatly reduced, with a 1:3 ratio being recorded for the PAS **2** and HBP **3** respectively (a 1:6 ratio expected). The DHP **1** was completely soluble in DMSO-d_6, and when this solvent was used to obtain an NMR spectrum, it was satisfying to note that it had an identical ratio of linear to branched monomers to that obtained when $CDCl_3$ was used as solvent. The solubility data therefore demonstrate that the product has a behavior different than either its constituent parts or their blend, which again provides further support for the DHP product **1** shown in Scheme 1.

Taking all of the thermal, viscosity, and solubility data into account, along with the GPC analysis and the ^{1}H NMR data described earlier, we can conclude that a dendronized (HBP) polymer (represented by structure **1**) can be obtained in a single synthetic step by polymerizing the linear monomer 4-acetoxystyrene with the AB_2 monomer 3,5-diacetoxybenzoic acid under thermal conditions. At this point it is not clear whether or not the hyperbranched polymer is first initiated/grown from a styrene monomer, giving an initial macromonomer that then polymerizes, or whether the linear polymer forms first and then initiates/seeds the hyperbranched polymerization. We are currently exploring these systems for use in a variety of applications.

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Supporting Information Available: Details of the synthesis and characterization for all molecules described. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) For synthetic details see the Supporting Information.
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