Functionalized Hyperbranched Polymers via Olefin Metathesis

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Hyperbranched polymers are highly branched, three-dimensional macromolecules which are closely related to dendrimers and are typically prepared via a one-pot polycondensation of $AB_{n\geq 2}$ monomers.[1] Although hyperbranched macromolecules lack the uniformity of monodisperse dendrimers, they still possess many attractive dendritic features such as good solubility, low solution viscosity, globular structure, and multiple end groups.[1−3] Furthermore, the usually inexpensive, one-pot synthesis of these polymers makes them particularly desirable candidates for bulk-material and specialty applications. Toward this end, hyperbranched polymers have been investigated as both rheology-modifying additives to conventional polymers and as substrate-carrying supports or multifunctional macroinitiators, where a large number of functional sites within a compact space becomes beneficial.[1a,b,2,4]

The properties of a polymeric material are considerably influenced by its end groups.[5] Compared to a linear polymer, this effect is more pronounced for a hyperbranched architecture simply because of a significantly larger number of end groups per single polymer chain (there is one end group per every monomer) and their exposed placement (most of the ends are thought to be located on the periphery of the spherically shaped units). In fact, it has been demonstrated that the chemical nature of the end-group functionalities of a hyperbranched polymer dominates not only the material's solubility in various solvents[2,6−8] but also melt and thermal properties such as the glass transition temperature[1e,2,6−9] and crystallinity.[9] Consequently, it is desirable to have a simple, convenient, and modular method for postsynthetic functionalization of hyperbranched polymers.

Within the past 10 years, the development of new synthetic routes to hyperbranched polymers has surpassed the detailed investigation of these materials. As a result, a great variety of dendritic backbones is now available, while information on their physical properties, especially when compared to linear analogues, remains limited.[10] In particular, despite the importance of the end groups for both property-tuning and substrate-carrying applications of hyperbranched polymers, little is known about the dendritic chain termini microenvironments and branch folding.[4,11]

We have recently reported a facile approach to the synthesis of hyperbranched polymers via acyclic diene metathesis polymerization (ADMET).[12] This method is based on the selectivity of N-heterocyclic carbene catalyst **1** (Figure 1) in the cross-metathesis of different types of olefins. Since **1** promotes a selective reaction between an electron-rich terminal aliphatic alkene and an electron-poor acrylate, compounds such as AB_2 monomer **2** (Scheme 1) form highly branched structures such as **3** (Scheme 1) in its presence. Moreover, given that there are twice as many acrylates (B functionalities) as terminal alkenes (A functionalities) in the reaction mixture during the polymerization of **2**, half of the acrylates remain available for further manipulation.

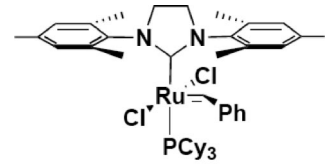

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Figure 1. Imidazolinylidene-based ruthenium olefin metathesis catalyst **1**.

This report describes our advances in the functionalization of **3** by a second cross-metathesis reaction with a small fluorescent analyte—alkene-modified pyrene. Although there have been numerous reports on the fluorescent properties of pyrene-functionalized dendritic and linear macromolecules, these studies have typically focused on comparing polymers to small molecules.[13−22] Here, the comparison of the absorption and emission spectra of the decorated hyperbranched polymer with not only the spectra for a monomeric fluorophore but also the spectra of a similarly labeled linear polymeric analogue provides improved insight into the polymer end-group environment.

Functionalization of the Hyperbranched Polymer. Although a variety of chemical transformations can be employed in the functionalization of the terminal acrylates of **3**, olefin cross-metathesis with **1** and an aliphatic alkene is the most advantageous route for several reasons. First, and most importantly, this selective reaction proceeds in excellent yields and does not produce any nonvolatile, stoichiometric byproduct. Second, this method is inherently compatible with any functionality incorporated within the polymer backbone because it is the same reaction as the polymerization itself; notably, the synthesis and functionalization can be efficiently performed in tandem. Finally, substrates with functionalities not already present in the polymer can be introduced into the polymer because of the excellent functional group tolerance of **1**.

Modified pyrene **4** (Scheme 1) was selected for functionalization of the hyperbranched polymer **3** due to its attractive fluorescent properties. Pyrene is recognized as a particularly useful handle for the study of polymer dynamics and structure in solution.[13−20] This well-studied fluorophore is characterized by long lifetimes and sensitive solvatochromic shifts.[21,22] Furthermore, pyrene is known to associate through π-stacking interactions at millimolar concentrations, leading to the formation of highly stable excimers with red-shifted emission.[21,22] Consequently, this analyte allows for a ratiometric and quantitative measurement of pyrene−pyrene interactions, such as those resulting from a high local concentration of the substrate enforced by a covalent attachment to a polymeric backbone.[13−20] Therefore, the functionalization of dendritic end groups with pyrene is instrumental for the study of their microenvironments.

1-Pyrenebutanol was modified with an aliphatic alkene to produce **4**, which is suitable for selective cross-metathesis with an acrylate and **1**. The functionalization method works according to the same principles as the polymerization itself: **1** selectively crosses the electron-deficient acrylates with the electron-rich

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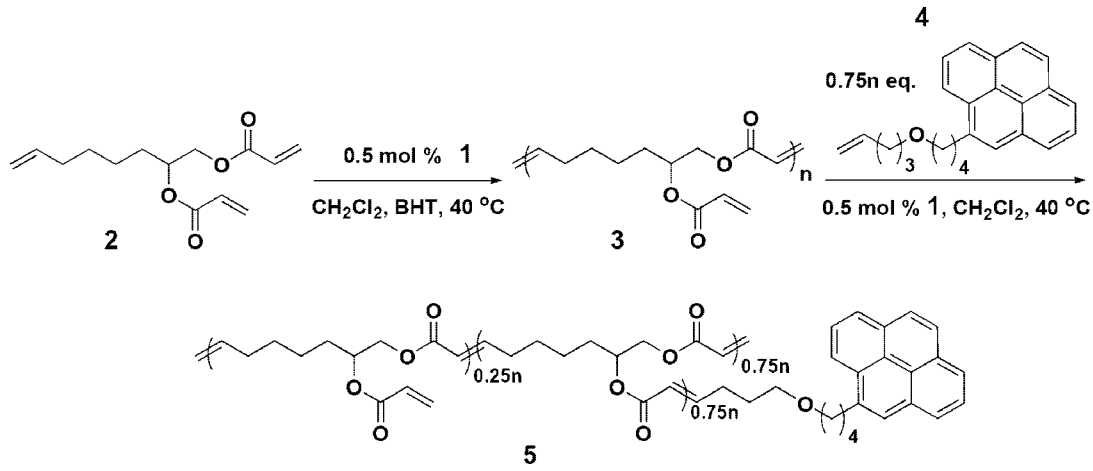
Scheme 1. Hyperbranched ADMET Polymer Synthesis[12] and Subsequent Functionalization with Pyrene



alkene of **4**.[12] Furthermore, this approach only affects the terminal acrylates, since the internal, disubstituted acrylates of the polymer are too sterically hindered to participate in cross-metathesis. In fact, if the internal acrylates could participate in the cross-metathesis with **4**, degradation of the backbone would be unavoidable. However, the polymer modification proceeds to completion, and **5** is produced cleanly according to analysis by ^{1}H NMR and size-exclusion chromatography (SEC) (Figures 2 and 3).

The ^{1}H NMR spectra in Figure 2 show the polymerization progression of **2** to **3** and the subsequent modification of crude **3** with **4** (Scheme 1). In the spectrum of **2**, the peaks downfield of the solvent peak correspond to the six acrylate protons (**a**) and one terminal alkene proton (**d**). As polymer **3** is formed, all terminal alkenes of **2** are consumed (**d** disappears) and half of the free acrylates are internalized, thereby producing peaks **b** in the corresponding integration ratios.[12] Finally, when the remaining terminal acrylates of **3** are reacted with ~0.75 equiv (per end group) of **4**, the amount of free acrylates is reduced to ~0.25 equiv (for each peak **a**). Consequently, ~0.75 equiv of internal, pyrene-functionalized acrylates (for each peak **c**) are added to the existing internal acrylates within the polymer backbone (1 equiv for each peak **b**). As expected, the integration values for the backbone protons **e** of **2** remain constant throughout all of these transformations (Figure 2). However, although the presented ^{1}H NMR analysis strongly supports successful functionalization of **3**, it provides little definitive information on the integrity of the polymer's backbone.

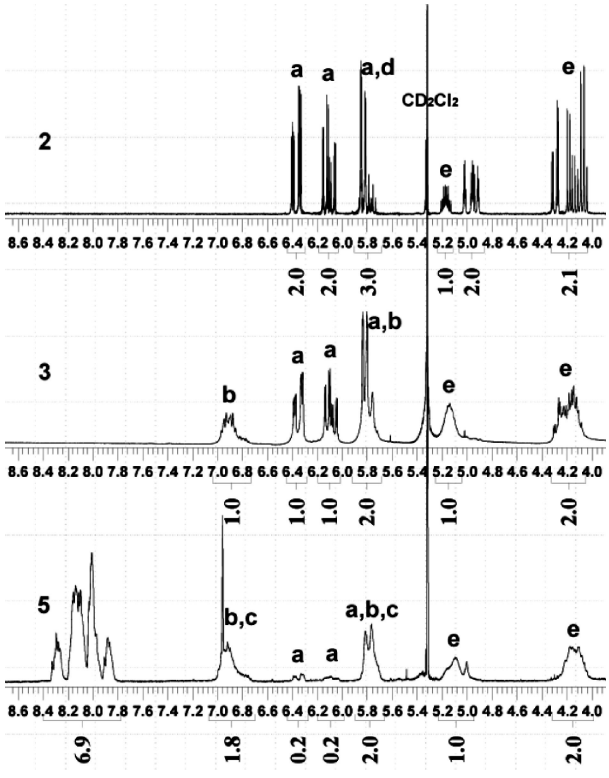


Figure 2. ^{1}H NMR spectra with integration values for **2**, **3**, and **5**. Peaks **a** correspond to the protons of the free terminal acrylate groups. Peaks **b** correspond to the protons of the internal acrylates within the polymer backbone. Peaks **c** correspond to the protons of the internal acrylates resulting from the functionalization with **4**. Peak **d** is due to the proton of the terminal alkene of **2** (which is consumed during the polymerization), and peaks **e** correspond to backbone protons of **2**.

Figure 3 compares the SEC traces of the polymer before (**3**) and after functionalization with **4** (**5**). Although crude **3** (purple trace) was used in the functionalization studies, the resulting **5** (pink trace) was later purified (red trace) for further fluorescence investigations. In spite of the broad polydispersity typical of hyperbranched polymers, the evaluation of the SEC traces obtained for crude **3** and **5** clearly demonstrates that no observable backbone degradation occurs as a result of func-

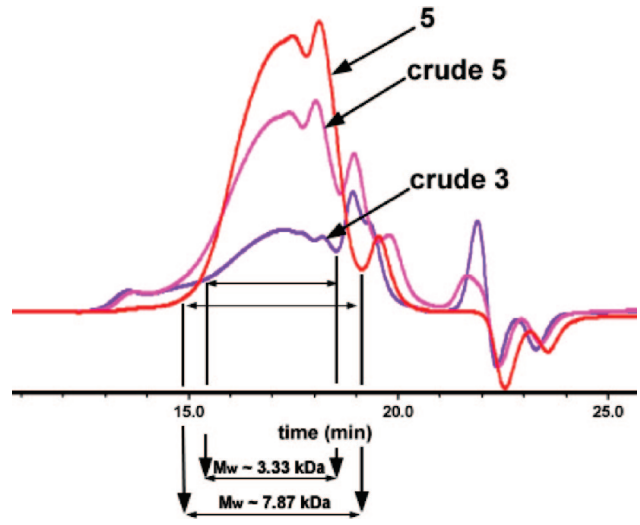
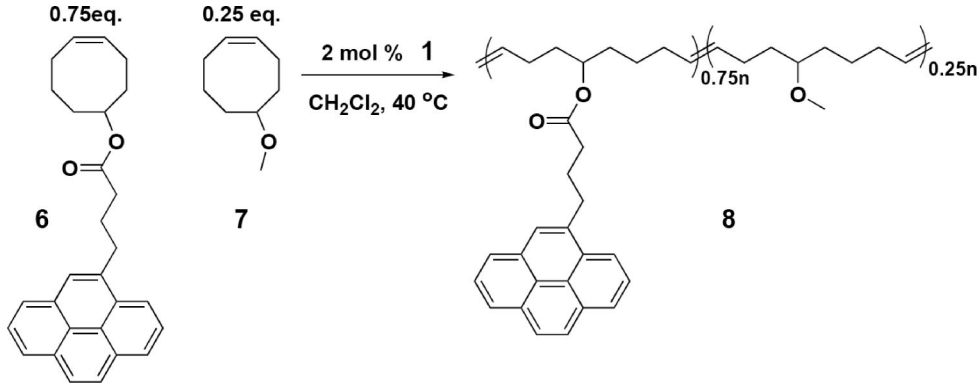


Figure 3. SEC traces (RI) for crude **3** (purple), crude **5** (pink), and purified **5** (red). The molecular weight of the *major* peak is approximately doubled after functionalization.

Scheme 2. Synthesis of the Pyrene-Functionalized Linear Polymeric Analogue



tionalization. Moreover, the absolute molecular weight corresponding to the major peak of **5** ($M_w \sim 7.87$ kDa, measured by a triple angle light scattering technique) is approximately double that of the major peak of **3** ($M_w \sim 3.33$ kDa), which is in agreement with the postulate that ~75% of the end groups of **3** are functionalized with **4** (Figure 3). In addition, as expected for a compact dendritic architecture, only a very slight elution time shift is observed for **5** relative to **3** despite the significant molecular weight difference between the two. Overall, both ^{1}H NMR and SEC analysis indicate that only terminal acrylates participate in the postsynthetic functionalization of hyperbranched polymer **3**.

Preparation of the Pyrene-Modified Linear Analogue. Another significant advantage of the olefin metathesis route to the synthesis and functionalization of hyperbranched polymers is that very similar linear polymers can be prepared via the same methodology. This aspect of the synthetic strategy outlined here is crucial for the direct comparison of hyperbranched polymers to suitable linear analogues. Moreover, there is more than one way to approach this task, as either ADMET of AB monomers[12,23] or ring-opening metathesis polymerization (ROMP) of appropriately functionalized cyclic monomers can be utilized. In fact, the synthesis of pyrene-functionalized linear polymers via ADMET has been previously reported.[23]

We chose to prepare a linear analogue by ROMP of pyrene-functionalized cyclooctene (**6**) in order to simplify molecular weight control over the polymerization reaction (Scheme 2). Since ROMP is a chain-growth-type polymerization which relies on monomer ring strain, it can be simply and efficiently controlled the by catalyst loading. In addition, to ensure that the linear polymer had a similar pyrene-per-chain content as the hyperbranched version, **6** was copolymerized with a corresponding amount of "blank" methoxy-functionalized monomer **7**. The resulting random copolymer **8** had ~75 pyrenes per 100 monomers, as did the hyperbranched polymer **5** (Figure 4).

Fluorescence Properties of Functionalized Hyperbranched and Linear Polymers. Figure 5A compares the UV−vis absorbance and steady-state fluorescence emission spectra for solutions of monomeric pyrene **4**, pyrene-functionalized hyperbranched polymer **5**, and similarly functionalized linear analogue **8**. The normalized UV−vis spectra of all three compounds overlap almost perfectly with no observed spectral broadening or red shift of the linear and hyperbranched polymer (relative to the pyrene monomer). This indicates that the polymeric scaffold does not dramatically influence the interaction of the pyrene moieties in the ground state. On the other hand, the fluorescence emission spectra of the three compounds at the identical concentrations are quite distinct. For all three samples, peaks which correspond to emission from the monomeric pyrene are evident at 380 and 400 nm. In addition, for the hyperbranched polymer **5** and linear analogue **8**, a broad and featureless excimer emission centered at 480−500 nm is also evident. Therefore, the pyrene moieties must interact strongly in the excited-state due to constraints imposed by the backbones of **5** and **8**.

As can be seen in Figure 5B, the ratios of the monomer to excimer emission intensity indicate that the degree of pyrene association is different for **5** and **8**. At a low pyrene concentration of ~80 μM, the ratio of the excimer to monomer emission intensity (I_E/I_M) is 1.5 for the hyperbranched polymer and 7.9 for the linear analogue. As expected, no stacking is observed for free pyrene **4** at micromolar concentrations. For both **5** and **8**, over the concentration range tested, there is only a slight change in the excimer-to-monomer ratio, indicating that the pyrene interactions are intramolecular rather than intermolecular. Therefore, although both polymers do serve to effectively increase the local pyrene concentration, the hyperbranched architecture promotes stacking less effectively than the linear scaffold. Given the nearly identical backbone chemical com-

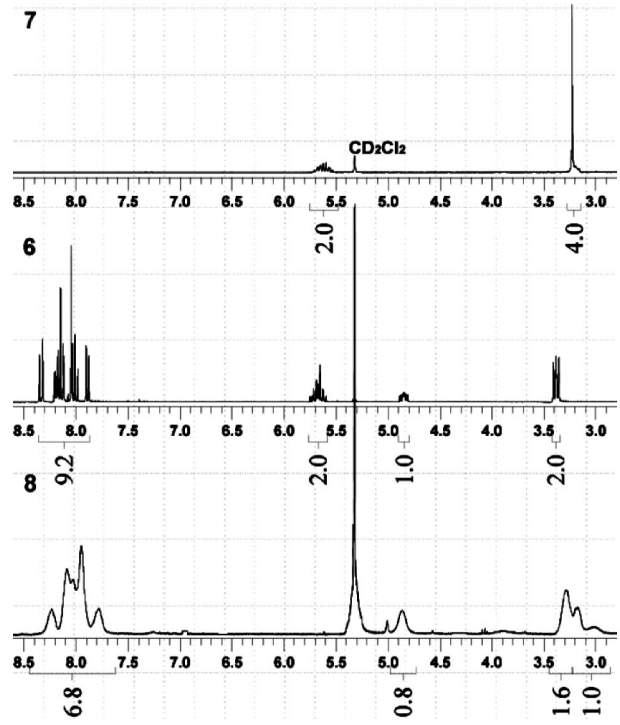


Figure 4. ^{1}H NMR spectra with integration values for **6**, **7**, and **8**.

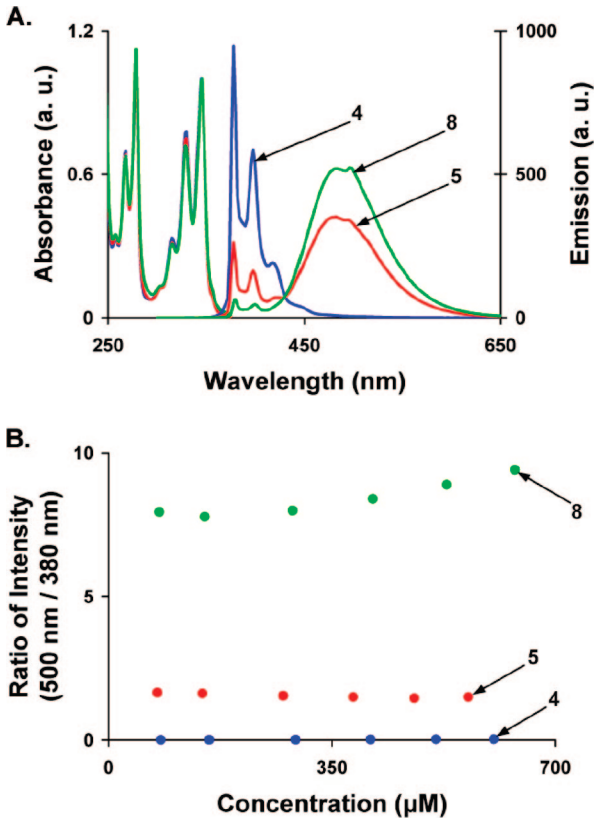


Figure 5. (A) UV−vis absorbance and fluorescence emission spectra for **4** (blue), **5** (red), and **8** (green) in dichloromethane. The absorbance spectra have been normalized for clarity, and the fluorescence spectra were obtained at an 80 μM concentration. (B) Plot of the monomer (380 nm) to excimer (500 nm) intensity emission ratio at various concentrations.

positions, concentrations, and degrees of functionalization for samples **5** and **8**, these observations suggest that some of the pyrene moieties are confined to the interior of the hyperbranched polymer and are, thus, shielded from adjacent pyrenes.

In conclusion, hyperbranched polymers were prepared via ADMET with catalyst **1** and efficiently functionalized at their periphery by further cross-metathesis. This strategy should prove general for the postpolymerization modification of ADMET hyperbranched polymers with a variety of terminal alkene-modified substrates. Moreover, this simple olefin metathesis approach to the synthesis of functionalized hyperbranched polymers can be easily extended to the preparation of linear analogues, which are useful for the investigations of the influence of different polymeric architectures on material properties. In particular, our studies of pyrene-functionalized hyperbranched and linear polymers showed that while both polymeric backbones enforce higher local concentrations of a bound fluorophore relative to its free form, only the hyperbranched scaffold appears to partially shield the analytes from each other, possibly through absorption into the dendritic interior. The differences between the two polymeric architectures may hold implications for the use of hyperbranched polymers as drug-delivery systems.[24]

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Supporting Information Available: Experimental protocols with full characterizations for the synthesis of **4**, **6**, and **7**; functionalization procedure for **5** and polymerization procedure for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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