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Hyperbranched Macromolecules via Olefin Metathesis

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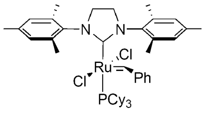
Hyperbranched polymers are highly branched macromolecules typically prepared via a one-pot polymerization of AB$_{n\geq 2}$ monomers.[1] The A and B functionalities of these monomers readily react with each other, but neither one reacts with itself. The unique macromolecular architecture of dendritic polymers gives rise to attractive features such as multiple end groups, improved solubility, and lower solution viscosity (compared to those of linear analogues of the same molecular weight).[1] Dendrimers—structurally perfect hyperbranched macromolecules[2]—have already found applications in medicine,[2,3] catalysis,[2,4] and nanofabrication.[2,5] Unfortunately, dendrimer synthesis can be rather labor-intensive and, thus, expensive.[2] As such, the preparation and study of hyperbranched polymers, which typically exhibit properties similar to those of monodisperse dendrimers,[6] have been extensively pursued in recent years.[1] However, many of the current methods for the synthesis of hyperbranched polymers also have significant drawbacks, including the need for complex monomers and harsh reaction conditions. Herein, we report a simple method for the preparation of hyperbranched polymers via acyclic diene metathesis polymerization (ADMET)[7] of easily synthesized monomers under mild conditions.

Chart 1. Acyclic Diene Metathesis Polymerization Catalyst



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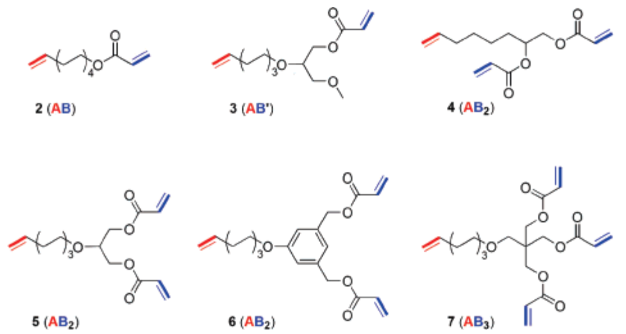
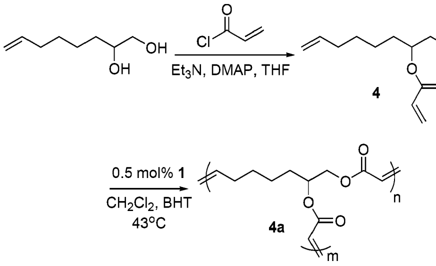
Catalyst **1** (Chart 1) was selected for ADMET hyperbranched polymerization. This imidazolinylidene-based catalyst is tolerant to many functional groups, stable to air and moisture, and readily promotes cross metathesis between electron-rich primary olefins. Furthermore, it can catalyze the cross metathesis involving low metathesis-reactive olefins, such as electron-deficient alkenes. When treated with **1**, electron-poor olefins do not homodimerize (or do so very slowly) but do participate in a secondary metathesis reaction with homodimers of more reactive olefins.[8] Therefore, any molecule functionalized with one electron-rich olefin, such as a terminal alkene, and two or more electron-poor olefins, such as acrylates, is an AB$_n$-type monomer (Chart 2) that can be polymerized into a hyperbranched structure using catalyst **1** (Scheme 1).[9]

Monomers **2**−**7** (Chart 2) were utilized for the ADMET hyperbranched polymerization. They were prepared in one to four steps from commercially available starting materials such as glycerol, Pentaerythritol, and 5-hydroxyisophthalic acid. **2** and **3** were prepared as linear analogues to AB$_2$ monomers **4** and **5**, as well as the AB$_3$ monomer **7**. To further demonstrate the inherent flexibility of the presented method, monomer **6** was also synthesized to make a hyperbranched polymer with a different backbone.

Chart 2. Monomers for Hyperbranched ADMET Polymerization



Scheme 1. Hyperbranched ADMET Polymerization



The polymerization of each monomer is easily monitored by ^{1}H NMR spectroscopy.[9a,10] For example, Figure 1 shows the ^{1}H NMR spectra of **4** and the resulting crude polymer **4a**. Some peak broadening due to formation of macromolecules can be observed in the spectrum of **4a**, especially for the backbone proton **b**. It can also be seen that the terminal olefins (**a**) completely disappear during the polymerization. Moreover, as expected, a new peak (**g**), a doublet of triplets, appears at 6.95 ppm due to formation of internal acrylates (AB olefins). An integration ratio of 1:1 is observed between **g** and the remaining unreacted acrylate peak **c** in the spectrum of **4a**, in accord with the fact that there are twice as many B groups as A groups in an AB$_2$ monomer.[11]

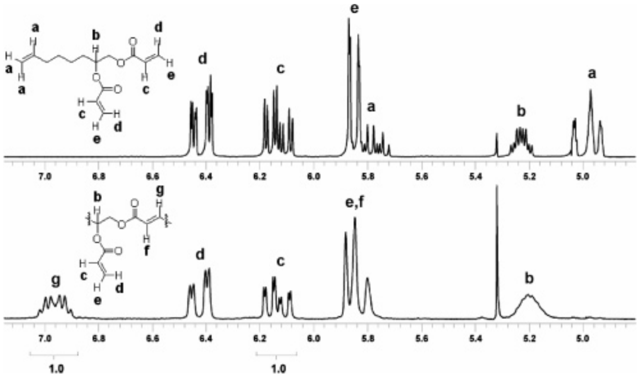


Figure 1. ^{1}H NMR spectra of monomer **4** and hyperbranched polymer **4a**.

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Table 1. Results of Polymerizations of **2**−**7**[a]

polymer	M_w (kDa)	M_n (kDa)	PDI	$\alpha \times 10^{-1}$
2a	4.31	2.07	2.1	4.45 ± 0.01
3a	21.43	4.44	4.8	4.12 ± 0.02
4a	3.61	0.55	6.5	3.82 ± 0.02
5a	14.77	3.08	4.8	3.24 ± 0.02
6a	10.24	3.17	3.2	3.34 ± 0.03
7a	30.90	5.00	6.2	2.69 ± 0.02

[a] Polymerization conditions: 0.5 mol % of **1** was used and the polymerizations were conducted in near-refluxing methylene chloride (45 °C) with venting. M_w, M_n, and PDI were calculated from triple-angle laser light-scattering and refractive index measurements. α was measured with the help of an on-line differential viscometer.

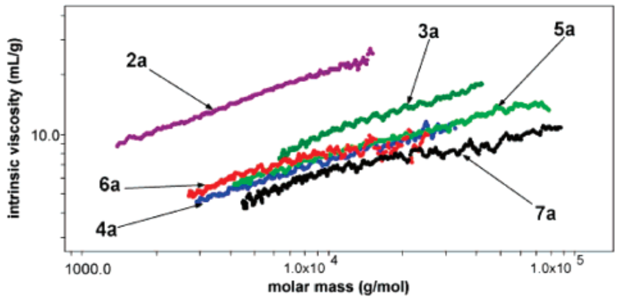

Figure 2. Mark−Houwink−Sakurada plots for polymers **2a**−**7a**.

A multiangle light-scattering (MALS) detector combined with a differential refractometer and an on-line viscometer (all from Wyatt Technology Corporation) following size exclusion chromatography (SEC) was used to determine the molecular weights and PDIs of the obtained polymers. Additionally, viscometer data helped to characterize branching of the macromolecules resulting from ADMET of **2**−**7**. Table 1 summarizes the typical crude polymerization results. The PDI values observed are quite high, which is not surprising for a hyperbranched step-type polymerization.[12]

Figure 2 compares the plots of intrinsic viscosity (IV) vs molecular weight (Mark−Houwink−Sakurada plots) for polymers **2a**−**7a**. As expected, the IV of branched polymers **4a**−**7a** is much lower than that of the linear polymer **2a** for any given molecular weight. Interestingly, the supposedly linear polymer **3a** has a drastically reduced intrinsic viscosity compared to that of **2a**, although not quite as low as the viscosities of branched polymers. We attribute this property of **3a** to the presence of a methoxymethyl pendant group in each monomer unit. This group is inert during the polymerization, but its length is comparable to the monomer's overall size. Such an architecture results in a "comb"-type polymer with a lower than expected IV (relative to that of a linear analogue).[13] Across the molecular weight range studied, the viscosity of polymer **7a**, based on an AB_3 monomer **7**, is even lower than that of AB_2 polymers **4a**−**6a**. This observation indicates even more branching in the AB_3-based polymer. On the other hand, the intrinsic viscosity does not change dramatically with slight variations in the backbone; it can be seen from Figure 2 that the Mark−Houwink plots for **4a**−**6a** completely overlap.

To extend our analysis, we compared the Mark−Houwink shape parameter α ($[\eta] = KM^{\alpha}$) for polymers **2a**−**7a** (Table 1). An α parameter of 0.5−1.0 is typical for randomly coiled linear polymers.[14] Polymers with a rigid-rod shape have an α of 2.0, and spherically shaped macromolecules are expected to have an $\alpha < 0.5$.[14] The linear polymer **2a** was found to have the highest α value of 0.45 (Table 1), closely followed by an α of 0.41 for **3a**. This observation confirms that **3a** is a linear polymer despite its low viscosity. It also validates that polymers **4a**−**7a** are not simply linear, alternating AB comb-shaped polymers. Branched AB_2-based polymers **4a**, **5a**, and **6a** all have α parameters indicative of a spherical shape in solution. Moreover, polymer **7a** yielded the lowest α value, which is in agreement with the AB_3-based polymer having the lowest intrinsic viscosity and, thus, the most branching. Overall, the α values found strongly suggest a spherical shape in solution and, therefore, hyperbranching for polymers **4a**−**7a**.

In summary, we have demonstrated that olefin metathesis can be used to prepare hyperbranched polymers with a variety of backbones. The monomer synthesis is simple, and the polymerization is conducted under very mild conditions. It is easy to envision that functionalization of these hyperbranched polymers could lead to a number of applications. Therefore, as an extension of this work, we are currently investigating functionalization of the peripheral groups (acrylates) of the hyperbranched polymers presented here.

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Supporting Information Available: Experimental procedures with full characterizations for the synthesis of **2**−**7** and the polymerization procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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