

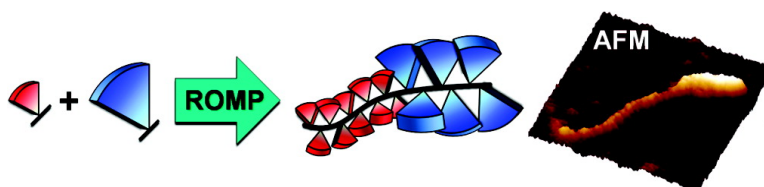
Communication

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Synthesis of Dendronized Diblock Copolymers via Ring-Opening Metathesis Polymerization and Their Visualization Using Atomic Force Microscopy

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Dendronized diblock copolymers are a class of highly modular macromolecules. The nature of the polymer backbone, the length of the constituent blocks, and the nature of the dendritic wedges can be independently varied to yield polymers with precisely controlled nanostructures. This allows the preparation of polymers with different shapes and function that can be directly visualized and manipulated by atomic force microscopy (AFM).¹

Dendronized linear polymers² have been synthesized via a graft from approach,^{1b-c,3} a graft to approach,^{1d,4} and a macromonomer approach.^{1e,5,6} In the first two methods, the synthesis of a defect-free dendronized linear polymer requires the use of reactions that proceed in quantitative yield. This can be especially challenging at high degrees of dendronization owing to the increased steric crowding around the polymer backbone. In contrast, the macromonomer approach uses a highly pure dendrimer with a polymerizable end group^{5a} to ensure complete dendritic coverage of the polymer backbone. When living polymerization conditions are used, the synthesis of block copolymers can be envisaged by the sequential addition of different dendritic monomers.

Despite these advantages, implementation of the macromonomer approach is a formidable synthetic task owing to the steric bulk of the monomer. Often, this hinders polymerization and leads to low molecular weight products.^{5g,j} The use of a highly reactive monomer-catalyst combination, as in the case of ring-opening metathesis polymerization (ROMP), can help overcome this limitation.⁷ Typically, to facilitate ROMP, a norbornene unit is used at the focal point of the dendron. Relief of ring strain upon ring opening of the norbornene provides the necessary thermodynamic driving force for the polymerization. We have recently reported the synthesis of a block copolymer derived from norbornene-type monomers, the first bearing a small aliphatic ester dendron made of 2,2'-bishydroxymethyl propanoic acid and the second carrying a functionalized fullerene using the third generation Grubbs catalyst.⁸ Hult and co-workers subsequently described the homopolymerization of the same monomer containing aliphatic ester dendrons with the second generation Grubbs catalyst.^{5c} However, the polymerization of dendritic monomers containing the more sterically demanding Fréchet-type aryl ether dendrons⁹ or the synthesis of fully dendronized diblock copolymers has not been reported using this approach. Herein, we report the synthesis of dendronized diblock copolymers containing a third generation aryl ether dendron and a second generation polyester dendron (Figure 1). Direct visualization of the products containing blocks of varying lengths was performed by atomic force microscopy of individual polymer chains deposited on mica.

Initially, a series of test reactions were performed to interrogate the reactivity of monomers containing the poly aryl ether dendron.

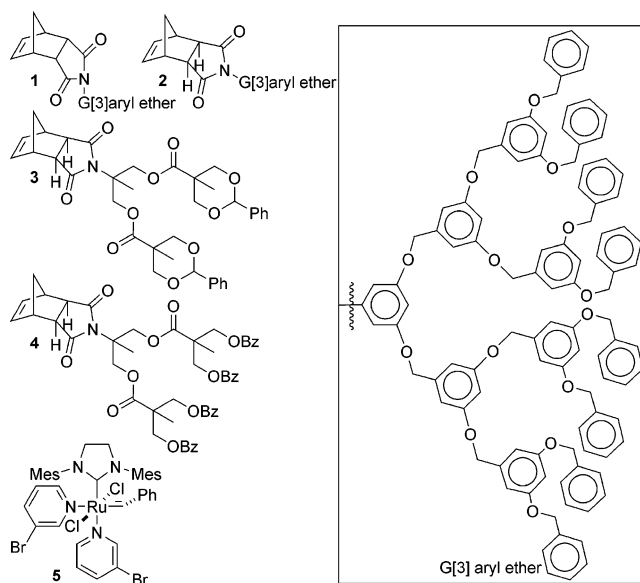
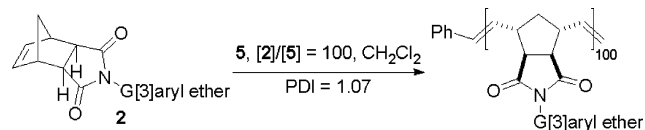


Figure 1. Structure of monomers (1–4) and catalyst (5) used in this study

Polymerization of the endo isomer **1** was attempted with the fast initiating third generation Grubbs catalyst (**5**).⁷ Analysis of the reaction mixture by size exclusion chromatography (SEC) revealed that the polymerization did not proceed even after extended reaction times.¹⁰ The endo orientation of the dendron seemed to effectively shield the alkene from the catalyst and, based on this hypothesis, we synthesized the exo monomer **2**.¹¹ When a dichloromethane solution of this monomer was treated with catalyst **5**, the monomer was completely consumed within 3 h and a polymer with a narrow molecular weight distribution (SEC, polystyrene standards) was obtained as shown in Scheme 1.

Scheme 1. Polymerization of Aryl Ether Dendron



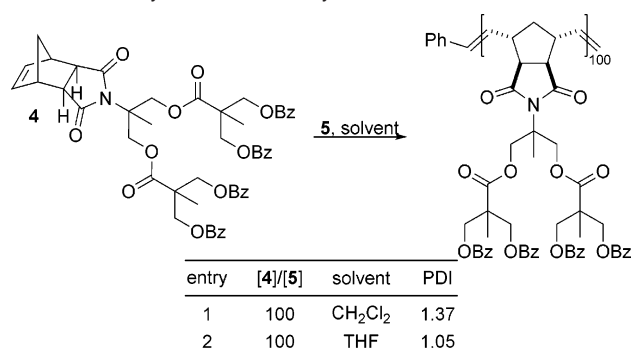
However, when a solution of the ester dendron **3** was added to this reaction, we failed to observe clean conversion to the diblock copolymer. To evaluate the order of addition of the monomers, monomer **3** was polymerized with catalyst **5**. The monomer was consumed within 1 h to yield a polymer with low polydispersity index (PDI). At this point a solution of monomer **2** in dichloromethane was added to the reaction. This resulted in the formation of a polymer with a high PDI, probably due to the occurrence of some crosslinking by transacetalization.¹²

To overcome this, we replaced the terminal benzylidene acetal groups of **3** with benzoate ester groups (monomer **4**, Figure 1).

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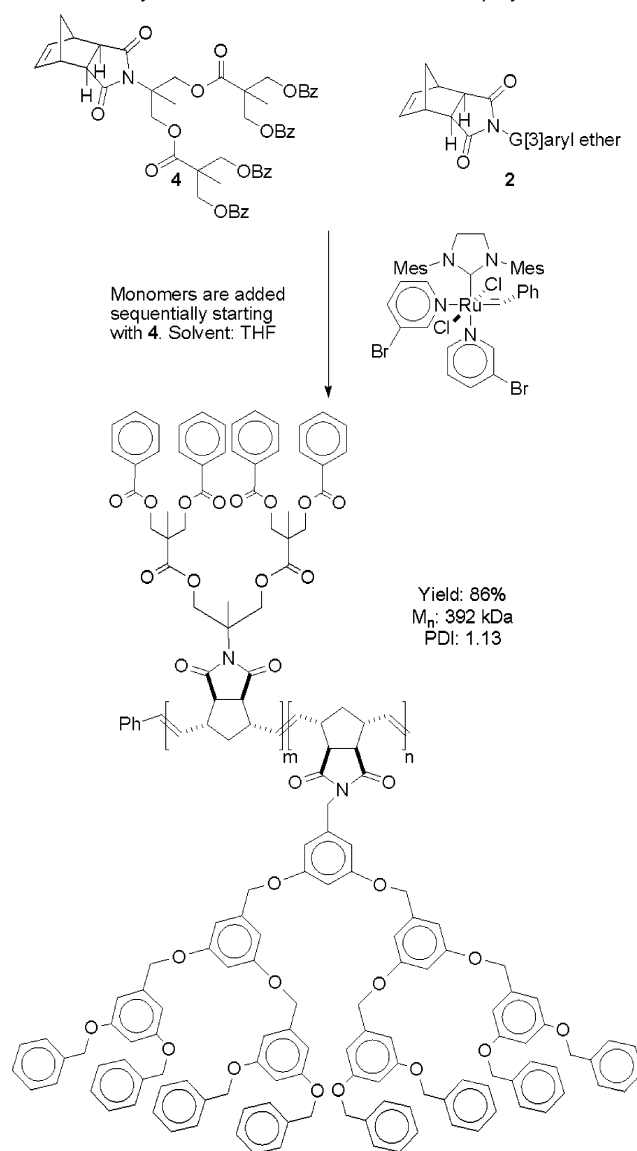
Scheme 2. Polymerization of Polyester Monomer

Treatment of a dichloromethane solution of this monomer with catalyst **5** resulted in complete consumption of the monomer in 1 h (Scheme 2). However, the resulting polymer had a PDI of 1.37, in sharp contrast to the low PDIs obtained with the other monomers. Careful examination of the SEC trace showed the increased PDI was due to considerable tailing of the polymer peak. This suggests that decomposition of the catalyst took place during the reaction. Considering that the reaction conditions for the polymerization of all the monomers were identical, this signifies a lowered stability of the catalyst to monomer **4**. We hypothesized that carrying out the reaction in a mildly Lewis basic solvent might be beneficial for catalyst stability and reduce the polydispersity of the resulting polymer. Indeed, when the polymerization of monomer **5** was performed in THF, a polymer with a PDI of 1.05 was obtained.

On the basis of this result, we attempted the preparation of a block copolymer by sequential polymerization of the benzoate monomer **4** followed by the aryl ether monomer **2** (Scheme 3). Polymerization was initiated by the addition of catalyst to a THF solution of monomer **4** (ratio of **4** to **5**, 100:1); after complete consumption of the monomer, a solution of the Fréchet-type monomer **2** (ratio of **2** to **5**, 150:1) in THF was rapidly injected into the reaction mixture. SEC analysis of an aliquot of this reaction indicated the complete disappearance of the Fréchet-type monomer in 3 h and the formation of a copolymer with a PDI of 1.13 and a M_n value of 392 kDa (by SEC, multiangle laser light scattering analysis). A detectable amount of the homopolymer remained, suggesting that chain termination had occurred with a small number of the initial polymer chains. Precipitation of a dichloromethane solution of the polymer into methanol did not significantly change the PDI of the sample. Additionally, the proton NMR and IR spectra were consistent with the incorporation of both monomers

The scope of this protocol for the synthesis of dendronized diblock copolymers of varying block lengths was studied. Various ratios of catalyst to dendronized ester monomer **4** were examined while keeping the ratio of catalyst to aryl ether monomer **2** constant (Table 1, entries 2–4). As the ratio of the monomer **4** increases, small increments in the amount of chain-terminated homopolymer were observed. This led to an increase in the overall polydispersity of the sample. However, the PDI of the polymer samples were remarkably low and made clear the utility of this method for the synthesis of dendronized diblock copolymers.

Further evidence for the nature of the copolymer was provided by direct AFM visualization of individual molecules on mica (Figure 2). This clearly confirmed the presence of distinct blocks. The polymers synthesized with variable block lengths (Table 1, entries: 2–4) are shown in decreasing order of dendronized ester block size from Figure 2a to Figure 2c. Although the molecules on mica predominantly assume a conformation that resembles a tadpole, which renders length determination of the aggregated block difficult, a qualitative correlation between the “tail” length and the

Scheme 3. Synthesis of Dendronized Diblock Copolymer**Table 1.** Scope of Dendronized Diblock Copolymer Synthesis

entry	ratio of monomer 4 to 5	ratio of monomer 2 to 5	% yield after precipitation	PDI from MALLS	obsd M_n (kDa) ^a	calcd M_n (kDa)
1	100	150	86	1.13	392	351
2	50	100	56	1.02	249	219
3	100	100	85	1.17	299	264
4	200	100	88	1.18	430	354

^a Obtained from MALLS analysis.

number of ester dendron units can be easily inferred. In these images, the contour lengths of the tails were estimated as 83, 37, and 19 nm for polymers synthesized with 200, 100, and 50 ester dendron units, respectively. Despite the approximate nature of these values owing to uncertainties associated with the AFM technique (tip convolution), the measured variation in the chain length is consistent with the catalyst monomer feed ratio and the ¹H NMR data.¹³ Supporting the previous observation, the “head” of the

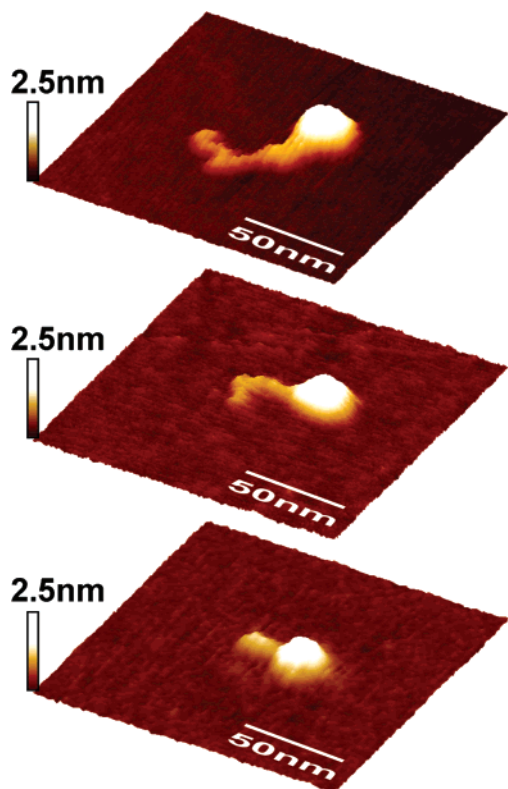


Figure 2. Tapping AFM images acquired on dendronized diblock copolymers spun cast from 0.5 $\mu\text{g}/\text{mL}$ CHCl_3 solution onto mica. The polymers synthesized with a constant number of aryl ether dendron monomer units (100) and decreasing number of ester dendron monomer units: (a) 200 units, (b) 100 units, and (c) 50 units.

tadpole has a constant diameter (ca. 20 nm) for the different polymers. The observed shape is attributed to the block containing the aryl ether dendron aggregating onto itself to minimize its interaction with the hydrophilic mica, while the more polar polyester dendronized block stretches out to maximize the contact area with the surface.

In conclusion, we have established a platform for the synthesis of fully dendronized block copolymers using the ROMP reaction. While the living nature of the polymerization provides a format suitable for the synthesis of block copolymers, the macromonomer approach ensures the high fidelity of dendritic coverage on the linear polynorbornene backbone. The inherent curtailment of reactivity^{5a} of a monomer containing bulky dendritic wedges such as the aryl ether dendron is overcome by the use of the fast initiating Grubbs third generation catalyst. Direct AFM visualization of the individual polymer molecules confirms the diblock structure and demonstrates the capability of precise control of block length through synthetic routes. This platform establishes an opportunity for the synthesis of modular and well-defined macromolecules. Using this strategy, the variation in polymer property as a function of nanostructure can be studied. Potential application of this system in catalysis and organic electronics are currently being explored.

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Supporting Information Available: Complete ref 5d, procedures for synthesis, and characterization of monomers and polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) See Supporting Information ¹HNMR data.

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