

Synthesizing Dendronized Linear Polymers using “Click Chemistry”

Justin L. Mynar,¹ Brett Helms,¹ Craig J. Hawker,² and Jean M. J. Fréchet*,¹

¹Department of Chemistry, University of California, Berkeley, CA, 94720-1460 and Lawrence Berkeley National Laboratory Berkeley, CA

² Materials Research Laboratory, University of California, Santa Barbara, CA

Introduction

Dendronized linear polymers have recently come forward as new materials for nanoscale applications. These “molecular cylinders” may be modified with specific chemical makeup, rigidity, surface decoration, and backbone properties much like their spherical complements, dendrimers.¹ This unique architecture may be valuable in certain nanoscale applications where the spherical conformation afforded by classical dendrimers is not desirable.

There are three main pathways (Routes I, II & III) for synthesizing dendronized polymers. Route I is a “graft-to” approach in which a polymer contains pendant groups that can be coupled with a preformed dendron. This route has the advantage of convergent synthesis, but complete coverage of the backbone has thus far been an elusive goal using high generation dendrons (G3 or larger).²

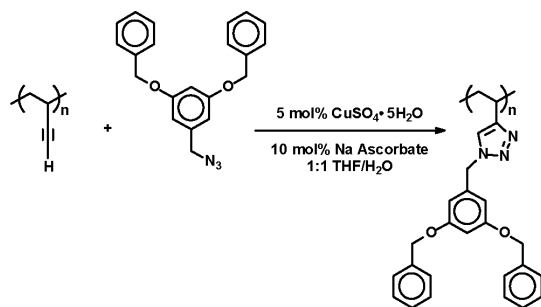
Route II, or the “graft-from” approach, proceeds via a step growth process from the polymer backbone. This route does provide a way to achieve the maximum degree of dendronization but the structures usually exhibit defects due to the route being synthetically difficult. Route II has been favored in literature over Route I and was first reported by Tomalia, although other groups including our own have improved upon it.³

Route III, the macromonomer approach, starts with the dendrons coupled with the monomer. The advantages of this approach is that each repeat unit in the polymer has a perfect pendant dendron, and maximum dendronization can therefore be accomplished. However, macromonomers with high generation dendrons usually do not polymerize with high degree of polymerization.⁴

Experimental

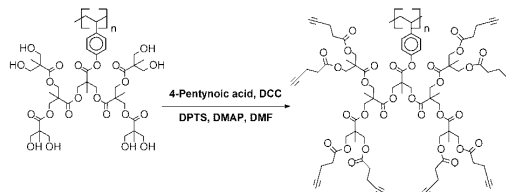
Our group has reported a graft-to pathway via “click chemistry”⁵ which allowed us to successfully obtain a dendronized linear polymer with Fréchet-type dendrons up to G3.⁶ We, however, failed to achieve complete coverage of the polymer backbone with dendrons above G3. We decided to utilize the “graft-from” approach to yield a dendronized linear polymer and then employed the “graft-to” approach to yield an even larger dendronized polymer with two different concentric layers of dendrons.⁷

Dendronized linear polymers were synthesized using poly(vinylacetylene) (PVAcet) as the polymer backbone and G1, G2, and G3 Fréchet type dendrons as the grafting moiety. PVAcet was synthesized using a modified literature procedure.⁸ Click reactions were carried out in a 1:1 solvent ratio of H₂O to THF using 5 mol% CuSO₄·5H₂O with 10 mol% sodium ascorbate as the *in situ* reducing agent to generate the active Cu(I) species (Scheme 1).



Scheme 1. G1 dendronized linear polymer via “click chemistry.”

To obtain doubly dendronized polymers, the synthesis began with the divergent dendronization of a 60,000 g/mol PHS with a polyaliphatic ester.⁹ The PHS-60K-[G2]-OH and PHS-60K-[G3]-OH were functionalized with 4-pentynoic acid under carbodiimide coupling conditions (Scheme 2). Click reactions were carried out in the same conditions as before using G3 Fréchet type dendrons as the grafting moieties.



Scheme 2

Results and discussion

Coverage along the polymer backbones was extremely high. Inspection of the ¹H NMR for the dendronized material clearly indicates the disappearance of the alkyne peak at δ 2.12 ppm. IR was also utilized to confirm that neither alkyne (3289 cm⁻¹) nor azide (2098 cm⁻¹) residues remain in the final polymer.

Along with the NMR and IR data, size-exclusion chromatography (SEC) was used to determine the coupling efficiency. SEC, however, grossly underestimates the true molecular weight (MW) of these polymers. Further structural and MW characterization was carried out using size exclusion chromatography coupled to multi-angle laser light scattering (SEC-MALLS). Both dendronized linear polymers and doubly dendronized polymers exhibited complete coverage.

Conclusions

The “graft-to” approach towards dendronized microstructures based on click chemistry has been demonstrated. This synthetic route is now being pursued to yield dendronized microstructures for microelectronics and drug delivery.

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