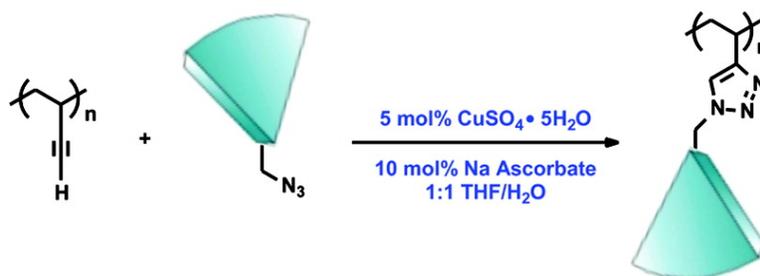


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Dendronized Linear Polymers via “Click Chemistry”

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Dendronized linear polymers have recently emerged as new materials for nanoscale applications. These “molecular cylinders” may be tailored with specific chemical constitution, stiffness, surface decoration, and backbone properties much like their spherical counterparts, dendrimers.¹ For example, Schlüter has shown that sufficiently long dendronized polymers can be visualized as well as manipulated by scanning force microscopy (SFM), leading the way to a bottom-up approach to more complex nanoscale features on surfaces.² Our own group has recently developed chemistry for patterning these dendronized materials on surfaces using SFM.³ Dendronization of linear polymeric materials has also been used for site-isolation in catalysis as well as in OLED formulations.⁴ Thus, the growing need to synthesize dendronized materials for applications, such as catalysis, drug delivery, and nanoscale electronics, recently led us to further expand the methodologies by which they are prepared.

There are three main pathways (Routes I, II, and III) for synthesizing dendronized polymers (Figure 1). Route I is a “graft-to” approach whereby a preformed dendron is coupled to a polymer that contains pendant groups for attachment. This route has the attractiveness of convergent synthesis, but complete coverage of the backbone has thus far been an elusive goal using high generation dendrons (G3 or larger).⁵

Route II, or the “graft-from” approach, proceeds via a step growth process from the polymer backbone. Although this route appears synthetically challenging given the likelihood of defects in the structure, it does provide a way to achieve the maximum degree of dendronization. Route II has been favored in the literature over Route I and was first reported by Tomalia, although other groups, including our own, have improved upon on it.^{2,6}

Route III, the macromonomer approach, incorporates dendrons into the monomer. Advantages are that each repeat unit in the polymer has a perfect pendant dendron, and maximum dendronization has been achieved. The disadvantage is that macromonomers with high generation dendrons usually reach only low degrees of polymerization.^{4c,7}

Given the success in using “click chemistry” in the synthesis of dendritic materials,⁸ we hypothesized that the “spring-loaded” nature of the Cu(I)-catalyzed Huisgen [2 + 3] dipolar cycloaddition reaction between an organic azide and a terminal alkyne would permit exhaustive dendronization of linear polymeric materials via Route I. The synthetic appeal of click reactions relies upon their high yields, simple reaction conditions, tolerance of oxygen and water, and simple product isolation.⁹ While these reactions occur between two highly energetic moieties, they exhibit quite narrow chemoselectivity. To apply the click chemistry concept to dendronized linear materials, we devised a system whereby a Fréchet-type dendritic azide reacts with the pendant alkynes of poly(vinylacetylene), or PVacet (Scheme 1). Given the modular nature

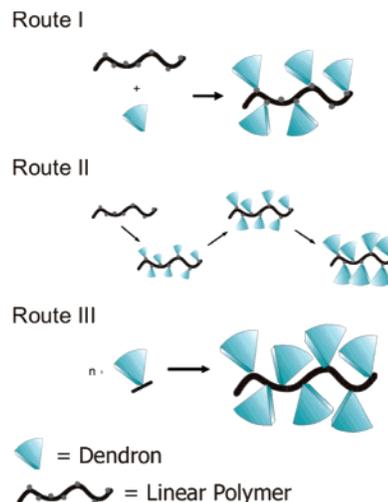
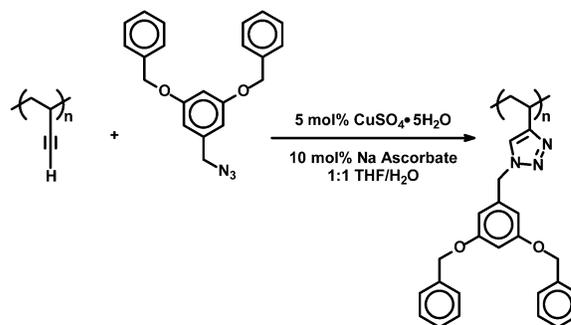
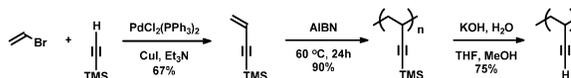


Figure 1. Synthetic routes to dendronized linear materials.

Scheme 1. First-Generation Dendronized Linear Polymers via “Click Chemistry”



Scheme 2. Synthesis of Poly(vinylacetylene)



of this scheme, we felt that our results with this methodology could prove useful in the preparation of more-elaborate dendronized materials in a single step from readily accessible dendritic azides.

PVAcet was synthesized using a modified literature procedure (Scheme 2).¹⁰ We found that 4-TMS-1-buten-3-yne was best prepared using a Sonogashira reaction between vinyl bromide and TMS-acetylene. This monomer was polymerized in bulk at 60 °C with AIBN. The TMS-protected polymer could be fractionated to the desired molecular weight with relatively narrow polydispersities (PDI = 1.2–1.3). Subsequent hydrolysis of the TMS groups afforded PVAcet with >98% alkynes available for reaction with dendritic azides. The preparation of benzyl ether dendritic azides has been described in previous work.^{5b}

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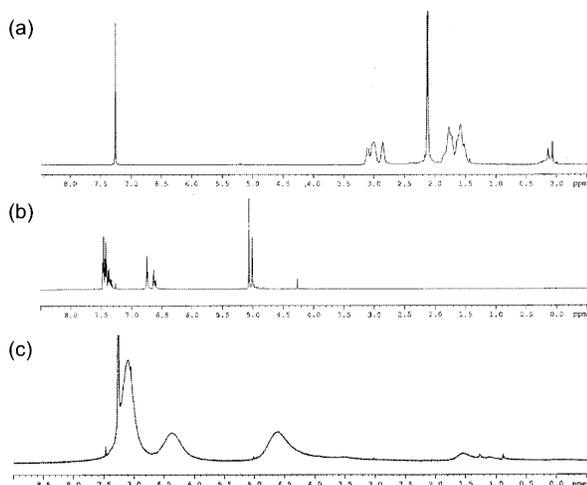


Figure 2. ^1H NMR spectra of (a) PVAcet, (b) G3 azido dendron, and (c) G3-dendronized linear polymer.

Click reactions were carried out in a 1:1 solvent ratio of H_2O to THF using 5 mol % $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with 10 mol % sodium ascorbate as the in situ reducing agent to generate the active Cu(I) species. Reactions with the first generation dendron (G1) reached completion in the course of a few hours, while coupling of the G2 dendron was slower and G3 required repeated exposure to freshly prepared catalyst. The G4 dendritic azide was found to be unreactive using these and other reaction conditions. These data led us to hypothesize that the reaction between the dendritic azide and the polymer was kinetically controlled; specifically, that the formation of the Cu(II)–acetylide was rapid, and the accessibility of the azide was rate determining. The absence of reactivity in the G4 material suggests that in a pseudo-aqueous environment, the azide moiety is buried within the benzyl ether polymer and hence unavailable for reaction.

The integrity of these materials with respect to coupling efficiency is extremely high. The reaction involving dendritic azides G1 and G2 were quantitative, and that for G3, proceeded in >98% yield. Inspection of the ^1H NMR for the G3-dendronized material clearly indicates the disappearance of the alkyne peak at δ 2.12 ppm (Figure 2). In addition, the absence of a sharp benzylic azide peak at δ 4.27 ppm implies excess dendron has been successfully removed by fractional precipitation. IR data also confirm that neither alkyne (3289 cm^{-1}) nor azide (2098 cm^{-1}) residues remain in the final polymer.

These dendronized linear polymers show concomitant increases in molecular weight with increasing generation (Figure 3). While we did observe an increase in the polydispersity for the third generation fully dendronized material, we attributed the tail in the SEC curve to interactions with the column. However, we could not rule out the possibility of a change in conformation from a random coil to a rigid rod between the second and third generations, respectively. AFM height images taken for the third-generation dendronized polymer suggest a rigid morphology has been reached (Figure 4). We plan to investigate this further.

We have presented a novel extension of click chemistry to prepare near-perfect high-generation dendronized polymers from simple building blocks. Applying this methodology to the synthesis

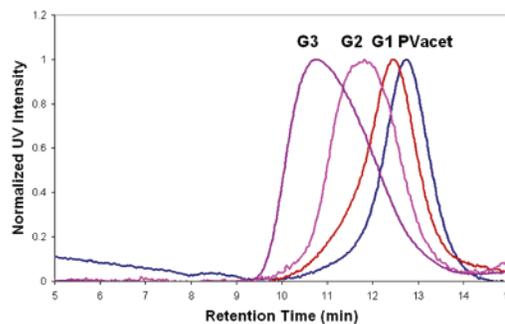


Figure 3. DMF-SEC traces for PVAcet and dendronized linear polymers (G1–G3).

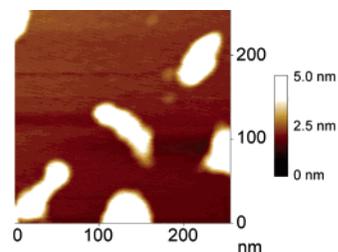


Figure 4. AFM height image of G3-dendronized polymers on mica.

of nanomaterials for catalysis, patterning, and molecular electronics is currently under way.

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Supporting Information Available: Detailed experimental procedures are described. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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