

Doubly-dendronized linear polymers†

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Received (in Cambridge, UK) 5th July 2005, Accepted 24th August 2005

First published as an Advance Article on the web 20th September 2005

DOI: 10.1039/b509398h

Doubly-dendronized polymers were synthesized by grafting polybenzyl ether dendrons onto a poly(hydroxy) styrene polymer with polyaliphatic esters.

Dendronized linear polymers constitute a class of macromolecules that can be uniquely fashioned into different sizes and shapes with a high degree of structural control.¹ At high degrees of dendronization, dendronized linear polymers gain stiffness and adopt a cylindrical shape.² This unique architecture may be useful in certain nanoscale applications where the spherical conformation afforded by classical dendrimers³ is not desirable. Previously, we have described a double-stage convergent growth approach for the preparation of large dendrimers which allowed for quicker and easier synthesis than the classical convergent growth while maintaining monodispersity.⁴ This inspired us to manipulate dendronized linear polymers in the same way to yield doubly-dendronized linear polymers. With this method, higher degrees of dendronization can be achieved, and different nanoenvironments can be attained inside the molecular cylinders by using different inner and outer dendrons. We report a novel microstructure in which a doubly-dendronized polymer is obtained by grafting Fréchet-type dendrons onto a dendronized linear polymer consisting of a poly(*p*-hydroxystyrene) (PHS) backbone dendronized with bis(hydroxymethyl)propionic acid dendrons.

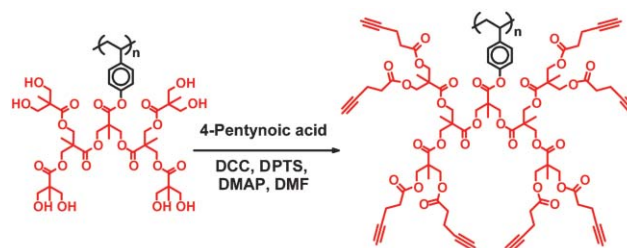
The most common synthetic pathways to dendronized linear polymers are the macromonomer approach,⁵ and the “graft-from”⁶ or “graft-to”⁷ approaches. Our group recently reported a successful graft-to pathway *via* “click chemistry”⁸ which led to complete coverage of a linear polymer backbone with Fréchet-type dendrons up to G3.^{7b} We were not, however, able to achieve complete coverage of the polymer backbone with dendrons above G3, an observation attributed to the low accessibility of the azide group at the focal point of the dendron in the aqueous medium used. To achieve a higher degree of dendronization as well as a new microstructure, we have now employed the “graft-from” approach to prepare a dendronized linear polymer and then have enlarged it using the “graft-to” approach thus obtaining a larger dendronized polymer with two different concentric layers of dendrons. This novel microstructure amounts to a copolymer with the characteristics of a “diblock copolymer” along its radial axis.

The synthesis began with the divergent dendronization of a 60,000 g mol⁻¹ PHS with a polyaliphatic ester.^{6d} The PHS-60K-[G2]-OH and PHS-60K-[G3]-OH were functionalised with 4-pentynoic acid under carbodiimide coupling conditions (Scheme 1).

This yielded second and third generation dendronized polymers with acetylene groups along their peripheries (PHS-60K-[G2]-yne and PHS-60K-[G3]-yne). The preparation of azido poly(benzyl ether) dendrons has been described in previous work.^{7a}

G3 Fréchet-type dendrons containing azide moieties at their focal point were coupled to the acetylene functionalised dendronized linear polymers utilizing a Cu(I)-catalyzed [3 + 2] cycloaddition. The reaction was carried out in a 1 : 1 mixture of H₂O and THF using 5 mol% of CuSO₄·5H₂O with 10 mol% of sodium ascorbate as the reducing agent to produce Cu(I) *in situ* (Scheme 2). The reaction mixtures were repeatedly exposed to freshly prepared catalyst until reaction completion. Coupling of the G3 azide to the PHS-60K-[G2]-yne afforded a pseudo-G5 dendronized linear polymer in 44% yield while the coupling of the G3 azide to the PHS-60K-[G3]-yne afforded a pseudo-G6 dendronized polymer in 10% yield. Final yields for these reactions are low due to the small sample size subjected to purification by both precipitation and preparative size exclusion chromatography (SEC). Analysis by ¹H NMR and IR indicated that the pseudo-G5 and pseudo-G6 dendronized linear polymers were synthesised with near structural perfection. The IR spectra for the conversion of PHS-60K-[G3]-yne to pseudo-G6 shows the disappearance of the acetylene peak at 3300 cm⁻¹ (Fig. 1) while the ¹H NMR revealed no alkyne peak at δ 2.03 ppm.

Fig. 2 compares (a) the SEC traces for DMF solutions of PHS-60K-[G2]-OH, PHS-60K-[G2]-yne, and pseudo-G5, while (b) compares those for PHS-60K-[G3]-OH, PHS-60K-[G3]-yne, and pseudo-G6. There is a monotonic increase in size from the starting polyhydroxyl polymers to pseudo-G5 and pseudo-G6 doubly dendronized polymers. However, the SEC grossly underestimates the true molecular weight (MW) of these polymers, especially for the pseudo-G5 and pseudo-G6, given their highly branched nature. For example, the polymethylmethacrylate equivalent



Scheme 1

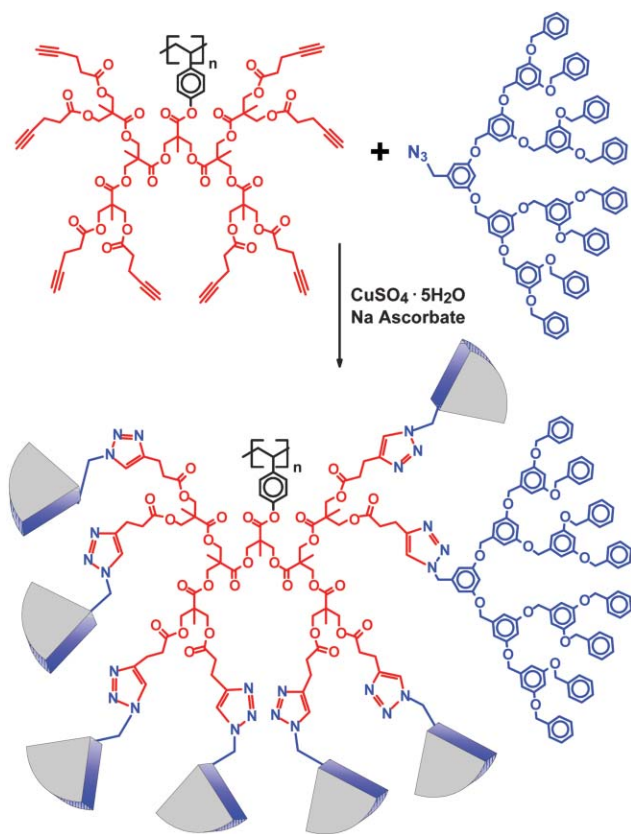
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† Electronic supplementary information (ESI) available: Experimental details. See <http://dx.doi.org/10.1039/b509398h>



Scheme 2

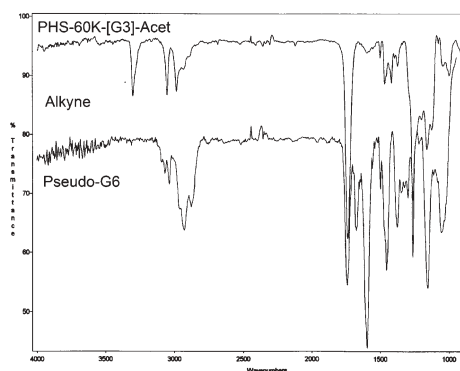


Fig. 1 IR spectra for PHS-60K-[G3]-yne and pseudo-G6.

MW (M_w PMMA) of the pseudo-G6 was estimated at 360k, more than an order of magnitude smaller than expected. Further structural and MW characterization was carried out using SEC coupled to multi-angle laser light scattering (SEC-MALLS). The MW data for the pseudo-G5 and pseudo-G6 compares favorably to the theoretical M_w for a $DP_w = 500$ (Table 1). Along with the NMR and IR data, these provide substantial evidence for the efficiency of this methodology to prepare highly dendronized materials. The small increase in polydispersity observed upon dendronization is consistent with that reported in the literature for other high generation dendronized structures.^{9,6d}

In conclusion, we have successfully prepared dendronized polymers with a very high degree of dendronization and the

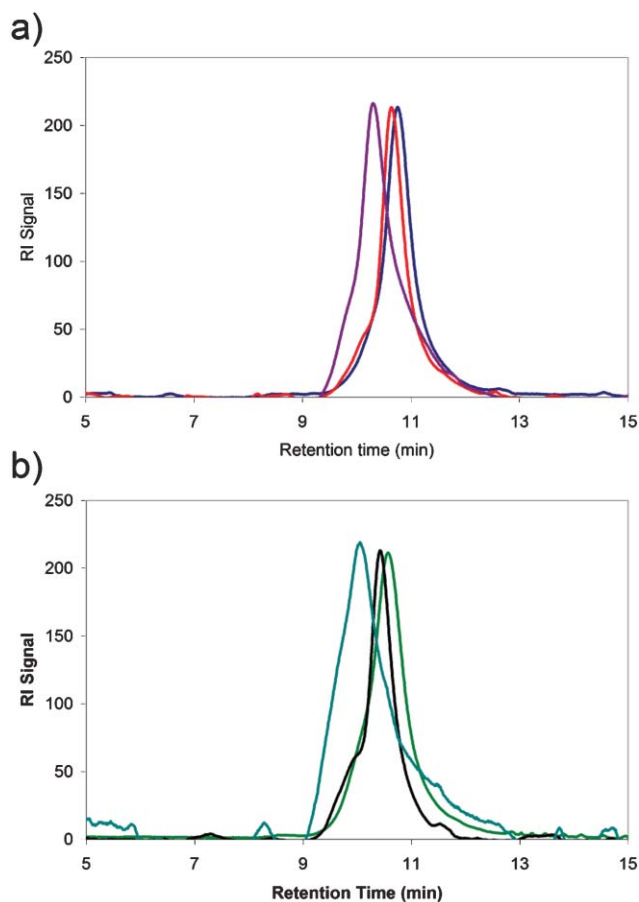


Fig. 2 (a) SEC of PHS-60K-[G2]-OH (blue), SEC of PHS-60K-[G2]-yne (red), pseudo-G5 (purple); (b) SEC of PHS-60K-[G3]-OH (green), SEC of PHS-60K-[G3]-yne (black), pseudo-G6 (teal).

Table 1

Compound	Theoretical M_w ($DP_w = 500$)/g mol ⁻¹	SEC M_w PMMA/ g mol ⁻¹	SEC-MALLS M_w /g mol ⁻¹
Pseudo-G5	3 600 000	365 000	3 490 000
Pseudo-G6	6 900 000	272 000	7 020 000

microstructure of a radial dendritic diblock copolymer. We now plan to probe the microenvironments resulting from encapsulation by the second dendron for use in mimicking molecular transport.

We thank the NSF-DMR and DOE-BES for support of this research. We also thank Marian Snauko and Brett Helms for their help on certain aspects of this project.

Notes and references

- (a) A. D. Schlüter, *Top. Curr. Chem.*, 1998, **197**, 165; (b) A. D. Schlüter and J. P. Rabe, *Angew. Chem., Int. Ed.*, 2000, **39**, 864; (c) C. J. Hawker and K. L. Wooley, *Science*, 2005, **309**, 1200–1205.
- I. Shu, A. D. Schlüter, C. Ecker, N. Severin and J. P. Rabe, *Angew. Chem., Int. Ed.*, 2000, **40**, 4666.
- (a) C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638; (b) D. A. Tomalia, A. M. Naylor and W. A. Goddard III, *Angew. Chem., Int. Ed.*, 1990, **29**, 138.

- 4 K. L. Wooley, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4252.
- 5 (a) C. J. Hawker and J. M. J. Fréchet, *Polymer*, 1992, **33**, 1507; (b) V. Percec, C.-H. Ahn and B. Barboiu, *J. Am. Chem. Soc.*, 1997, **119**, 12978; (c) Z. Bo and A. D. Schlüter, *Chem. Eur. J.*, 2000, **6**, 3235.
- 6 (a) D. A. Tomalia and P. Kirchoff, *U. S. Pat.*, 4 694 064, 1987; (b) R. Yin, Y. Zhu, D. A. Tomalia and H. Ibuki, *J. Am. Chem. Soc.*, 1998, **120**, 2678; (c) S. M. Grayson and J. M. J. Fréchet, *Macromolecules*, 2001, **34**, 6542; (d) M. Yoshida, Z. M. Fresco, S. Ohnishi and J. M. J. Fréchet, *Macromolecules*, 2005, **38**, 334.
- 7 (a) A. Desai, N. Atkinson, F. Rivera, Jr., W. Devonport, I. Rees, S. E. Branz and C. J. Hawker, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 1033; (b) B. Helms, J. L. Mynar, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 15020.
- 8 (a) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004; (b) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596.
- 9 V. Percec, C.-H. Ahn, W. D. Cho, A. M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S. A. Prokhorova, S. S. Sheiko, S. Z. D. Cheng, A. Zhang, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 1998, **120**, 8619.