

Solid-Supported Hyperbranched Polymerization: Evidence for Self-Limited Growth

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In recent years there has been considerable interest in topologically complex polymers such as dendrimers and hyperbranched macromolecules.^{1–5} Hyperbranched polymers are prepared by a one-step synthetic process, yet they maintain many of the architectural features found in their more perfectly defined dendrimer counterparts (i.e., multiple terminal groups, unique focal point functionality, and globular shape). An undesirable feature of the one-step polymerization process is the loss of control in molecular weight, accompanied by a broad molecular weight distribution.⁶ A significant goal, therefore, would be the development of a one-step, AB₂ polymerization process which has built-in molecular weight control and produces substances of low polydispersity. In this paper, we describe a new hyperbranched procedure which takes place on an insoluble solid-support, providing polymers with polydispersity < 1.3 and good molecular weight control in the range of 5–25 kDa. The observed behavior suggests that growth is regulated by a feedback mechanism due to confinement imposed by the support.

We previously reported a solid-supported convergent method for synthesizing well-defined phenylacetylene monodendrons.⁷ Higher generations were difficult to prepare by this method, even though these same generations had been synthesized in solution. On the basis of these findings, we hypothesized that the confined spaces that exist when a dendrimer attaches to a solid-support might provide a means to control the molecular weight in hyperbranched polymerizations. To test this idea, we examined the polymerization reaction shown in Figure 1.⁸ The diiodo focal point monomer was tethered to an insoluble solid-support through a triazene linkage producing **1**.⁹ Dropwise addition of the AB₂ monomer **2** at room temperature to a suspension of **1** in piperidine¹⁰ containing [Pd₂(dba)₃] (dba = dibenzylideneacetone) led to the formation of a white insoluble solid which was determined to be hyperbranched polymer unattached to the support. Examination of the support between crossed polarizers in an optical microscope showed that the beads changed significantly in their appearance (vide infra). We suspected that hyperbranched polymerization was taking place both on and off the support. Cleavage of the polymer-bound

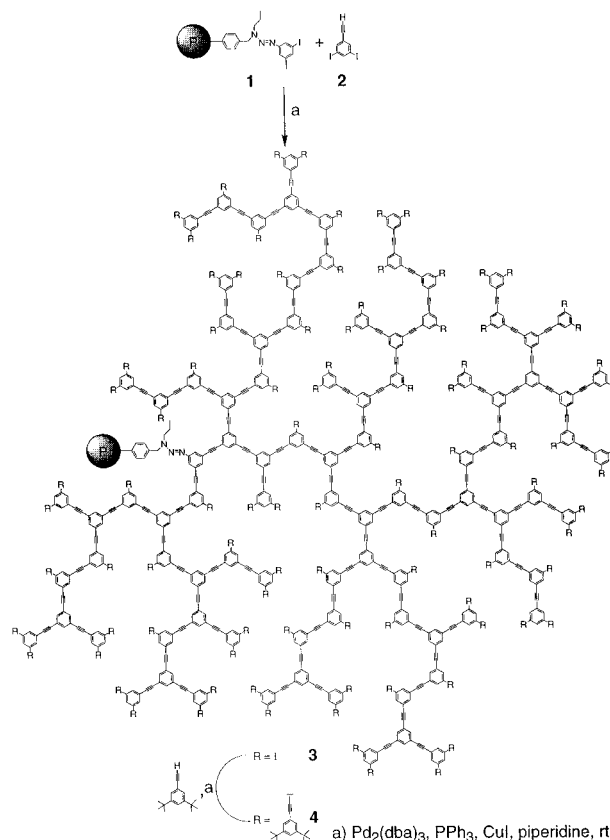


Figure 1. Schematic showing hyperbranched polymerization on a solid-support. The chemical structure represents a polymer with a degree of branching of *ca.* 40% and a molecular weight of *ca.* 25 kDa (for R = (3,5-di-*tert*-butylphenyl)acetylene).

material (**3**) without modifying the terminal iodo groups gave an insoluble product. Therefore, to increase solubility,¹¹ the mixture of support-bound and unattached polymers was reacted with a large excess of (3,5-di-*tert*-butylphenyl)acetylene in presence of [Pd₂(dba)₃] prior to cleaving the hyperbranched polymer from the support. After this capping reaction was complete, hyperbranched polymer **4** was obtained by washing the support with a series of solvents to remove the excess monomer, residual catalyst, and the unattached hyperbranched polymer. At this point, the percent mass increase of the support was noted as a qualitative means of determining the extent of polymerization that took place on the support. Finally, the support-bound hyperbranched polymer was cleaved from the resin by reaction with iodomethane.¹²

The resulting soluble polymer was characterized by ¹H NMR and size exclusion chromatography (SEC). Interestingly, SEC data showed a striking difference between the hyperbranched polymers prepared in solution and those attached to the solid-support. The hyperbranched polymer isolated from the solid-support gave a symmetrical SEC elution profile with narrow polydispersity (1.3). In contrast, a hyperbranched polymer prepared in solution under identical conditions but without the solid-support had a bimodal elution profile characterized by a relatively narrow peak at very high molecular weight and a long tailing (integration of the entire area including the tail gave a polydispersity of >2.5). SEC traces similar to the solution polymerization were also recorded for unbound polymer isolated from the filtrate of the solid-support washings. Characterization by ¹H NMR indicated near complete substitution of iodo termini

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(1) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *I. Angew. Chem.* **1990**, *102*, 119–157.

(2) Kim, Y. H. *Adv. Mater.* **1992**, *4*, 764–766.

(3) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 193–313.

(4) Fréchet, J. M. J. *Science* **1994**, *263*, 1710–1715.

(5) Voit, B. I. *Acta Polym.* **1995**, *46*, 87–99.

(6) Hult and co-workers reported moderate success with a staged polyesterification process in which stoichiometric amounts of monomer corresponding to each generation were added successively. Polymers of molecular weight in the range of 1.4–5.6 kDa and of polydispersity 1.4–1.9 were produced. Malmstrom, E.; Johansson, M.; Hult, A. *Macromolecules* **1995**, *28*, 1698–1703.

(7) Bharathi, P.; Patel, U.; Kawaguchi, T.; Pesak, D. J.; Moore, J. S. *Macromolecules* **1995**, *28*, 5955–5963.

(8) All new monomeric compounds were characterized by ¹H and ¹³C NMR, mass spectrometry, and elemental analysis. Polymers were characterized by ¹H NMR and size exclusion chromatography.

(9) Young, J. K.; Nelson, J. C.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 10841–10842.

(10) Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403–6406.

(11) Xu, Z. F.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 246–248.

(12) Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, 2465–2466.

Table 1. Yield and Polydispersity Data of Hyperbranched Polymers Obtained as a Function of the Monomer:Focal Point Monomer Molar Ratio on Different Solid-Supports^a

monomer:focal point monomer (molar ratio)	mass increase of solid-support (%) ^b			yield of solid-supported hyperbranched polymer ^c (%)			polydispersity of solid-supported hyperbranched polymer		
	I	II	III	I	II	III	I	II	III
17.5:1	200	100	26	53	7	19	1.37	1.46	1.56
35:1	250	190	120	35	21	9	1.33	1.57	1.41
70:1	470	550	55	35	18	7	1.28	1.38	1.51
140:1	760	900	190	19	17	8	1.34	1.42	1.49
280:1	1025	1230	235	20	14	4	1.29	1.44	1.89
560:1	1245	1350	305	12	6	3	1.47	1.73	1.74

^a Support I: initial degree of functionalization 0.7 mmol/g, 200–400 mesh, crosslinked with 1% divinyl benzene. Support II: initial degree of functionalization 1.7 mmol/g, 200–400 mesh, crosslinked with 1% divinylbenzene. Support III: initial degree of functionalization 1.7 mmol/g, 200–400 mesh, crosslinked with 2% divinylbenzene. ^b Calculated as $(\Delta m/m_0) \times 100\%$, where Δm is the change in mass of the support and m_0 is the initial mass of the support. ^c Yield of hyperbranched polymer obtained after cleavage from the solid-support (theoretical yield based on amount of monomer added). See Supporting Information for details.

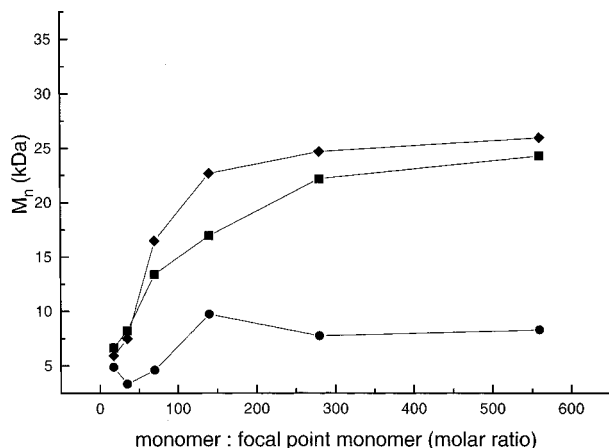


Figure 2. Plots showing the number average molecular weight (M_n) versus the monomer:focal point monomer molar ratio for solid-supported hyperbranched polymerization: (◆) solid-support I (0.7 mmol/g, 200–400 mesh, crosslinked with 1% divinylbenzene); (■) solid-support II (1.7 mmol/g, 200–400 mesh, crosslinked with 1% divinylbenzene); (●) solid-support III (1.7 mmol/g, 200–400 mesh, crosslinked with 2% divinylbenzene).

by (3,5-di-*tert*-butylphenyl)acetylene, as judged by the integral ratio of aromatic to *tert*-butyl proton signals.¹³ However, inadequate chemical shift dispersion made it impossible to determine the degree of branching.¹⁴

We expected the competition between polymerization on and off the support to be influenced strongly by the instantaneous concentration of free monomer, with higher concentrations favoring unbound polymerization. Extensive experimentation with variables such as rate of monomer addition and influx monomer concentration gave results consistent with this notion, as judged by the percent mass increase of the support (see Supporting Information). These variables did not appreciably influence polydispersity.

Interestingly, we found that the molecular weight of the hyperbranched polymer on the solid-support could be controlled over the range of *ca.* 5–25 kDa by the amount of monomer added relative to the support and also on the nature of the solid-support (e.g., percent crosslinked and initial loading). Plots of M_n versus the monomer to focal point monomer molar ratio with three different solid-supports are shown in Figure 2. It can be seen that molecular weight reaches a limiting value in all three cases. The limiting molecular weights decrease as the loading or degree of crosslinking increases. The polydispersity is nearly constant for a particular support, as shown in Table 1. The percent mass increase of the support follows a similar pattern. The yield of hyperbranched polymer isolated

after cleaving the polymer from the support (yield based on added **2**) decreases as the monomer to focal point monomer ratio increases (Table 1), further suggesting that growth on the beads reaches a limit. Excess monomer apparently polymerizes in solution, never attaching to the support.

Examination of the dry solid-support by polarized optical microscopy reveals that the beads become birefringent and grow in size as they take up more monomer. We believe that the birefringence is caused by internal stress within the expanded polymer beads. Interestingly, at high monomer to focal point monomer ratios, the spherical beads shatter into a fine powder. These observations together with the low polydispersity and asymptotic approach to a limiting M_n suggest that growth on the support is self-regulated. Possible feedback mechanisms responsible for this control may be confinement of the growing hyperbranched polymer within the boundaries of the support or the impingement of adjacent dendrimers on one another.

In addition to the benefits of molecular weight control, there are several other potential advantages of solid-supported hyperbranched polymerizations. First, since the focal point functional group is bound to the solid-support, intramolecular cyclization between the focal point and a peripheral group is not possible. This problem has been implicated as limiting solution grown hyperbranched polymers.¹⁵ Second, the terminal ends of the hyperbranched polymer can easily be modified with different monomers, thus providing many new varieties of hyperbranched polymers from a common internal structure. This type of modification can be extended to other monomers to make hyperbranched copolymers with concentric layered structures.¹⁶ Third, cleavage of the hyperbranched polymer from the support after terminal group capping insures one unique focal point functional group per molecule. This site could be used to construct multidendron architectures or hybrid structures. Finally, use of a solid-support greatly simplifies the purification of these polymers. Excess reagents, monomers, and unbound polymer can easily be washed away. We are currently extending these methods to other hyperbranched polymers and other supports¹⁷ as well as probing the mechanism of molecular weight control.

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Supporting Information Available: Experimental procedures for the synthesis, calculation of theoretical yield, and tables of variables such as rate of monomer addition and influx monomer concentration (10 pages). See any current masthead page for ordering and Internet access instructions.

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(15) Percec, V.; Chu, P. W.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441–4453.

(16) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1992**, *114*, 8405–8413.

(17) Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Wells, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 3773–3774.

(13) Xu, Z.; Kahr, M.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537–4550.

(14) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583–4588.