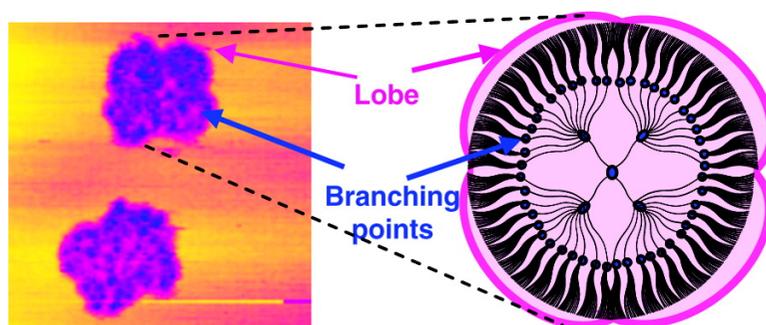


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## Synthesis and AFM Structural Imaging of Dendrimer-Like Star-Branched Polystyrenes

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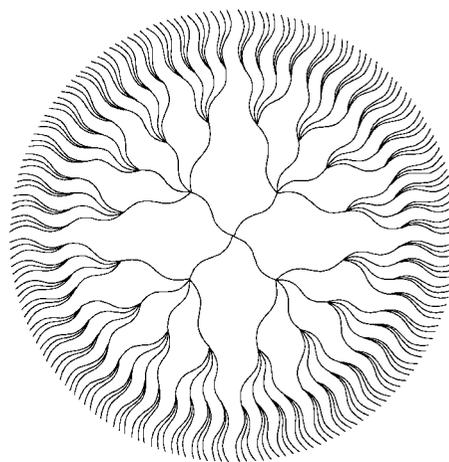
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Dendrimer-like star-branched polymers similar to dendrimers in branched architecture have recently appeared as a new class of hyperbranched polymers<sup>1–4</sup> and have been synthesized by a stepwise iterative methodology based on either a “core-first” divergent<sup>5–7</sup> or an “arm-first” convergent approach.<sup>8–10</sup> Since these polymers are constructed by several layers (or generations) consisting of two or more polymer chains as repeating units, they are much higher in molecular weight and much larger in molecular size than dendrimers. Some examples were actually over 1 million g/mol in molecular weight and several 10 nm in size.<sup>10b,d</sup>

Isolated dendrimers have been visualized as spherical dome-shaped molecules<sup>11a,b</sup> by AFM and STM, but although they are believed to be also globular macromolecules, no direct information on the shape and internal structure of dendrimer-like star-branched polymers is available at the present time. Recently, the direct visualization of high molecular weight architectural polymers such as combs, dendrigrafts, and comb-star polymers by AFM imaging has been reported with great success.<sup>12,13</sup> Therefore, we attempted to visualize dendrimer-like star-branched polymers poly(methyl methacrylate) by AFM tapping mode. A first attempt was performed on a fourth-generation star-branched polymer poly(methyl methacrylate),<sup>14</sup> Figure 1, which possesses branches interconnected by tetrafunctional branching points from the first to third layers and by trifunctional branching points on the average in the outer fourth layer and is  $3.8 \times 10^6$  g/mol in  $M_n$  value and 30.2 nm in hydrodynamic radius,  $R_h$ .

On highly oriented pyrolytic graphite (HOPG), several isolated polymer molecules appeared on the AFM image as diffuse, completely flattened objects with an average square size close to 100 nm and height very small of about 0.6 nm, indicating that the molecules that were too soft and spread out on HOPG and AFM images could not show their internal structure.

In order to obtain clear AFM images which give us information on shape and architectural organization of dendrimer-like star-branched polymers, we decided to synthesize larger and more densely tough dendrimer-like star-branched polystyrene. For this purpose, the following iterative methodology involving the sequential three stages has been adopted: (a) preparation of living anionic AB diblock copolymer of 3-*tert*-butyldimethylsilyloxymethylstyrene (**1**)<sup>15</sup> with styrene, (b) linking reaction of the living anionic block copolymer thus synthesized with either a core compound substituted with four benzyl bromide



**Figure 1.** Structure of fourth-generation dendrimer-like star-branched poly(methyl methacrylate) with tetrafunctional and trifunctional branching points.

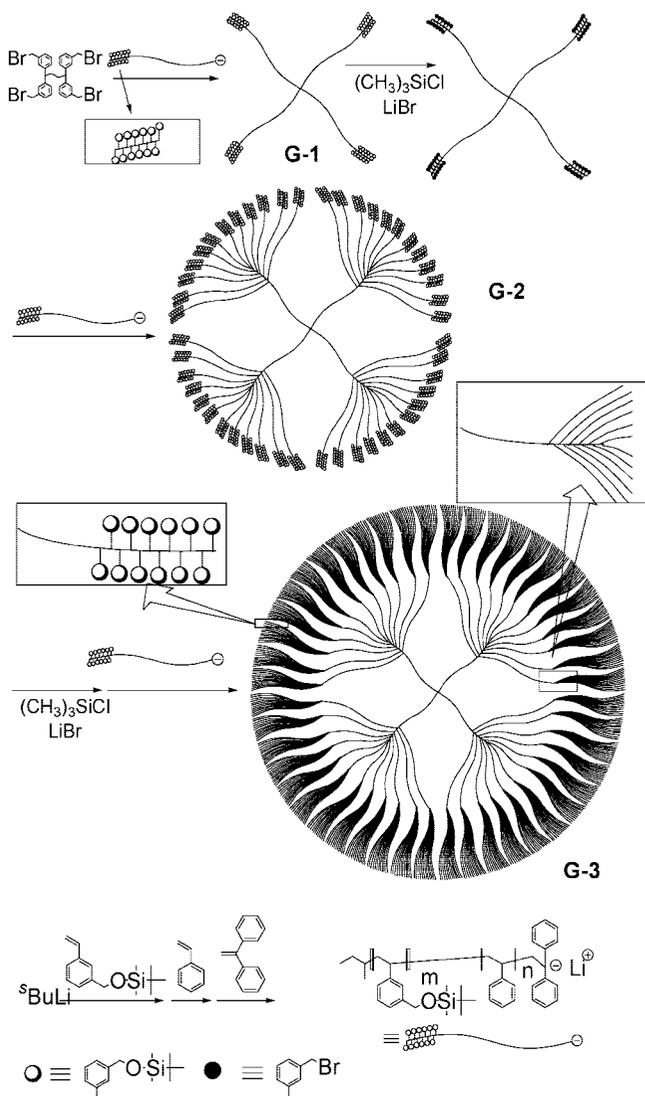
(BnBr) functions to yield G-1 or BnBr chain-multifunctionalized polystyrene (PS) (G-1 to G-2 and G-2 to G-3), and (c) transformation reaction for regeneration of BnBr functions usable as next reaction sites. In practice, the BnBr functions were quantitatively regenerated by treatment of the poly(**1**) block with  $(\text{CH}_3)_3\text{SiCl}/\text{LiBr}$ . Accordingly, the number of BnBr reaction sites per branch is not exactly but averagely defined by the living anionic polymerization of **1**.<sup>15</sup> The synthetic outline is illustrated in Scheme 1.

In the first iteration step, the living anionic block copolymerization was carried out by the sequential addition of **1** followed by styrene in THF at  $-78^\circ\text{C}$  for 20 and 10 min, respectively, and 1,1-diphenylethylene (DPE) was subsequently added for end-capping. Then, the resulting living anionic block copolymer ( $M_n = 2.53 \times 10^4$  g/mol,  $M_w/M_n = 1.02$ ,  $\text{DP}_{\text{P}(1)}/\text{DP}_{\text{PS}} = 12.3/216$ ) was in situ added to react with the core compound substituted with four BnBr moieties at  $-78^\circ\text{C}$  for 20 min. A 1.2-fold excess of living polymer was used toward the BnBr function. SEC chromatogram of the reaction mixture (available as Supporting Information) shows two distinct sharp peaks corresponding to the linked product and the deactivated living block copolymer used in excess in the reaction. On the basis of the two peak areas, the reaction was found to proceed quantitatively. The objective polymer isolated in 90% yield by fractional precipitation exhibits a sharp monomodal SEC distribution. The  $M_n$  value of  $1.02 \times 10^5$  g/mol determined by RALLS in THF was in excellent agreement with that predicted

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**Scheme 1.** Iterative Methodology Followed for the Synthesis of Large and More Densely Tough Dendrimer-Like Star-Branched Polystyrene of Third Generation



( $1.03 \times 10^5$  g/mol), and the molecular weight distribution was narrow, the  $M_w/M_n$  value being 1.03.

In the second iteration, the polymer G-1 was brominated with  $\text{Me}_3\text{SiCl}/\text{LiBr}$  and then reacted with living anionic block copolymer end-capped with DPE ( $M_n = 2.34 \times 10^4$  g/mol,  $M_w/M_n = 1.02$ ,  $\text{DP}_{\text{P}(1)}/\text{DP}_{\text{PS}} = 12.4/195$ ) in THF at  $-40^\circ\text{C}$  for 2 h. The reaction proceeded virtually quantitatively under such conditions, and the linked product was isolated in 80% yield by fractional precipitation. The  $M_n$  value determined by RALLS was  $1.23 \times 10^6$  g/mol, in agreement well with that predicted ( $1.25 \times 10^6$  g/mol). A sharp monomodal distribution was attained ( $M_w/M_n = 1.05$ ). Thus, the analytical results clearly confirm the successful synthesis of the second-generation dendrimer-like star-branched polystyrene (G-2).

The third iterative process involved the bromination of the G-2 by the same treatment with  $\text{Me}_3\text{SiCl}/\text{LiBr}$  and the subsequent linking reaction with a living anionic block copolymer end-capped with DPE ( $M_n = 2.33 \times 10^4$  g/mol,  $M_w/M_n = 1.02$ ,  $\text{DP}_{\text{P}(1)}/\text{DP}_{\text{PS}} = 12.5/192$ ) in THF at  $-40^\circ\text{C}$  for a longer reaction time of 6 h. The objective third-generation polymer G-3 isolated in 80% yield by fractional precipitation shows a sharp monomodal SEC distribution ( $M_w/M_n = 1.08$ ). The molecular weight

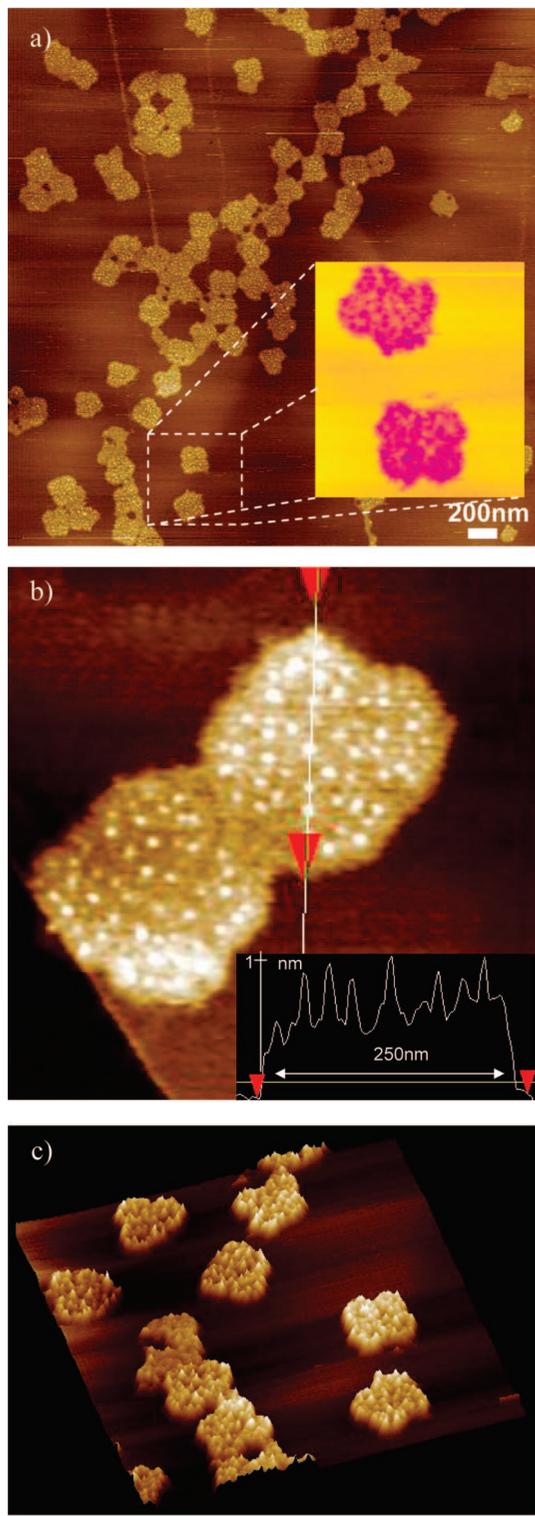
determined by RALLS in THF was  $1.43 \times 10^7$  g/mol, very close to the predicted value of  $1.49 \times 10^7$  g/mol. Large numbers of up to 608 ( $12.4 \times 12.3 \times 4$ ) branches carrying 7600 ( $608 \times 12.5$ ) termini were introduced into the third layer. Thus, the methodology readily allows the synthesis of a much higher molecular weight and more densely branched polymer than the fourth-generation PMMA studied above ( $M_n = 3.8 \times 10^6$  g/mol) only by repeating the iterative process three times. The  $R_h$  and  $R_g$  values of this G-3 were determined by dynamic light scattering to be 46.5 and 46.7 nm, respectively. The ratio of  $R_g$  to  $R_h$  is 1.00 and relatively higher than the value of 0.775 of the Pyun–Fixman prediction theoretically representing compact sphere shape.<sup>16</sup>

The direct visualization of this polymer sample has been conducted by the similar AFM analysis on HOPG in the light tapping mode. Deposits of the G-3 dendrimer-like polystyrene were obtained by spin casting of their  $\text{CH}_2\text{Cl}_2$  solutions (0.1 mg/mL) on graphite plates.

The G-3 polymers appear on topographic AFM images, Figure 2a, as completely flattened objects with a relatively homogeneous and symmetrical square-like or rectangle-like shape, in contrast to most AFM pictures of hyperbranched polymers which generally display spherical or cylindrical objects.<sup>12,13</sup> Considering a square shape, the isolated G-3 dendrimers show an average diagonal size of 250 nm and a height of less than 1 nm. This very low last value is consistent with the spreading out of the macromolecule as a monolayer on HOPG, suggesting that most of the PS aromatic rings are lying flat on the graphite surface due to the still low polymer compactness and strong interactions. A rough calculation of the diameter of the third generation macromolecule in a fully extended conformation, considering the sum of the PS DPn of the different generations, that is,  $D = 0.25 \times 2(243 + 225 + 224) = 346$  nm, is in satisfactory agreement with the measured value and confirms the important spreading of the molecule.

Among the molecules observed, a large number clearly appears as constituted of four interconnected lobes; see colored inset in Figure 2a. This corresponds to the building of the dendrimer-like polymer in four substructures issued from the tetrafunctional core used as precursor for the covalent assembly of the macromolecular dendrimer. Interestingly, the image of magnified macromolecules, Figure 2b, shows the presence inside the objects of a large number of regularly distributed white spots that correspond to more compact and harder zones in the polymer. Their number, around 50 per dendrimer, closely corresponds to the calculated 52 connecting domains between G-1 and G-2 (4) and G-2 and G-3 (48); see Scheme 1. In the cross-section given as an inset in Figure 2b, the harder domains appear as a series of peaks of about 2 times the height of the less dense and softer domains constituted by PS branches with an average molar mass between branching segments of  $2.5 \times 10^4$  to  $2.3 \times 10^4$  for the different generations. This particular topology is highlighted in 3D in Figure 2c, in which the harder domains appear as white peaks over the less dense and softer PS domains. This represents one of the first examples of direct visualization of the internal structure of a macromolecular dendrimer.

On these grounds, we are now synthesizing high generation dendritic polymers using different core and branching point functionalities to investigate the impact of these parameters on their shape, dimensions, and physico-chemical characteristics.



**Figure 2.** Topographic AFM images of PS dendrimer of generation 3 obtained from deposits of their  $\text{CH}_2\text{Cl}_2$  solution on HOPG: (a) general view; (inset) selected objects showing clearly a 4 lobes architecture; coloration helps to better visualize the molecule shape and enhances the contrast between soft and hard regions; (b) magnified objects showing the presence in their structure of internal white spots corresponding to harder zones; (inset) cross-section of one dendrimer showing the relative height of alternating soft domains and hard branching points; (c) three-dimensional image emphasizing the presence and distribution of hard and soft domains.

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**Supporting Information Available:** Materials, experimental procedures, and characterization methods (SEC, RALLS, AFM). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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