Improvements in the Synthesis of Phenylacetylene Monodendrons Including a Solid-Phase Convergent Method

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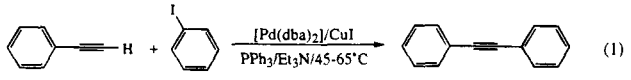
Received April 19, 1995; Revised Manuscript Received June 12, 1995[⊗]

ABSTRACT: A new scheme for the synthesis of phenylacetylene dendritic macromolecules is described which greatly facilitates the large-scale production of high molecular weight monodendrons. Simply by inverting the monomer protecting group scheme from B_2A_p to A_2B_p (where A = ArC≡CH; B = ArI; A_p and B_p are protected versions of these groups), we show that the repetitive synthesis can be propagated through at least one higher generation on reaction scales 2 orders of magnitude greater than previously possible. Using this new scheme, we have prepared gram quantities of phenylacetylene monodendrons through generation four (**I-M$_{63}$-(*t*-Bu)$_{64}$**), in high yields. Possible reasons for the improvements are discussed. We furthermore show that the new route is amenable to a solid-phase convergent dendrimer synthesis which involves tethering the focal point monomer to an insoluble support. Preparation of phenylacetylene monodendrons by the solid-phase method is demonstrated through generation four, yielding monodendron products identical to those synthesized by solution methods. However, at generation four, coupling reactions using polymer supports can only be driven to completion with light loading of the focal point monomer. The solid-phase convergent method offers several advantages, especially in the synthesis of early generation monodendrons.

Introduction

Dendrimer syntheses[1] provide a unique opportunity to study chemical reactivity as a function of molecular size in well-defined systems. In previous work from our laboratory, we described the synthesis of dendritic macromolecules based on phenylacetylene monomers.[2] The coupling step involves palladium-catalyzed carbon-carbon bond formation between aryl halides and terminal acetylenes (eq 1).[3] A major side reaction is oxidative



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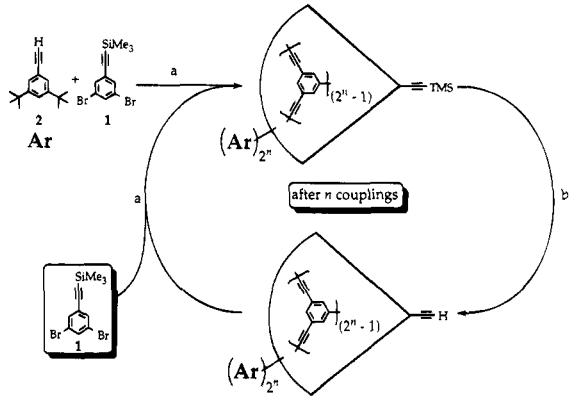
dimerization leading to symmetrical diacetylenes.[2] In early generations, the amount of diacetylene is low and relatively insensitive to reaction conditions (typically <2%). There is a significant increase in diacetylene formation as the generation increases. Minimization of this product could be realized by careful adjustment of reaction conditions. However, synthesis of the fourth generation monodendron was impossible as the diacetylene reaction manifold becomes dominant. These observations point to an interesting, yet poorly understood, molecular size-dependent switch in chemical reactivity.

From a practical standpoint, there is much to be gained by optimizing reaction conditions and improving methods for manipulating and purifying the high molecular weight products from dendrimer preparations. These aspects become especially significant as the reaction scale increases. In our original report we described procedures that were suitable only for producing milligram quantities of the third generation monodendron.[2] We report here alternative chemistry to prepare related phenylacetylene monodendrons, including the synthesis of monodendrons on an insoluble solid support. This new scheme, either in solution or on the solid support, greatly improves the yield and simplifies purification, making possible the preparation of gram quantities, up to generation four, of phenylacetylene monodendrons. This corresponds to one generation higher than we were previously able to realize, and the reaction scale is more than 100-fold larger than that in our earlier work. This example illustrates how molecular weight dependent reactivity can potentially derail the development of new dendrimer syntheses, even when reactions are high-yielding and well-optimized on small-molecule substrates. It furthermore illustrates how subtle changes in monomer protecting group chemistry can have significant consequences on the ability to sustain a dendrimer reaction sequence.

Scheme 1. Synthetic Route to Phenylacetylene Monodendrons As Reported in Reference 2a[a]



[a] (a) $Pd(dba)_2$, CuI, PPh_3, TEA, 75 °C. (b) K_2CO_3, rt, MeOH/CH_2Cl_2.

Results and Discussion

Our original convergent synthesis was based on the repetitive chemistry shown in Scheme 1. The terminal

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.

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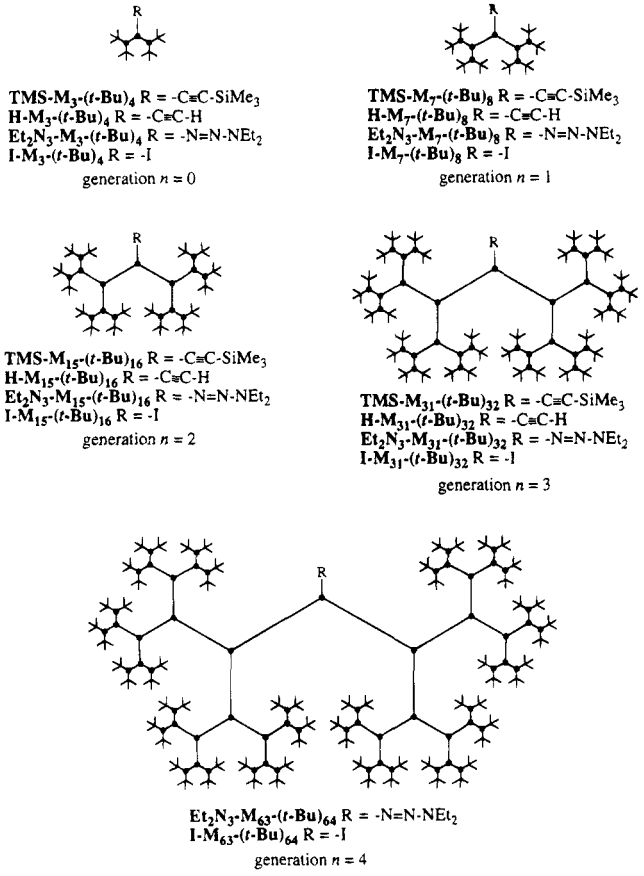
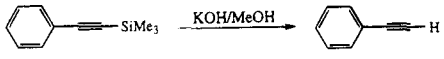


Figure 1. Chemical structure of phenylacetylene monodendrons. Each 1,3,5-triconnected arene vertex of the dendrimer fragments is shown as a filled circle (●), and the acetylene linkages are shown as solid lines (—).

acetylene of a focal point monomer is suitably masked as its trimethylsilyl derivative which can be deprotected in high yield as shown in eq 2. The initial cycle involves



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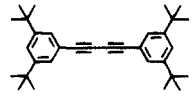
coupling focal point monomer **1** with 2.2 equiv of a terminal alkyne **2** to construct the dendrimer's periphery (n = 0 at the completion of this stage) yielding monodendron **TMS-M3-(*t*-Bu)4**.[4] High yields are obtained, and only a small amount of diacetylene byproduct **3** is noted. Removal of the TMS group leaves a



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terminal acetylene at the focal point (**H-M3-(*t*-Bu)4**), completing one cycle. Palladium-catalyzed cross-coupling of 2 equiv of the new monodendron with focal point monomer **1** provides a first generation (n = 1) product, **TMS-M7-(*t*-Bu)8**. Continuation of this process produced the family of monodendrons shown in Figure 1, up to **TMS-M31-(*t*-Bu)32**.

It is noteworthy that, for the convergent synthesis shown in Scheme 1, monodendron yield steadily diminishes as a function of generation, with the monodendron product being accompanied by an increasing proportion of symmetrical diacetylene resulting from oxidative dimerization. This made it increasingly difficult to purify the desired monodendron by silica gel chromatography since the R_f value of the monodendron is similar to that of the diacetylene byproduct. Attempts to prepare the next generation monodendron, **TMS-M63-(*t*-Bu)64**, were unsuccessful by this route. In the attempted coupling, only the byproduct **4** was isolated (eq 3). However, it should be noted that we successfully

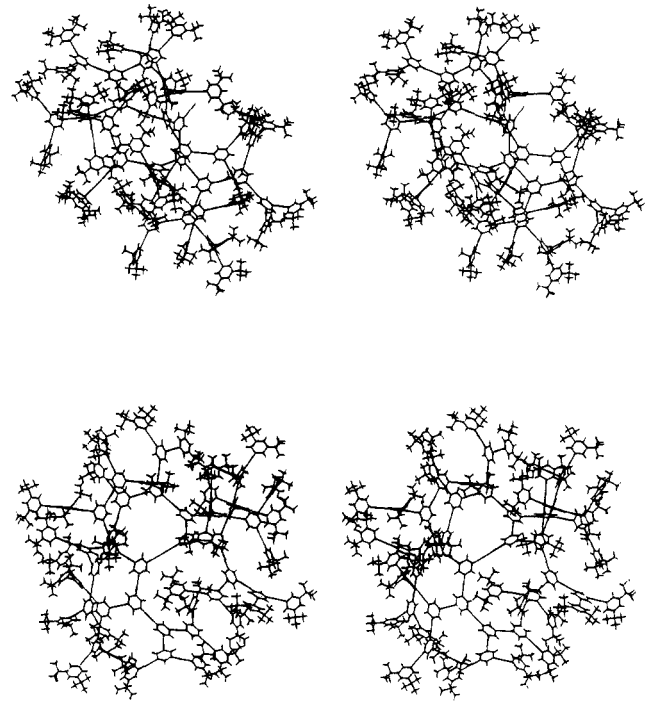
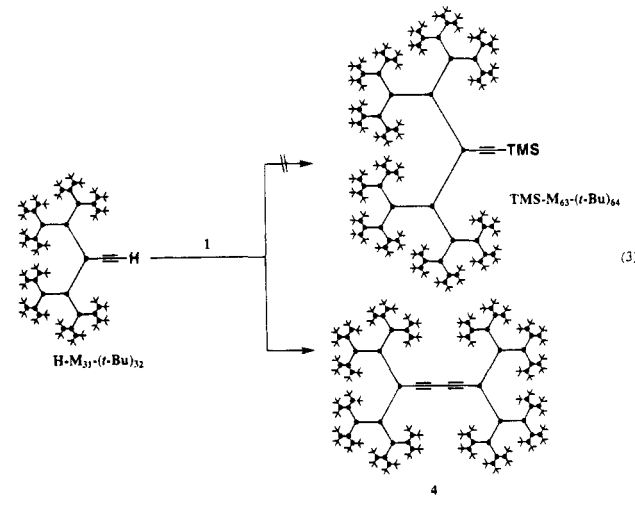


Figure 2. Stereodiagrams of **H-M63-(*t*-Bu)64** and diacetylene **4**.



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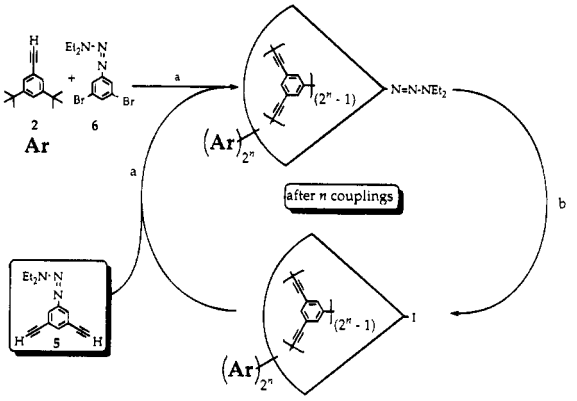
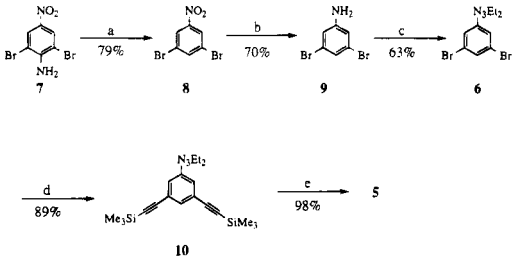
coupled 3 equiv of **H-M31-(*t*-Bu)32** with 1,3,5-triiodobenzene to prepare the corresponding tridendron, **D-94**. Thus, it was evident that monodendron **TMS-M63-(*t*-Bu)64** could be made. We attribute the failed synthesis of **TMS-M63-(*t*-Bu)64** to the lower reactivity of aryl bromide verses aryl iodide groups, since **D-94** could not be prepared from 1,3,5-tribromobenzene. Although we cannot provide a detailed explanation as to why the reaction manifold progressively shifts toward the diacetylene pathway for aryl bromides at increasing generation, we speculate that it is related to the severe steric crowding around the focal point group of the product **TMS-M63-(*t*-Bu)64**. Stereodiagrams of the two products from eq 3, **H-M63-(*t*-Bu)64** and diacetylene **4**, are shown in Figure 2. In **H-M63-(*t*-Bu)64**, the halves

Scheme 2. Synthetic Route to Phenylacetylene Monodendrons Using Focal Point Monomer 5[a]



[a] (a) $Pd(dba)_2$, CuI, PPh_3, TEA, 75 °C. (b) MeI, 110 °C.

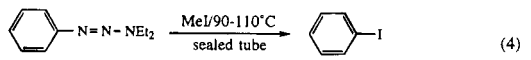
Scheme 3. Synthesis of Monomer 5[a]



[a] (a) (1) AcOH, H_2SO_4, $NaNO_2$, (2) EtOH, Cu_2O. (b) $SnCl_2{\cdot}2H_2O$, EtOH, 75 °C. (c) (1) HCl, H_2O, MeCN, (2) $NaNO_2$, H_2O, 0 to −5 °C, (3) H_2O, MeCN, K_2CO_3, $NHEt_2$. (d) $HC{\equiv}CSiMe_3$, $Pd(dba)_2$, CuI, PPh_3, NEt_3, 70 °C. (e) MeOH, CH_2Cl_2, K_2CO_3, room temperature.

of the molecule (31-mer segments) are oriented into similar regions of space, while in **4** the 31-mer segments radiate away from one another. Thus, we suspect that **4** becomes kinetically preferred due to its less severe steric requirements.

It is evident from the above discussion that a significant improvement in the convergent synthesis of phenylacetylene monodendrons could be gained by using aryl iodides in the cross-coupling step. The aryl iodide of a focal point monomer is suitably masked as its dialkylaryltriazene derivative which can be deprotected in high yield as shown in eq 4.[5] A readily available focal point



(4)

monomer for convergent synthesis which employs aryl iodide cross-coupling is triazene **5**, as shown in Scheme 2. An important difference between Schemes 1 and 2 is the switch in focal point functional group from terminal acetylene to aryl iodide. Overall, this corresponds to inverting the monomer protecting group scheme from B_2A_p to A_2B_p. In this way, aryl iodides can be used in the cross-coupling reaction for all but the initial cycle. Besides the enhanced reactivity, we also anticipated that the large difference in polarity between the triazene group and the corresponding aryl iodide would aid in chromatographic separation. Monomer **5** could be conveniently prepared on the 50-g scale using the sequence of reactions outlined in Scheme 3, starting from commercially available 2,6-dibromo-4-nitroaniline (**7**). Complete details for these preparations are provided in the Experimental Section.

Entry into the repetitive cycle of Scheme 2 involves coupling **6** with 2.2 equiv of 3,5-di-*tert*-butylphenylacetylene, to give zero generation monodendron **Et_2N_3-M_3-(*t*-Bu)$_4$**, having two peripheral units in 74% yield. A small amount of an impurity, confirmed as diacetylene byproduct **3**, was easily removed by chromatography due to its high R_f value relative to the desired product. This first reaction was very similar to the preparation of zero generation monodendron **TMS-M_3-(*t*-Bu)$_4$** in Scheme 1, which involves an aryl dibromide focal point monomer and a terminal alkyne peripheral group. Therefore, it is not surprising that the diacetylene impurity **3** was observed in this first step. This reaction and corresponding separation could be conducted conveniently on scales of more than 20 g. Following this initial coupling reaction, the triazene group was deprotected, leaving an aryl iodide at the monodendron focal point (**I-M_3-(*t*-Bu)$_4$**) in 84% yield. Monomer **5** was then coupled with 2.2 equiv of **I-M_3-(*t*-Bu)$_4$** to give the first generation (n = 1) monodendron, **Et_2N_3-M_7-(*t*-Bu)$_8$**, having four peripheral units. Continuation of this process gave the series of monodendrons shown in Figure 1. The synthesis was carried out successfully through generation n = 4 (**Et_2N_3-M_{63}-(*t*-Bu)$_{64}$**) in high yield.

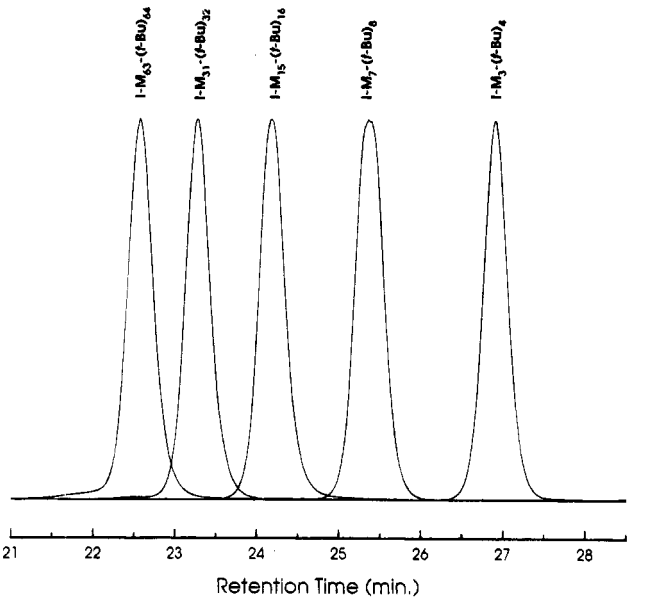


Figure 3. Size-exclusion chromatographs of **I-M_y-(*t*-Bu)$_{y+1}$**. From left to right: y = 63, 31, 15, 7, and 3.

It is noteworthy that, with the reaction sequence shown in Scheme 2, diacetylene byproducts from oxidative dimerization were no longer generated in detectable levels. The absence of the diacetylene dimer can be attributed to several factors, the most significant perhaps being the use of the more reactive aryl iodides. An additional reason is that the reagent in excess changes from a terminal acetylene to an aryl iodide. Consequently, the rate of bimolecular self-coupling is reduced due to the lower concentration of terminal acetylene. Even if the diacetylene byproduct formed, the side products have at least two triazene groups, making them relatively polar and therefore easily separated chromatographically from the desired monodendron.

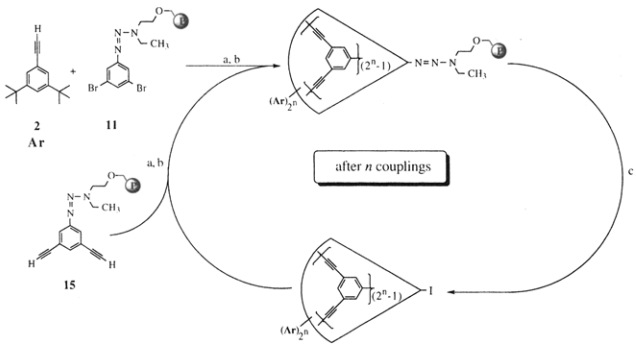
The purity of the monodendrons obtained by Scheme 2 is at least as high as that of those prepared using Scheme 1. Figure 3 shows size-exclusion chromatographic (SEC) traces for the iodide-terminated monodendrons. All of the monodendrons gave a single, sharp, symmetrical peak of low polydispersity (≤1.03). In addition to SEC, all monodendrons were characterized by ^1H NMR and elemental analysis (see the Experi-

Table 1. Yield Data for Monodendrons Prepared by Solution and Solid-Phase Methods

		isolated yield (%)[a]			
	generation	Scheme 1 X = −C≡C−H	Scheme 2 X = −I	Scheme 4 X = −I	wt % monodendron on solid support
0	**X-M**$_3$-(*t*-Bu)$_4$	93	88	85	9.7
1	**X-M**$_7$-(*t*-Bu)$_8$	80	82	80	33
2	**X-M**$_{15}$-(*t*-Bu)$_{16}$	51	84	78	53
3	**X-M**$_{31}$-(*t*-Bu)$_{32}$	27	81	77	70
4	**X-M**$_{63}$-(*t*-Bu)$_{64}$	0[b]	85	*c* and *d*	83[c]
4	**X-M**$_{63}$-(*t*-Bu)$_{64}$			68[e]	76[d]

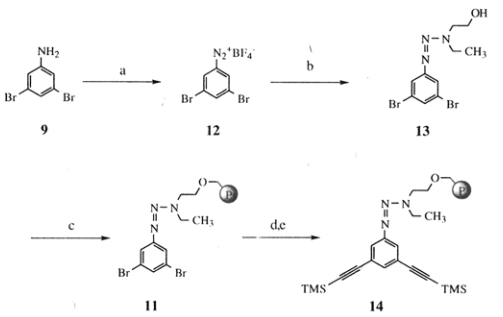
[a] Overall yield of purified products for the complete cycle. [b] Diacetylene from oxidative dimerization is the only product isolated. [c] Solid support functionality: 0.7 mequiv/g. [d] Mixture of monocoupled product and **I-M**$_{63}$-(*t*-Bu)$_{64}$ observed. [e] Solid support functionality: 0.45 mequiv/g.

Scheme 4. Convergent Solid-Phase Synthesis of Phenylacetylene Monodendrons[a]



[a] (a) Pd(dba)$_2$, CuI, PPh$_3$, 2:1 (v/v) TEA/DMF. 75 °C. (b) Wash solid support (3 × 30 mL/g of polymer) with methanol, DMF, dichloromethane, methanol, $(C_2H_5)_2NCS_2Na{\cdot}3H_2O$, DMF, dichloromethane, and methanol. (c) MeI, 110 °C.

Scheme 5. Synthesis of a Focal Point Monomer Tethered to an Insoluble Support[a]



[a] (a) $BF_3{\cdot}OEt_2$, *t*-$BuNO_2$, −15 °C. (b) 2-(Ethylamino)ethanol, K_2CO_3, DMF, 0 °C. (c) NaH, Merrifield's peptide resin [(chloromethyl) divinylbenzene, 1% cross-linked]. (d) (Trimethylsilyl)acetylene, Pd(dba)$_2$, CuI, PPh$_3$, 2:1 (v/v) NEt_3/DMF, 70 °C. (e) Wash solid support (3 × 30 mL/g of polymer) methanol, DMF, dichloromethane, methanol, $(C_2H_5)_2NCS_2Na{\cdot}3H_2O$, DMF, dichloromethane, and methanol.

mental Section). Table 1 provides a comparison of the yield data for monodendrons prepared by Schemes 1 and 2. It is apparent that the process shown in Scheme 2 sustains a nearly constant high yield over the first five generations, while monodendron yields from Scheme 1 decrease to zero in nearly linear fashion. Overall the scheme based on focal point monomer **5** offers many advantages compared to the original approach.

In an effort to simplify purification, we developed a solid-phase method[6] for preparing monodendrons (Scheme 4) based on the chemistry described above. The polymer-supported aryl dibromide **11** was obtained by etherification of Merrifield's chloromethylated polymer using a five-fold excess of the alcohol−triazene **13** and 3 equiv of sodium hydride (Scheme 5). We discovered that a small amount of reductive debromination occurs as a side product if care is not taken in this reaction. Using the conditions reported, less than 1% of this product is observed (as determined by removal of the focal point monomer with methyl iodide). Polymer-supported bisacetylene **15**, was obtained by Pd(0)-catalyzed coupling of the (trimethylsilyl)acetylene with aryl bromide **11**, followed by deprotection of the trimethylsilyl group with tetrabutylammonium fluoride. The coupling and deprotection of the trimethylsilyl group were monitored by infrared spectroscopy as shown in Figure 4 (spectra a and b). The band at 2153 cm^{-1} (spectrum a) is characteristic of carbon−carbon triple bond stretching of trimethylsilyl-protected acetylenes, and the 3311 cm^{-1} (strong) and 2109 cm^{-1} (weak) bands are the terminal carbon−hydrogen stretching vibrations and carbon−carbon triple bond stretching vibrations, respectively. Most of the preparations described below were conducted with chloromethylated polymer functionalized to a degree of 0.7 mequiv/g. Lighter loadings

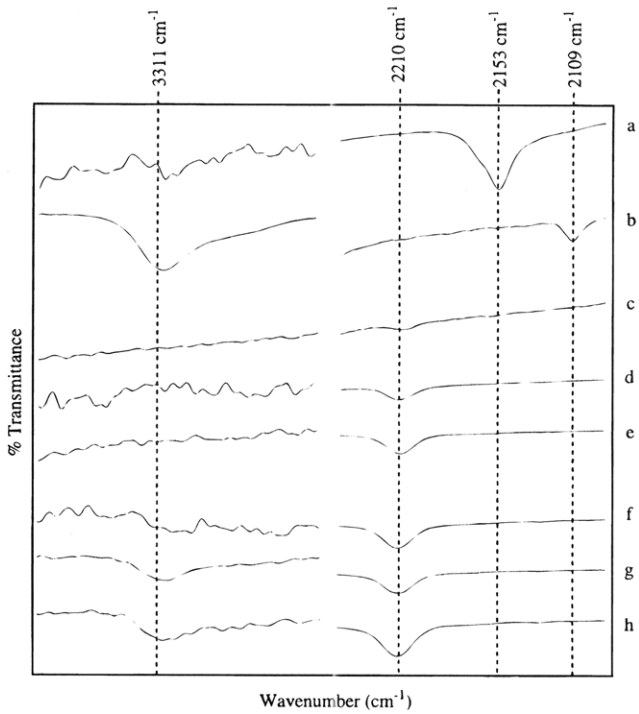


Figure 4. IR spectra of monodendrons supported on polystyrene beads swollen with CCl_4: (a) **14**, (b) **15**, (c) polymer−**N-M**$_3$-(*t*-Bu)$_4$, (d) polymer−**N-M**$_7$-(*t*-Bu)$_8$, (e) polymer−**N-M**$_{15}$-(*t*-Bu)$_{16}$, (f) polymer−**N-M**$_{31}$-(*t*-Bu)$_{32}$, (g) polymer−**N-M**$_{63}$-(*t*-Bu)$_{64}$, (h) polymer−**N-M**$_{63}$-(*t*-Bu)$_{64}$. See text for details.

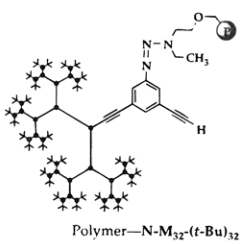
were investigated only at the highest generation (vida infra).

Coupling of polymer **11** with 2.2 equiv of 3,5-di-*tert*-butylphenylacetylene in the presence of Pd(0) catalyst

resulted in the polymer-supported monodendron polymer–$\mathbf{M_3}$-(t-$\mathbf{Bu})_4$. The completeness of the coupling reaction was monitored by infrared spectroscopy until a null signal was observed in the 3311 cm^{-1} band as in Figure 4 (spectrum c). The band at 2210 cm^{-1} corresponds to stretching vibrations of internal carbon–carbon triple bonds. Once the coupling reaction was judged to be complete, the catalyst and excess monodendron were removed by a series of washings as outlined in Scheme 4. To complete the first cycle, the triazene tether was cleaved with iodomethane to provide the zero generation monodendron, **I-M$_3$-(t-Bu)$_4$**, in 85% yield as shown in Scheme 4.

The first generation monodendron, **I-M$_7$-(t-Bu)$_8$**, was obtained by reacting 2.2 equiv of **I-M$_3$-(t-Bu)$_4$** with the polymer-supported focal point monomer **15**, followed by removal of the monodendron from the polymeric support with iodomethane. This repetitive process was repeated through generation three without complication. All coupling reactions are followed by infrared analysis of the polymer-bound substrate as shown in Figure 4 by the disappearance of the terminal carbon–hydrogen acetylene stretch at 3311 cm^{-1}. As the generation increases, the band intensity at 2210 cm^{-1} of internal carbon–carbon triple bond stretching increases. The spectral data of the monodendrons obtained from the solid-phase method are identical with those obtained by the solution process. Table 1 shows that the yields of the monodendrons from the solid-phase synthesis are comparable to the values obtained in solution.

Attempts to continue the solid-phase process to the generation four met with some difficulty. Polymer-supported monomer **15** reacted with 4 equiv of **I-M$_{31}$-(t-Bu)$_{32}$** but failed to reach completion (Figure 4, spectrum g). Instead, a significant amount of a mono-coupled product, presumed to be polymer–**N-M$_{32}$-(t-Bu)$_{32}$**, was obtained. This was confirmed by removal



of the product from the solid support, yielding a mixture of **I-M$_{63}$-(t-Bu)$_{64}$** and a compound whose molecular weight corresponded to a 32-mer by SEC (presumably **I-M$_{32}$-(t-Bu)$_{32}$**). The SEC trace of the crude mixture is shown in Figure 5a. Attempts to drive the reaction to completion at this degree of loading were not successful. Although this mixture of monodendrons could be separated chromatographically, we sought ways to improve the coupling efficiency in these higher generation products.

For an initial degree of functionalization of 0.7 mequiv/g, the total weight percent of monodendron on the polymeric support increases rapidly to more than 80% for generation four (Table 1). Undoubtedly, this leads to densification of the support and is likely related to the incomplete reactivity observed in higher generations. When the coupling reaction was attempted using a support of a lighter loading (0.45 mequiv/g) but with otherwise identical conditions, it resulted in a decrease in the amount of polymer–**N-M$_{32}$-(t-Bu)$_{32}$**, as shown by the IR spectrum (Figure 4, spectrum h) and by the SEC

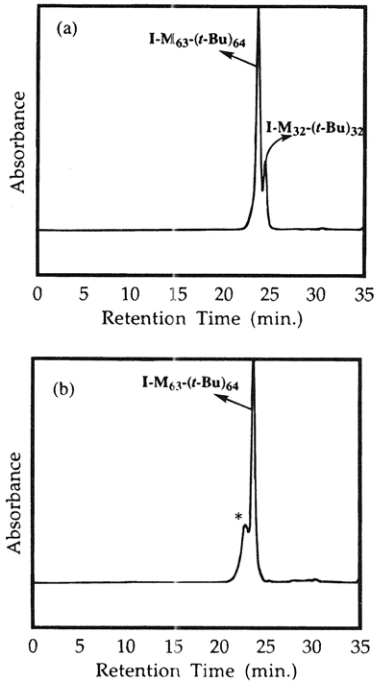


Figure 5. Size-exclusion chromatographs of the crude reaction mixture from the fourth generation monodendron, **I-M$_{63}$-(t-Bu)$_{64}$**, after cleavage from the solid support. (a) Product obtained from **15** loaded at an initial level of 0.7 mequiv/g. (b) Product obtained from **15** loaded at an initial level of 0.45 mequiv/g. The peak marked with an asterisk corresponds to an unknown high molecular weight impurity which could be removed by chromatographic separation on silica gel.

trace of the crude product obtained upon removal by iodomethane treatment (Figure 5b). An unknown high molecular weight impurity was observed with this support (Figure 5b) which required careful chromatographic separation to obtain pure **I-M$_{63}$-(t-Bu)$_{64}$**. The purified monodendron was obtained in 68% isolated yield. Attempted synthesis of higher generation monodendrons using the polymeric support loaded to the level of 0.45 mequiv/g was not successful. Examination of the cross-linked beads by optical microscopy reveals a dramatic change in their appearance from generation three to four. The swelling properties of the polymeric support were significantly reduced at this stage, apparently making the reactive sites inaccessible. Matrix effects of a related nature have long been known in solid-phase peptide synthesis.[7]

In spite of these limitations, the solid support convergent method offers several advantages, especially in preparing early generation monodendrons which are the building blocks for higher generation dendrons. First, excess monodendron reactant can now conveniently be used to drive the couplings to completion. The unreacted monodendrons and the catalyst are easily washed away and recovered, without the need for chromatographic separation as is required by the solution method. Thus, for each generation, the solid-phase method requires one less chromatographic purification. Because of these features, the solid-phase approach is ideal for large-scale syntheses of early generation monodendrons. Second, the coupling reactions can be monitored by infrared spectroscopy without requiring product isolation. Third, handling of the toxic triazenes can be minimized since they are bound on the solid phase. A fourth advantage of the method, not yet demonstrated, is the possibility of a convenient route to site-specifically functionalized monodendrons.

Conclusions

The procedures described in this paper make possible the preparation of gram quantities of phenylacetylene monodendrons. Relatively minor changes in the protecting group scheme from our original approach have made significant improvements in yield and ease of purification. This chemistry was ideally suited for the development of a solid-phase convergent synthesis, which is especially useful for large-scale preparation of early generation monodendrons.

Experimental Section

General Procedures. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, Fischer, Mallincrodt, J. T. Baker, EM Science) and were used without purification. Hexane, dichloromethane, and ethyl acetate were distilled before use. All atmosphere-sensitive reactions were done under nitrogen using a vacuum line or in a drybox. Bulb to bulb distillation was done with a Kugelrohr distillation apparatus. Analytical TLC was performed on Kieselgel F-254 precoated silica gel plates. Visualization was accomplished with UV light or phosphomolybdic acid stain. Flash chromatography was carried out with silica gel 60 (230–400 mesh) from EM Science. Dry triethylamine was obtained by vacuum transfer from calcium hydride. Dry THF was obtained by vacuum transfer from sodium benzophenone.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-360, a Varian Unity 400, or a Varian XL-200 spectrometer. Chemical shifts were recorded in parts per million (δ), and splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants, J, are reported in hertz (Hz). The residual proton signal of the solvent was used as an internal standard for spectra recorded in chloroform-d (δ 7.26 for ^{1}H, δ 77.0 for ^{13}C), benzene-d_6 (δ 7.15 for ^{1}H, δ 128 for ^{13}C), and DMSO-d_6 (δ 2.49 for ^{1}H, δ 39.5 for ^{13}C). Gas chromatography (GC) was performed on a HP-5890 Series II gas chromatograph equipped with a 12.5 m × 0.2 mm × 0.5 μm HP-1 methylsilicone column and fitted with a flame ionization detector and helium carrier gas at 30 mL/min. Low-resolution mass spectra were obtained on either a Hewlett-Packard GC-MS equipped with a 30 m HP-1 capillary column operating at 70 eV or a Finnigan-MAT CH5 spectrometer operating at 70 eV. High-resolution electron impact mass spectra were obtained on a Finnigan-MAT 731 spectrometer operating at 70 eV. Low- and high-resolution fast atom bombardment (FAB) mass spectra were obtained on VG ZAB-SE and VG 70-SE-4F spectrometers. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory using a Leeman Labs CE440. Melting points were reported as the onset temperature from differential scanning calorimetry traces run at a heating rate of 20 °C·min^{-1} on a Perkin-Elmer Series 7 thermal analysis system. Infrared spectra were recorded on an IBM IR/32 FTIR spectrometer. The dry polymer beads were placed on NaCl plates, and a few drops of carbon tetrachloride were added to swell the material. The swollen beads were placed between a pair of NaCl plates and the infrared spectrum was immediately recorded. Cascade nomenclature followed the description outlined by Newkome et al.[8]

3,5-Dibromonitrobenzene (8). To a solution of sodium nitrite (47.11 g, 680 mmol) in concentrated sulfuric acid (450 mL) was added slowly a suspension of 2,6-dibromo-4-nitroaniline (134.6 g, 450 mmol) in glacial acetic acid (1.65 L), maintaining an internal temperature below 20 °C. After stirring for 30 min, the resulting diazonium salt was then slowly added to a suspension of cuprous oxide (9.8 g, 68 mmol) in 95% ethanol (1220 mL). After stirring overnight, the mixture was quenched with water (300 mL). The organic layer was separated, washed with saturated $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated to afford a brown solid. The aqueous layer from the extracts was diluted, in portions, into 4 times the volume of water, causing precipitation of additional product which was collected by suction filtration. The combined lots of crude product were recrystallized from 95% EtOH to afford analytically pure **8** (101.38 g, 79%): R_f 0.36 (1:4 dichloromethane/low petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J =1.7 Hz, 2H), 7.99 (t, J =1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 140.0, 125.6, 123.4; IR (KBr) 3077, 1531, 1337, 883, 749, 743, 735 cm^{-1}. MS (EI). Calcd for $C_6H_3NO_2Br_2^+$: m/e 278.8531. Found: m/e 278.8532. Anal. Calcd for $C_6H_3NO_2Br_2$: C, 25.65; H, 1.08; N, 4.99. Found: C, 25.66; H, 1.06; N, 5.01.

3,5-Dibromoaniline (9). A homogeneous solution of 3,5-dibromonitrobenzene (70 g, 249 mmol) and stannous chloride dihydrate (282.2 g, 1.25 mol) in EtOH (500 mL) was heated at 70 °C for ca. 100 min under N_2. Upon cooling, the solvent was removed under reduced pressure and the residue diluted with excess 20–30% aqueous NaOH. The aqueous layer was extracted with ether (4 × 200 mL). The organic extracts were washed with saturated aqueous NaCl, dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford a brown solid of analytically pure **9** (43.69 g, 70%): R_f 0.33 (1:1 dichloromethane/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (t, J = 1.7 Hz, 1H), 6.74 (d, J = 1.7 Hz, 2H), 3.77 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 123.6, 123.3, 116.4. MS (EI). Calcd for $C_6H_5Br_2N^+$: m/e 248.8789. Found 248.8788. Anal. Calcd for $C_6H_5Br_2N$: C, 28.72; H, 2.01; N, 5.58. Found: C, 28.98; H, 2.04; N, 5.61.

1-(3,5-Dibromophenyl)-3,3-diethyltriazene (6). To a solution of 3,5-dibromoaniline (**9**; 52.8 g, 210 mmol) in acetonitrile (ca. 200 mL) was added 6 N hydrochloric acid (80 mL, 484 mmol). The resultant heterogeneous mixture was then heated to ca. 70 °C for 15 min and cooled to <10 °C. To this stirred suspension was added dropwise an aqueous solution of sodium nitrite (19.02 g, 276 mmol in ca. 30 mL of water). This solution was then slowly added to a stirred mixture of potassium carbonate (146 g, 1.05 mol), diethylamine (33 mL, 319 mmol), water (ca. 300 mL), and acetonitrile (ca. 100 mL) at <10 °C. Upon completion of the addition, the mixture was taken out of the ice bath and stirred for 1 h. The mixture was extracted with ether (4 × 200 mL). The organic extracts were combined, washed with saturated aqueous NaCl, dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford a dark red oil. Kugelrohr distillation of the crude product afforded **6** as an orange oil (44.2 g, 63%): R_f 0.36 (1:4 dichloromethane/low petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 1.7 Hz, 2H), 7.37 (t, J = 1.7 Hz, 1H), 3.76 (br, 4H), 1.22 (br d, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 129.7, 122.8, 122.3, 49.3, 41.4, 14.4, 11.1; IR (neat) 2977, 2934, 1576, 1551, 1466, 1429, 1397, 1341, 1250, 1227, 1111, 741 cm^{-1}. MS (EI). Calcd for $C_{10}H_{13}Br_2N_3^+$: m/e 332.9476. Found: m/e 332.9476. Anal. Calcd for $C_{10}H_{13}Br_2N_3$: C, 35.85; H, 3.91; N, 12.54. Found: C, 35.80; H, 3.92; N, 12.51.

1-[3,5-Bis[2-(trimethylsilyl)ethynyl]phenyl]-3,3-diethyltriazene (10). Into a heavy-walled tube fitted with a Teflon cap was added **6** (25.013 g, 74.7 mmol), (trimethylsilyl)-acetylene (26 mL, 184 mmol), $Pd(dba)_2$ (1.724 g, 3.00 mmol), cuprous iodide (0.566 g, 2.97 mmol), and triphenylphosphine (3.951 g, 15.1 mmol) in triethylamine (375 mL). The contents was reacted according to the general coupling procedure. The crude product was purified by flash column chromatography (eluting first with hexane to remove high R_f impurities and then with 1:4 dichloromethane/hexane) to obtain **10** (24.52 g, 89%) as a viscous orange oil: R_f 0.19 (1:5 dichloromethane/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 1.5 Hz, 2H), 7.34 (t, J = 1.5 Hz, 1H), 3.75 (q, J = 7.1 Hz, 4H), 1.25 (br, 6H), 0.23 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 131.8, 124.0, 123.5, 104.5 (C5), 94.1, −0.1; IR (neat) 2899, 2155, 1588, 1570, 1449, 1406, 1347, 1252, 1233, 1107, 982, 851, 760 cm^{-1}. MS (EI). Calcd for $C_{20}H_{31}N_3Si_2^+$: m/e 369.2058. Found: m/e 369.2058. Anal. Calcd for $C_{20}H_{31}N_3Si_2$: C, 64.98; H, 8.45; N, 11.37. Found: C, 64.72; H, 8.51; N, 11.23.

1-(3,5-Diethynylphenyl)-3,3-diethyltriazene (5). To a solution of **10** (11.5 g, 31 mmol) in MeOH (ca. 25 mL) and dichloromethane (ca. 30 mL) was added solid potassium carbonate (0.1 g, 1.78 mmol). The mixture was degassed and stirred under positive nitrogen pressure at room temperature for ca. 1 h. The mixture was then diluted with hexane (ca. 200 mL), extracted with water (3 × 100 mL), dried ($MgSO_4$),

filtered, and concentrated to afford a green oil. Purification by flash column chromatography gave **5** (6.87 g, 98%): R_f 0.32 (1:2 dichloromethane/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 1.7 Hz, 2H), 7.36 (t, J = 1.5 Hz, 1H), 3.76 (q, J = 7.1 Hz, 4H), 3.06 (s, 2H), 1.26 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 131.8, 124.6, 122.6, 83.0, 77.2, 49 (br), 41 (br), 14 (br), 11 (br); IR (neat) 3295, 2979, 2109, 1572, 1456, 1402, 1343, 1256, 1235, 1109 cm^{-1}. MS (GC-MS/EI). Calcd for $C_{14}H_{15}N_3^+$: m/e 225.1266. Found: m/e 225.1266. Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.67; H, 6.69; N, 18.65.

Synthesis of 3,5-Di-*tert*-butylphenylacetylene (2). A heavy-walled flask was charged with 3,5-di-*tert*-butylphenol (33.0 g, 0.16 mol) and pyridine (80 mL). The mixture was degassed and back-filled with nitrogen three times, and the contents were cooled to 0 °C. Trifluoromethanesulfonic anhydride (50.0 g, 0.177 mol) was added by syringe pump (13.3 mL/h). After the addition was complete, the mixture was warmed to room temperature and stirred for 2 h. When the reaction was finished, water was added and the product was extracted with hexane. The organic layer was washed with 10% HCl aqueous solution and NaCl saturated solution, dried over $MgSO_4$, and filtered. The solvent was evaporated to give 3,5-di-*tert*-butyl trifluoromethanesulfonate as a colorless oil (53.5 g, 98.8% yield, 99.6 % pure by GC). A heavy-walled flask was charged with 3,5-di-*tert*-butyl trifluoromethanesulfonate (47.6 g, 0.14 mol), 2-methyl-3-butyn-2-ol (47.6 g, 0.566 mol), bis(dibenzylideneacetone)palladium(0) (1.62 g, 2.8 mmol), triphenylphosphine (3.71 g, 14.1 mmol), copper(I) iodide (0.54 g, 2.8 mmol), lithium chloride (17.9 g, 0.42 mol), and triethylamine (480 mL). The flask was degassed and back-filled with nitrogen three times, sealed, and stirred at 80 °C for 86 h. The reaction mixture was then filtered, and the solvent was evaporated. The crude product was purified by recrystallization from hexane to give 1-(3-hydroxy-3-methyl-1-butynyl)-3,5-di-*tert*-butylbenzene as a white powder (36.35 g, 93% yield). This 1-(3-hydroxy-3-methyl-1-butynyl)-3,5-di-*tert*-butylbenzene (31.0 g, 0.114 mol) was dissolved in toluene (400 mL) containing potassium hydroxide (5.4 g) and methanol (250 mL) in a round-bottom flask equipped with a Dean–Stark trap fitted with a reflux condenser. The mixture was heated at 110 °C for 3.5 h. The reaction mixture was cooled to room temperature, washed with water, dried over $MgSO_4$, and filtered. The solvent was evaporated, and the resultant residue was passed through a short silica column, eluting with hexane to give 3,5-di-*tert*-butylphenylacetylene (**2**) as a white powder: overall yield 77.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, J = 1.8 Hz, 1H), 7.38 (d, J = 2.0 Hz, 2H), 3.05 (s, 1H), 1.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.82, 126.35, 123.22, 121.00, 84.81, 75.80, 34.76, 31.28. Anal. Calcd $C_{16}H_{22}$: C, 89.65; H, 10.34. Found: C, 89.83; H, 10.56.

2-Cascade: 1-phenyl-3,3-diethyltriazene[2–3,5]:(5-ethynyl-1,3-di-*tert*-butylbenzene (Et_2N_3-M_3-(*t*-Bu)$_4$). A heavy-walled flask was charged with 1-(3,5-dibromophenyl)-3,3-diethyltriazene (**6**; 15.6 g, 0.047 mol), 3,5-di-*tert*-butylphenylacetylene (**2**; 22 g, 0.1 mol), bis(dibenzylideneacetone)palladium(0) (1.07 g, 1.9 mmol), triphenylphosphine (2.45 g, 9.3 mol), copper(I) iodide (0.36 g, 1.9 mmol), and triethylamine (500 mL). The flask was degassed and back-filled with nitrogen three times, sealed, and stirred at 75 °C for 17 h. The disappearance of 1-(3,5-dibromophenyl)-3,3-diethyltriazene (**6**) was monitored by TLC. After the reaction was complete, the mixture was filtered and the solvent was evaporated. The product was purified by flash chromatography, eluting with 4:1 hexane/CH_2Cl_2 to give Et_2N_3-M_3-(*t*-Bu)$_4$ as a white amorphous solid: yield 74% (20.9 g); R_f 0.29 (3:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 8.10 (d, J = 1.5 Hz, 2H), 7.89 (t, J = 1.7 Hz, 1H), 7.66 (d, J = 2.0 Hz, 4H), 7.49 (t, J = 1.8 Hz, 2H), 3.4–3.1 (br, d, 4H), 1.22 (s, 36H), 0.9–0.8 (br, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.17, 150.78, 131.06, 125.91, 124.02, 123.39, 122.74, 122.17, 90.40, 87.86, 34.82, 31.33. Anal. Calcd: C, 83.81; H, 9.21; N, 6.98. Found: C, 83.78; H, 9.23; N, 7.10.

General Procedure for the Conversion of the Triazene Group of Et_2N_3-M_y-(*t*-Bu)$_x$ to Aryl Iodide. A heavy-walled glass tube joined to a Teflon screw valve was charged with the monodendron (Et_2N_3-M_y-(*t*-Bu)$_x$) and was taken up in freshly distilled iodomethane (ca. 0.1 M in monodendron). The solution was degassed and placed under a nitrogen head space, and the tube was sealed and heated at 110 °C for 12 h. After complete deprotection (monitored by TLC), the product was purified by flash chromatography to give I-M_y-(*t*-Bu)$_x$.

General Procedure for the Pd(0)-Catalyzed Coupling of Aryl Halides with Terminal Acetylenes (Et_2N_3-M_y-(*t*-Bu)$_x$). A heavy-walled flask was charged with monomer **5** (1.0 equiv), I-M_y-(*t*-Bu)$_x$ (2.2 equiv), Pd(dba)$_2$ (0.04 equiv), triphenylphosphine (0.20 equiv), copper(I) iodide (0.04 equiv), and triethylamine. The concentration of the reaction varied from 0.3 to 0.05 M depending on the solubility of the reactants and the scale of the reaction. The flask was then evacuated and back-filled with nitrogen three times, sealed, and stirred at 55 °C for 12 h or until the reaction was complete. The disappearance of monomer was monitored by TLC. When the reaction was finished, the mixture was filtered, the filter cake was washed with hexane, and the combined filtrates were evaporated to dryness. The product was purified as outlined below.

2-Cascade: iodobenzene[2–3,5]:5-ethynyl-1,3-di-*tert*-butylbenzene (I-M_3-(*t*-Bu)$_4$). Et_2N_3-M_3-(*t*-Bu)$_4$ (20.18 g, 33.5 mmol) was treated with iodomethane (100 mL) using the general triazene deprotection procedure, and the product was purified by flash chromatography eluting with hexane to give I-M_3-(*t*-Bu)$_4$ as a white, amorphous powder: yield 84.0% (17.7 g); R_f 0.77 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 7.78 (d, J = 1.5 Hz, 2H), 7.71 (t, J = 1.5 Hz, 1H), 7.65 (d, J = 2.0 Hz, 4H), 7.52 (t, J = 1.8 Hz, 2H), 1.24 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.93, 139.40, 133.68, 125.94, 125.48, 123.23, 121.52, 93.16, 92.35, 85.80, 34.83, 31.31. Anal. Calcd: C, 72.60; H, 7.21. Found: C, 72.36; H, 7.31.

4-Cascade: 1-phenyl-3,3-diethyltriazene[2–3,5]:5-ethynyl-1,3-phenylene: 5-ethynyl-1,3-di-*tert*-butylbenzene) (Et_2N_3-M_7-(*t*-Bu)$_8$). Monomer **5** and I-M_3-(*t*-Bu)$_4$ were reacted using the general coupling procedure, and the product was purified by flash chromatography eluting with hexane increasing to 8:2 hexane/CH_2Cl_2 to give Et_2N_3-M_7-(*t*-Bu)$_8$ as a white amorphous powder: yield 93.5%; R_f 0.41 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 8.08 (d, J = 1.5 Hz, 2H), 7.81 (t, J = 1.6 Hz, 2H), 7.74–7.73 (m, 5H), 7.69 (d, J = 2.0 Hz, 8H), 7.53 (t, J = 1.8 Hz, 4H), 3.45–3.22 (br d, 4H), 1.25 (s, 72H), 1.00–0.84 (br, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.32, 150.88, 134.11, 133.89, 130.99, 125.95, 124.21, 123.94, 123.82, 123.48, 123.07, 121.76, 91.63, 89.93, 87.99, 86.68, 34.82, 31.32. Anal. Calcd: C, 88.11; H, 8.46; N, 3.43. Found: C, 88.15; H, 8.44; N, 3.48.

4-Cascade: iodobenzene[2–3,5]:5-ethynyl-1,3-phenylene:5-ethynyl-1,3-di-*tert*-butylbenzene (I-M_7-(*t*-Bu)$_8$). Et_2N_3-M_7-(*t*-Bu)$_8$ (5.80 g, 4.7 mmol) was treated with iodomethane (50 mL) using the general triazene deprotection procedure, and the product was purified by flash chromatography, eluting with hexane to give I-M_7-(*t*-Bu)$_8$ as a white amorphous powder: yield 93.0% (5.48 g); R_f 0.72 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 7.84 (t, J = 1.5 Hz, 2H), 7.75 (d, J = 1.5 Hz, 4H), 7.72–7.69 (m, 10H), 7.53–7.50 (m, 5H), 1.25 (s, 72H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.92, 140.02, 134.55, 133.88, 133.78, 125.97, 124.95, 124.37, 123.15, 121.67, 93.26, 91.84, 89.90, 87.70, 86.51, 34.84, 31.33. Anal. Calcd: C, 82.40; H, 7.48. Found: C, 82.65; H, 7.58.

8-Cascade: 1-phenyl-3,3-diethyltriazene[2–3,5]:(5-ethynyl-1,3-phenylene)^2:5-ethynyl-1,3-di-*tert*-butylbenzene (Et_2N_3-M_{15}-(*t*-Bu)$_{16}$). Monomer **5** and I-M_7-(*t*-Bu)$_8$ were reacted following the general coupling procedure, and the product was purified by flash chromatography, eluting with hexane increasing to 8:2 hexane/CH_2Cl_2 to give Et_2N_3-M_{15}-(*t*-Bu)$_{16}$ as a white amorphous powder: yield 92.8%; R_f 0.48 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 8.17 (d, J =1.5 Hz, 2H), 7.85 (t, J = 1.5 Hz, 1H), 7.84 (t, J = 1.5 Hz, 8H), 7.70 (d, J = 1.7 Hz, 16H), 7.67 (d, J = 1.5 Hz, 4H), 7.65 (t, J = 1.5 Hz, 2H), 7.52 (t, J = 1.8 Hz, 8H), 3.43–3.20 (br d, 4H), 1.25 (s, 144H), 0.99–0.82 (br, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.34, 150.89, 134.43, 133.92, 130.81, 125.96, 124.33, 124.21, 124.13, 123.72, 123.37, 123.11, 121.72, 91.77, 90.29,

89.21, 88.61, 87.66, 86.58, 34.82, 31.32. Anal. Calcd: C, 90.20; H, 8.10; N, 1.70. Found: C, 90.25; H, 8.07; N, 1.73.

8-Cascade: iodobenzene[2−3,5]:(5-ethynyl-1,3-phenylene)^2:5-ethynyl-1,3-di-*tert*-butylbenzene (I-M_{15}-(*t*-Bu)$_{16}$). Et_2N_3-M_{15}-(*t*-Bu)$_{16}$ (6.70 g, 2.7 mmol) was treated with iodomethane (30 mL) using the general triazene deprotection procedure, and the product was purified by flash chromatography, eluting with hexane to give I-M_{15}-(*t*-Bu)$_{16}$ as a white amorphous powder: yield 87.0% (5.88 g); R_f 0.67 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 7.85(t, J = 1.5 Hz, 4H), 7.83−7.80 (m, 10H), 7.70 (d, J = 1.7 Hz, 18H), 7.68−7.66 (m, 7H), 7.53 (t, J = 1.8 Hz, 9H), 1.24 (s, 144H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.91, 140.27, 134.49, 134.36, 133.90, 133.64, 125.96, 125.82, 124.83, 124.36, 123.88, 123.44, 123.27, 123.13, 121.69, 93.33, 91.82, 89.53, 89.43, 88.42, 88.05, 86.55, 34.82, 31.32; Anal. Calcd: C, 87.32; H, 7.61. Found: C, 87.16; H, 7.69.

16-Cascade: 1-phenyl-3,3-diethyltriazene[2−3,5]:(5-ethynyl-1,3-phenylene)^3:5-ethynyl-1,3-di-*tert*-butylbenzene (Et_2N_3-M_{31}-(*t*-Bu)$_{32}$). Monomer **5** and I-M_{15}-(*t*-Bu)$_{16}$ were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with hexane increasing to 8:2 hexane/CH_2Cl_2 to give Et_2N_3-M_{31}-(*t*-Bu)$_{32}$ as a white amorphous powder: yield 90.6%; R_f 0.35 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 8.16 (d, J = 1.5 Hz, 2H), 7.85−7.81 (m, 25H), 7.77 (s, 6H), 7.72 (d, J = 1.5 Hz, 8H), 7.70−7.67 (m, 36H), 7.51 (t, J = 1.8 Hz, 16H), 3.45−3.20 (br d, 4H), 1.24 (s, 288H), 0.98−0.78 (br, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.95, 150.89, 134.62, 134.46, 133.91, 130.07, 125.95, 125.82, 124.37, 124.22, 123.89, 123.69, 123.64, 123.33, 123.11, 121.72, 91.83, 90.40, 89.38, 88.96, 88.88, 88.51, 87.59, 86.57, 34.81, 31.32. Anal. Calcd: C, 91.24; H, 7.92; N, 0.84. Found: C, 91.28; H, 7.82; N, 0.91.

16-Cascade: iodobenzene[2−3,5]:(5-ethynyl-1,3-phenylene)^3:5-ethynyl-1,3-di-*tert*-butylbenzene (I-M_{31}-(*t*-Bu)$_{32}$). Et_2N_3-M_{31}-(*t*-Bu)$_{32}$ (1.55 g, 0.31 mmol) was treated with iodomethane (20 mL) using the general triazene deprotection procedure, and the product was purified by flash chromatography, eluting with hexane to give I-M_{31}-(*t*-Bu)$_{32}$ as a white amorphous powder: yield 96.4% (1.49 g); R_f 0.63 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 7.84 (t, J = 1.5 Hz, 8H), 7.82−7.81 (m, 18H), 7.80 (t, J = 1.5 Hz, 2H), 7.77 (d, J = 1.5 Hz, 4H), 7.74 (d, J = 1.5 Hz, 8H), 7.70−7.68 (m, 36H), 7.65 (t, J = 1.5 Hz, 1H), 7.51 (t, J = 1.8 Hz, 16H), 1.24 (s, 288H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.90, 140.46, 134.67, 134.58, 134.49, 134.38, 133.91, 125.96, 125.90, 125.82, 124.37, 123.87, 123.79, 123.30, 123.12, 121.70, 93.26, 91.82, 89.46, 89.42, 89.08, 88.76, 88.47, 88.11, 86.56, 34.82, 31.32. Anal. Calcd: C, 89.79; H, 7.68. Found: C, 89.76; H, 7.71.

32-Cascade: 1-phenyl-3,3-diethyltriazene[2−3,5]:(5-ethynyl-1,3-phenylene)^4:5-ethynyl-1,3-di-*tert*-butylbenzene (Et_2N_3-M_{63}-(*t*-Bu)$_{64}$). Monomer **5** and I-M_{31}-(*t*-Bu)$_{32}$ were reacted using the general coupling procedure, and the product was purified by flash chromatography, eluting with 9:1 hexane/CH_2Cl_2 increasing to 8:2 hexane/CH_2Cl_2 to give Et_2N_3-M_{63}-(*t*-Bu)$_{64}$ as a white amorphous powder: yield 86.7%; R_f 0.38 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 7.94−7.91 (m, 3H), 7.87 (d, J = 1.2 Hz, 4H), 7.86−7.83 (m, 26H), 7.82 (d, J = 1.5 Hz, 32H), 7.79 (t, J = 1.2 Hz, 4H), 7.75 (d, J = 1.5 Hz, 16H), 7.70 (t, J = 1.5 Hz, 8H), 7.67 (d, J = 2.0 Hz, 64H), 7.50 (t, J = 1.8 Hz, 32H), 3.45−3.25 (br d, 4H), 1.24 (s, 576H), 0.99−0.88 (br, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.87, 134.67, 134.46, 134.36, 133.89, 125.94, 125.81, 124.47, 124.34, 123.84, 123.77, 123.71, 123.63, 123.59, 123.31, 123.09, 121.70, 91.81, 90.49, 89.38, 88.99, 88.90, 88.85, 88.76, 88.50, 87.33, 86.57, 34.80, 31.31. Anal. Calcd: C, 91.75; H, 7.83; N, 0.42. Found: C, 91.69; H, 7.89; N, 0.49.

32-Cascade: iodobenzene [2−3,5]:(5-ethynyl-1,3-phenylene)^4:5-ethynyl-1,3-di-*tert*-butylbenzene (I-M_{63}-(*t*-Bu)$_{64}$). Et_2N_3-M_{63}-(*t*-Bu)$_{64}$ (1.80 g, 0.18 mmol) was treated with iodomethane (20 mL) using the general deprotection of the triazene procedure, and the product was purified by flash chromatography, eluting with hexane to give I-M_{63}-(*t*-Bu)$_{64}$ as a yellowish amorphous powder: yield 88.4% (1.59 g); R_f 0.63 (2:1 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, benzene-d_6) δ 7.93−7.91 (m, 3H), 7.86 (d, J = 1.5 Hz, 4H), 7.86−7.81 (m, 56H), 7.78−7.75 (m, 22H), 7.70 (t, J = 1.3 Hz, 8H), 7.67 (d, J = 1.7 Hz, 64H), 7.50 (t, J = 1.7 Hz, 32H), 1.24 (s, 576H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.87, 140.44, 134.68, 134.65, 134.48, 134.35, 133.89, 125.95, 125.81, 124.35, 123.85, 123.74, 123.62, 123.31, 123.09, 121.72, 93.26, 91.82, 89.40, 89.05, 88.99, 88.95, 88.93, 88.90, 88.81, 88.50, 34.80, 31.31. Anal. Calcd: C, 91.02; H, 7.71. Found: C, 91.02; H, 7.72.

1-(3,5-Dibromophenyl)diazonium Tetrafluoroborate (12). A round-bottom flask was charged with BF_3·OEt_2 (522 mmol, 64.2 mL) and cooled to −15 °C (internal temperature). Then 3,5-dibromoaniline (**9**; 174 mmol, 43.5 g) in dry THF (120 mL) was added dropwise with an addition funnel so as to form a homogeneous solution. After stirring for 10 min, *tert*-butyl nitrite (522 mmol, 62.10 mL) in dry THF (75 mL) was added dropwise using an addition funnel so as to maintain the temperature at −15 °C. After stirring for 20 min, the reaction was warmed to 5 °C and hexane (25 mL) was added. The resulting diazonium tetrafluoroborate salt was isolated by suction filtration, washed with cold ether (100 mL), and air dried (57.85 g, 95% yield): ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.98 (d, J = 1.7 Hz, 2H), 8.86 (t, J = 1.7 Hz, 1H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 146.30, 133.83, 123.58, 119.34. Anal. Calcd: C, 20.61; H, 0.86; N, 8.01. Found: C, 20.91; H, 0.89; N, 7.67.

1-(3,5-Dibromophenyl)-3-(2-hydroxyethyl)-3-ethyltriazene (13). 2-(Ethylamino)ethanol (164 mmol, 15.99 mL), K_2CO_3 (656 mmol, 90.66 g), and DMF (400 mL) were taken up in an Erlenmeyer flask and cooled to 0 °C. The diazonium tetrafluoroborate salt (**12**) was added portionwise and stirred for another 30 min following the addition. Water (500 mL) was added, the mixture was extracted with dichloromethane (3 × 100 mL), and the organic layer was washed with water (3 × 100 mL), dried over Na_2SO_4, and concentrated. Purification using a short column of silica gel eluting with 4:1 hexane/CH_2Cl_2 afforded the triazene as a pale yellow oil in 93% yield (53.5 g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J =1.7 Hz, 2H), 7.38 (t, J = 1.7 Hz, 1H), 3.85−3.75 (br, 6H), 3.70 (br, 1H, −OH), 1.38−1.20 (br, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.94, 130.10, 122.77, 122.31, 60.66, 51.18, 14.26. MS (EI). Calcd for $C_{10}H_{13}Br_2N_3O^+$: m/e 351.04. Found: m/e 351.

Procedure to Link 13 onto the Polymer (11). A three-necked flask was charged with chloromethylated polystyrene (30.135 g, 21.09 mmol, 0.7 mequiv of Cl/g, 200−400 mesh, 1% cross linked with divinylbenzene), degassed, and backfilled with nitrogen. Triazene **13** (105 mmol, 37 g) dissolved in dry THF (100 mL) was transferred via cannula onto the swollen polymeric support under nitrogen. Additional dry THF (150 mL) was added to swell the polymer, facilitating free stirring. The reaction mixture was cooled to −78 °C, and NaH (60% dispersion in oil, 63.27 mmol, 2.53 g) was added portionwise under a nitrogen blanket. After the addition was complete, the reaction mixture was warmed to room temperature and heated at 75 °C with gentle stirring. After 48 h, the mixture was cooled, quenched with methanol (25 mL) and water (25 mL), and filtered. The polymer was washed with the solvents (3 × 30 mL/g) THF, water, methanol, ethyl acetate, *n*-hexane, dichloromethane, and methanol and dried under vacuum. The increase in the mass of the polymer roughly corresponds to that of the triazene monomer attached to the polymer. Anal. Found: C, 81.91; H, 6.95; N, 2.11.

Synthesis of Polymer-Supported Diacetylene (15). A heavy-walled flask was charged with polymer **11**, $Pd(dba)_2$ (0.04 equiv), and copper(I) iodide (0.04 equiv), triphenylphosphine (0.2 equiv), degassed, and back-filled with nitrogen three times. Then degassed triethylamine and DMF (2:1, ca. 8 mL/g of the polymer) were added followed by (trimethylsilyl)-acetylene (2.2 equiv). The contents were heated at 70 °C for 48 h with stirring, cooled, and washed with the solvents (3 × 30 mL/g of the polymer) methanol, DMF, dichloromethane, methanol, sodium diethyldithiocarbamate in DMF (550 mg of sodium diethyldithiocarbamate in 50 mL of DMF and 0.25 mL of *N,N*-diisopropylethylamine), dichloromethane, and methanol and vacuum dried to constant mass: IR (beads in CCl_4 between NaCl plates): 2152 cm^{-1}.

A round-bottom flask was charged with bis(trimethylsilyl) polymer **14**, THF (ca. 8 mL/g), and tetrabutylammonium

fluoride (1.0 M in THF, 2 equiv) and stirred at room temperature for 30 min. The diacetylenearyl polymer **15** was filtered, washed with THF, MeOH, CH_2Cl_2, and MeOH (3 × 30 mL/g), and dried to constant mass: IR (beads in CCl_4 between NaCl plates): 3308, 2108 cm^{-1}.

General Procedure for the Cross-Coupling Reaction Using the Convergent Solid-Phase Route. A heavy-walled flask was charged with polymer **15**, iodo-terminated monodendron (2.2 equiv), $Pd(dba)_2$ (0.04 equiv), copper(I) iodide (0.04 equiv), and triphenylphosphine (0.2 equiv), degassed, and back-filled with nitrogen three times. Degassed triethylamine and DMF (2:1, ca. 8 mL/g of the polymer) were added, and the contents was heated at 70 °C for 48 h with stirring. The suspension was cooled and washed with the solvents (3 × 30 mL/g of the polymer) methanol, DMF, dichloromethane, methanol, sodium diethyldithiocarbamate in DMF (550 mg of sodium diethyldithiocarbamate in 50 mL of DMF and 0.25 mL of *N,N*-diisopropylethylamine), dichloromethane, and methanol and vacuum dried to constant mass.

General Procedure for the Deprotection of the Triazene Linkage from the Solid Support. A heavy-walled, screw-capped sealed tube was charged with monodendron-attached polymeric beads, and iodomethane was added to wet the polymer (ca. 9 mL/g of the polymer). The contents was degassed and back-filled with nitrogen, sealed, and heated to 110 °C. After 12 h at this temperature the reaction mixture was cooled, and the excess iodomethane was removed by vacuum transfer. The monodendron product was extracted from the crude polymer by refluxing in dichloromethane for 30 min and filtering. The residue was washed with dichloromethane, and the washings were combined and concentrated. The monodendron was purified by column chromatography as noted above. NMR and mass spectral data were identical to the monodendrons prepared in solution.

Acknowledgment. J.S.M. acknowledges support from the National Science Foundation (Grant DMR 94-96225) and the NSF Young Investigator Program (Grant CHE 94-96105; 1992–1997). Additional support from Menicon Co., Ltd., and the Camille Dreyfus Teacher–Scholar Awards Program is gratefully acknowledged.

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MA950527+