A Simple Orthogonal Approach to Poly(phenylenevinylene) Dendrimers

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Dendrimers possess a multibranched structure that radiates out from a central core. The synthesis and characterization of these unique molecules have been the focus of attention of current polymer chemistry.[1] These molecules are not only aesthetically appealing but also possess some interesting physical properties, such as unusual glass transition behavior and viscosity, and an isolating effect with certain functional molecules (e.g., porphyrin and rare earth ions).[2,3] A wide range of synthetic methodologies have been applied toward the efficient syntheses of dendritic macromolecules.[4] Two general approaches have been developed to synthesize these molecules: a divergent growth approach and a convergent growth approach.[5,6] For the synthesis of well-defined dendritic molecules, the convergent approach is preferred, as exemplified by the excellent works of Frechet, Moore, and others.[7,8] A general feature of these works is that the synthesis of each generation of dendrons involves the protection and deprotection of certain functional groups. Zimmerman disclosed an orthogonal approach in which aromatic moieties are alternatively linked by flexible ester linkage and rigid acetylene linkages.[9] However, this approach leads to the formation of dendrimers that are not homogeneous in chemical constituents due to the presence of different linkages.

Recently, we described an orthogonal approach for the synthesis of functionalized oligophenylenvinylenes in our diblock copolymer project.[10] In that approach two reactions, the Heck and Horner−Wadsworth−Emmons reactions, were alternatively utilized to construct a vinylene linkage. Due to the fact that both reactions mutually tolerate the functional groups involved, protection chemistry was not needed in each step of growth. A logical extension of this approach is to the synthesis of dendritic molecules bearing phenylenevinylene linkages. We designed two AB₂ type building molecules (**A** and **B,** Scheme 1), one of which underwent the Horner−Wadsworth−Emmons reaction and the other underwent the Heck coupling reaction to produce higher generations of dendrimer bearing vinyl linkages. This strategy allows us to

Scheme 1. Syntheses of Dendritic Molecules

Reaction Conditions: i, NaH/NMP. ii, Pd(Ac)₂/N(n-Bu)₄Br/K₂CO₃
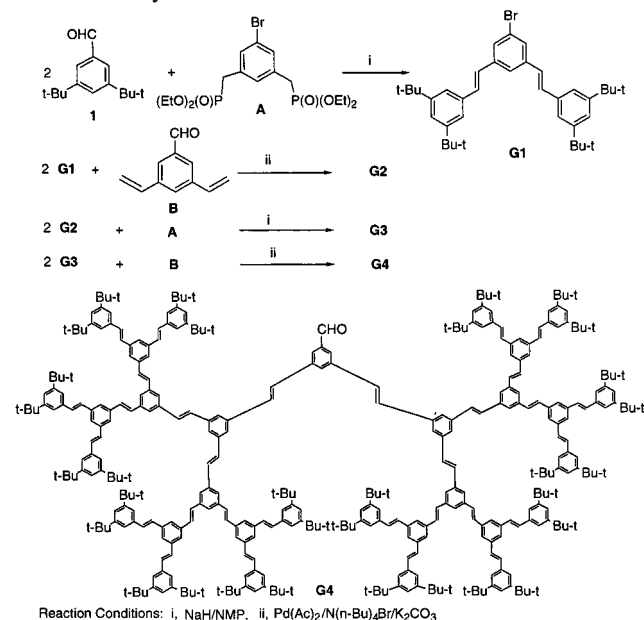
Scheme 2. Syntheses of **G3.5** and Compound **D**
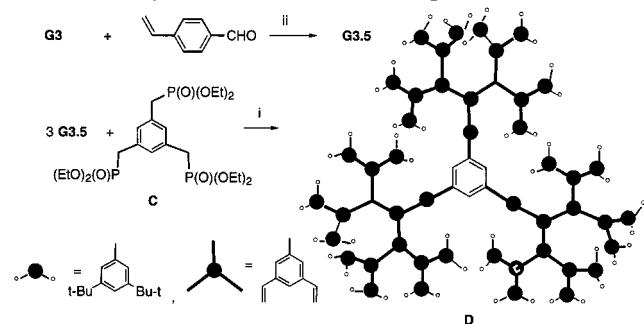
obtain homogeneous dendrons with a single functionality, which is either a bromo or formyl group, at the focal point.

Benzylic bromination of 5-bromo-*m*-xylene followed by an Arbuzov reaction yielded compound **A**. Compound **B** was synthesized by monoformylation of 1,3,5-tribromobenzene followed by exchange of the remaining two bromide groups by vinyl groups via the Stille coupling reaction. Compound **A** reacted with 3,5-di-*tert*-butylbenzaldehyde to obtain the first generation dendrimer, which was highly soluble in many common organic solvents such as CHCl₃, CH₂Cl₂, THF, toluene, etc. (see Scheme 1). The higher generations were obtained by orthogonally using the Heck and Horner−Wadsworth−Emmons coupling reactions between the preceding generation and the appropriate building molecules (see Scheme 1). The yield using the traditional Heck coupling conditions for the preparation of **G4** was poor.[11] However, higher yields (45%) were obtained using the protocol described by Meijere *et al.* which uses K₂-CO₃ as a base and tetra-*n*-butylammonium bromide as a solid-liquid phase transfer catalyst.[12]

Since each generation of the dendrimers is functionalized at the central core, further chemical manipulation is possible. For example, a generation 3 dendron can be used to react with vinylbenzaldehyde to generate a molecule that has the aldehyde functional group with less steric hindrance (**G3.5**, Scheme 2). This molecule can then be used to couple with benzotriphosphate (compound **C**) to obtain a molecule with a higher molecular weight (compound **D**). Due to solubility problems, the yield

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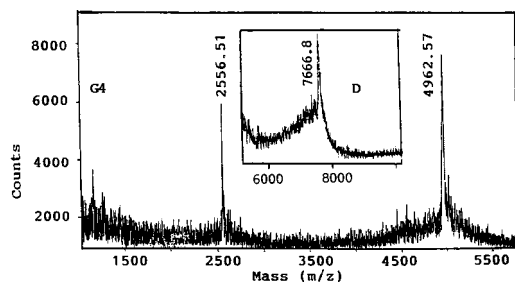(12) Lansky, A.; Reiser, O.; De Meijere, A. *Synlett* **1990**, 405.

Figure 1. Mass spectrum (MALDI) of **G4**. The calculated molecular weight is 4965.6. The molecular ion peak for compound **D** is shown in inset. The theoretical value for that is 7673.8.

of this coupling process is low (9%), but molecule **D** can be easily separated. It is a yellowish material with blue fluorescence. NMR and MALADI experiments have confirmed its structure (see the inset of Figure 1).[13]

All of the dendrimers were characterized by using various analytical techniques. ^{1}H NMR spectra of the dentrimers become complicated when the generations become higher but the higher generations do possess the correct ratio of aliphatic to aromatic protons. Monosubstitution was ruled out because of the absence of a chemical shift caused by the terminal vinyl proton or benzylic proton in the purified dendrimer. Dendrimers **G2, G3.5**, and **G4** all possess a proton chemical shift at about 10.15 ppm due to the formyl group. A chemical shift due to one of the vinyl protons can be identified as a doublet at about 7.2 ppm.

^{13}C NMR spectra of these dendrimers were very crowded in the 120−160 ppm region and it was difficult to assign every peaks. The aliphatic primary carbons and the tertiary carbons associated with the *tert*-butyl group appear around 32.5 and 35.9 ppm, respectively, for all of the dendrimers. The four different carbons associated with the peripheral benzene unit with two *tert*-butyl groups appeared around 152, 139.4, 123.3, and 121.9 ppm in each case. The aldehyde carbon for **G2** and **G4** had a chemcal shift at 193 ppm.

Combustion results were in excellent agreement with the theoretical composition within the experimental error.[14] Firm evidence for the molecular structure was obtained from mass spectrometry results, using laser desorption ionization (MALADI). The mass spectra of all of the dendrimers showed the molecular ion peak at the calculated position.[13] Figure 1 exemplifies the mass spectrum of **G4**. The purity of these dendrimers was confirmed by the SEC data where all showed polydispersity close to 1.[15] Since polystyrene was used as the calibration standard, the molecular weights in all the cases were more than doubled compared to the true value as obtained from mass spectrometry (MALADI).

These molecules are almost colorless and the UV−vis spectrum of the **G1** dendrimer shows an absorption maxima at 306 nm (see Figure 2). A red shift was observed from **G1** to **G2**−**G4** and was caused by substitution effect. Dendrimers **G2**−**G4** exhibit virtually identical absorption maxima at 320 nm because these molecules contain cross-conjugation, implying that the major absorbing unit is stilbene in all the cases (the λ_{max} corresponding to the $\pi-\pi^*$ transition of stilbene is 294 nm). However, as the generations increase, the steric hindrance
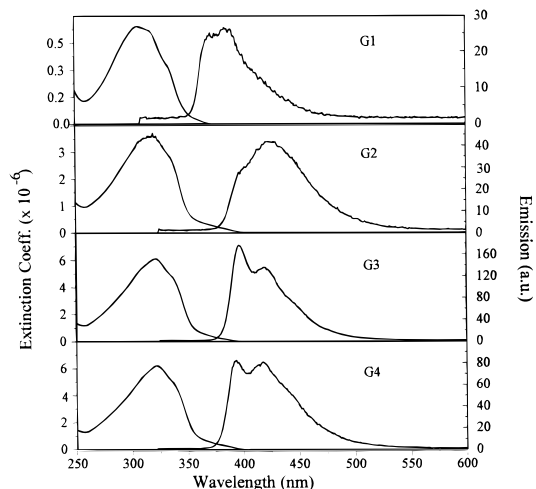

Figure 2. UV/vis and fluorescence spectra of **G1**−**G4.** The fluorescence spectra were taken from solutions having UV absorbance close to 0.2 AU and were normalized thereafter.

increases; the conjugation twists to different degrees from the periphery to the core. This effect is reflected by the fact that the extinction coefficient of **G4** is almost identical with that of **G3. G3.5** has a longer conjugation system at the aldehyde terminal and hence possesses a larger extinction coefficient.

These macromolecules fluoresce in the the near UV (**G1**) or blue (**D2-G4**) region of the spectrum (see Figure 2). **G1** showed a low fluorescent quantum yield, probably due to effective quenching by the bromine atom. **G3** possesses a much higher quantum yield than **G1,** although it also contains a bromine group in the core position. **G2, G3.5**, and **G4** all possess an aldehyde group at the core and they exhibited similar fluorescence spectra. Their fluorescence quantum yields increase as the generations increase.

G1 and **G2** are crystalline materials with melting points at 150 and 350 °C, respectively. **G3** and **G4** did not show any thermal transition between room temperature and 500 °C as indicated by the DSC studies, both formed glassy materials.

In this work, there are several important points worth emphasizing. First, the synthetic approach developed here avoids the need for protection chemistry, which is needed almost exclusively in all dendrimer syntheses, except for the work by Zimmerman *et al.*[9] The unique feature of this synthesis is that the orthogonal approach leads to the formation of a homogenous structure. This approach is also very versatile for the syntheses of different dendritic structures, which can be achieved through variation of the building molecules. The second point is that the dendrimers obtained contain π-electron systems which can be utilized in designing other functional materials, such as photorefractive materials.

In conclusion, the strategy outlined here enables us to construct phenylenevinylene dendrimers with high molecular weights and without carrying out any protection−deprotection chemistries. The resulting dendrimers maintain the uniformity of the structure in terms of linking units involved between the generations. The reaction conditions are mild and simple and can tolerate a large variety of functional groups. This approach will be applicable to build up other structurally uniform and well-defined conjugated functional dendrimers.

Supporting Information Available: Experimental details and MS spectra for all compounds (20 pages). See any current masthead page for ordering and Internet access instructions.

(13) MALADI results: **G1**, calcd for $C_{38}H_{49}Br$ 585.7, found 584.7; **G2**, calcd for $C_{87}H_{106}O$, 1167.8, found 1167.7; **G3**, calcd for $C_{182}H_{217}Br$, 2484.6, found 2482.5; **G3.5**, calcd for $C_{191}H_{224}O$, 2535.9, found 2534.6; **G4**, calcd for $C_{375}H_{442}O$, 4965.6, found 4962.6; compound D, calcd for $C_{582}H_{678}$ (trimer from G3.5) 7673.8, found 7666.8.

(14) **G1**: Calcd for $C_{38}H_{49}Br$, C, 77.93, H, 8.43, Br, 13.64. Found: C, 78.00, H, 8.42, Br, 13.58. **G2**: Calcd for $C_{87}H_{106}O$ C, 89.48, H, 9.15. Found: C, 89.49, H, 9.18. **G3**: Calcd for $C_{182}H_{217}Br$ C, 87.98, H, 8.80, Br, 3.22. Found: C, 87.97, H, 8.80, Br, 3.27. **G3.5**: Calcd for $C_{191}H_{224}O$ C, 90.47, H, 8.90. Found: C, 90.22, H 8.95. **G4**: Calcd for $C_{375}H_{442}O$, C, 90.71, H, 8.97. Found: C, 90.88, H, 8.99.

(15) **G1**: M_n 1224, M_w 1227; PD 1.003. **G2**: M_n 2898, M_w 2907; PD 1.003. **G3**: M_n 5278, M_w 5293; PD 1.003. **G4**: M_n 13416, M_w 13718; PD 1.022.