Conjugated Polymer Nanoparticles via Intramolecular Crosslinking of Dendrimeric Precursors

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π-Conjugated electro-optically active dendrimers are of current interest for developing efficient electroluminescent display devices and other photonic applications. They have unusual electronic and photophysical properties, for example, intramolecular energy transfer in multichromophoric systems, exciton and charge localization phenomena, and photovoltaic effects have been observed. A number of these conjugated polymer dendrimer systems are based on polyaniline, polyphenylenes, polythiophenes, etc. Conjugated polymers based on the carbazole unit are of interest because of their role in electrochromic devices, electrochemical transistors, microcavity photoconduction, electroxerography, and as photovoltaic components that can provide a very efficient matrix for current carrier transport. Polycarbazole and carbazole containing dendrimers that show efficient hole-transport properties and nonlinear optical properties have also been reported.

Intramolecular crosslinking of nano-objects after assembly has emerged as a viable strategy for imparting robustness created by intramolecular crosslinking. This allows expansion of applications for these objects as synthetic antibodies, core crosslinked nanoparticles, shell crosslinked nanoparticles, and shell crosslinked rods. An advantage is their environmental stability, i.e., both chemical and physical, compared to their noncrosslinked precursors. Chemical or physical crosslinking of dendrimers has attracted a lot of attention recently with focus on both inter- and intramolecular crosslinking. For example, the placement of functional groups at the termini or in well-defined segments can ultimately dictate their properties and provide highly controlled macromolecular systems.

In the present work, we have used a third generation carbazole-terminated Fréchet-type polybenzylether dendrimers (G3-D), which have been synthesized in our group. The concentration of the dendrimer was controlled in such a way that individual dendrimers are allowed to intramolecularly crosslink either chemically in solution or electrochemically at an interface. The crosslinking affects the size and rigidity of the electroactive dendrimer, which can be altered by controlling the extent of crosslinking of the peripheral carbazole groups using various polymerization methods. To our knowledge, this is one of the first attempts to produce intramolecularly crosslinked, conjugated dendrimers and investigate their nanoparticle properties. The crosslinking of the peripheral carbazole at the 3,6-positions leads to the formation of polycarbazole units. In order to make the crosslinked dendrimer nanoparticles soluble and processable, precautions were made to avoid having any high degree of intermolecular crosslinking between the dendrimers. Thus, even after crosslinking, the dendrimer was found to be soluble in common organic solvents such as CHCl₃, CH₂Cl₂, tetrahydrofuran, and other polar solvents. The chemical crosslinking was performed using FeCl₃ as an oxidizing agent. The electrochemical crosslinking was also performed in situ using electrochemical nanolithography, in which the crosslinking occurs at the interface of an electrode substrate in a conducting atomic force microscopy (AFM) setup.

Firstly, the chemical crosslinking was performed using an ultradilute concentration (6.2 × 10⁻⁷ M) of the dendrimer G3-D in chloroform. The molar ratio of FeCl₃ to G3-D was set as 200:1. At this dilution level, mostly intramolecular crosslinking occurs, i.e., formation of polycarbazole units at the surface of the dendrimer molecule, resulting in a crosslinked dendrimer (G3-D-CLK) as shown in Scheme 1. The extent of crosslinking was monitored using UV-vis spectroscopy. The G3-D shows an absorption peak at 325 nm and 345 nm, which are typically assigned to the π–π* and n–π* transitions of carbazole, respectively. After crosslinking, the π–π* transition is redshifted and observed as an adsorption tail extending into the visible range centered at 375 nm. This indicated the formation of higher π-conjugated species. The polymerization or crosslinking was performed until no further change was observed.

In addition to the electronic properties, one can utilize the fluorescent properties of polycarbazole to further confirm the crosslinking reaction. It was found that the dendrimer shows entirely different fluorescence spectra before and after crosslinking. The fluorescence of the carbazole units present on G3-D is observed at 360 nm (Figure 1B); this peak is...
Figure 1. A) UV-vis spectra recorded at various intervals to monitor the extent of crosslinking, and inset showing a solution of $1 \times 10^{-9}$ M G3-D dendrimer before and after crosslinking. Absorbance in absorbance units (a.u.). B) Fluorescence spectrum of G3-D at excitation of $\lambda = 325$ nm and inset showing the fluorescence spectrum G3-D-CLK (resulting from polycarbazole) after exciting at $\lambda = 375$ nm.

Figure 2. A) SEC analysis before and after crosslinking. B) NMR before and after crosslinking.

In order to further confirm the intramolecular crosslinking of the individual dendrimers based on a change in size, size exclusion chromatography (SEC) analysis was performed as shown in Figure 2A. A higher retention time was observed in going from G3-D (24.6 min) to G3-D-CLK (25.0 min), reflecting the more compact size of the crosslinked dendrimer, i.e., reduced hydrodynamic volume. In addition, at lower retention times the SEC elution curve of the G3-D-CLK also shows very small traces of dimer, trimer, or even higher analogs, which is evidence of some intermolecular crosslinking between dendrimer units. The extent of intramolecular crosslinking was also quantified using NMR spectroscopy. The integration of the peaks showed the extent of intramolecular crosslinking was more than 80%. The protons at the 3- and 6-positions of the carbazole have a distinct signal at around $\delta = 8.01$ ppm that decreases upon crosslinking, indicating the formation of polycarbazole, as shown in Figure 2B. It quenched in the case of G3-D-CLK, where a new peak arises at 420 nm resulting from the formation of polycarbazole (inset, Figure 1B).

Scheme 1. Intramolecular crosslinking of peripheral carbazole to form polycarbazole. Note that the diagram is just a 2D representation of the crosslinking process.
is highly unlikely to get complete intramolecular crosslinking within a dendrimer considering its 3D structure.

After crosslinking, both the crosslinked and uncrosslinked dendrimers were diluted to $1 \times 10^{-12}$ M in chloroform and subsequently spin-coated (5000 rpm for 2 min) on atomically flat mica (freshly cleaved). AFM was performed using an acoustic mode (238.143 kHz, 1.49 lines s$^{-1}$) to visualize the distribution in size, shape, and rigidity of the dendrimer before and after crosslinking. However, the lateral size could not be determined due to convolution effects created by the AFM tip. Figure 3A shows a random distribution of the G3-D dendrimer nanoparticles and upon analysis of the statistical distribution, the height profile revealed the particle size to be $2.46 \pm 0.24$ nm. Figure 3D shows a high-resolution AFM image and the line profile of an individual uncrosslinked nanoparticle which was found to be 2.4 nm in height.

The G3-D dendrimer was found to lie more flat on the surface of mica. It is quite rational to observe this behavior because the uncrosslinked G3-D is more flexible in its structure. On the other hand, G3-D-CLK was found to have a higher statistical distribution in height ($3.47 \pm 0.23$ nm) and a more compact shape, as shown in Figure 3B. Figure 3E shows a high-resolution AFM image and the line profile of an individual crosslinked nanoparticle which was found to be 3.48 nm in height.

Thus, the results show seemingly contradictory data in terms of change in height, while crosslinking results in the formation of a more rigid structure and a lower radius of gyration $R_g$ value, owing to the compact nature of the crosslinked dendrimer.$^{[12]}$

To delineate the effect of rigidity and dendrimer nanoparticle–substrate interaction, we also studied the uncrosslinked and intramolecularly crosslinked dendrimer on a low free-energy silanized silicon wafer as compared to the high free-energy surface of mica. The dendrimers were spin-coated following similar protocols and using exactly the same solution concentrations as before. The sizes of these nanoparticles were found to be 2.7 nm and 3.6 nm for G3-D and G3-D-CLK, respectively. (Supporting Information, Figure S1) Clearly, there is a height difference of the dendrimer nanoparticles in going from one substrate to the other. Thus, for the case of G3-D on mica, a pancakelike conformation is seen, while G3-D-CLK adopts a more egglike conformation and remains unchanged in either case, as observed by AFM. In order to further probe the observed disparity in shape and size, we performed theoretical calculations aimed at understanding the structural changes of the dendrimers upon crosslinking. Figure 4 shows the optimized structures that were obtained using a molecular mechanics force-field implemented in Spartan’04 starting from an initial structure (Spartan’04, Wavefunction Inc. Irvine, CA, see Supporting Information).
The data, and the images in Figure 4B and D illustrate the shape of the dendrimer before and after crosslinking, and are generated from the final optimized structure. The shapes of the dendrimer were predicted by calculating the moment of inertia for the G3-D dendrimer before and after crosslinking. The moments of inertia were obtained by diagonalizing the moment of inertia tensor, \( I \)

\[
I_{ik} = \sum_n m_n \left( r_{ni}^2 \delta_{jk} - x_{ni}x_{nk} \right)
\]

where \( x \) is the center of mass, \( m_n \) is the mass of the \( n \)th atom (not the total mass), \( x \) corresponds to the \((x,y,z)\) cartesian coordinates of the \( n \)th atom relative to center of mass of the molecule, and \( r \) is the distance between atom \( i \) and the center of mass. \( \delta \) corresponds to Kronecker delta; \( i, j, \) and \( k \) correspond to the Cartesian coordinates, and \( n \) corresponds to the index of the atom. \( I_A, I_B, \) and \( I_C \) are the components of the moment of inertia in the principal axis frame. Because \( I_A < I_B = I_C \) (conventionally \( I_C \geq I_B \geq I_A \)) in each case, the molecules are roughly prolate-shaped ellipsoids. The fact that the G3-D has less disparity between \( I_A \) and \( I_B = I_C \) than the G3-D-CLK case, indicates that the uncrosslinked molecule is less elongated (i.e., more spherical) than the crosslinked molecule, and that the chemically crosslinked versus the electrochemically crosslinked dendrimer. One possibility is that in the process of applying a bias voltage, neighboring dendrimers can collectively crosslink intermolecularly, e.g., two closely located dendrimers can come together and crosslink to form a dimer. This is not unreasonable considering the size of the cantilever probe surface and the distribution of the electric field on the substrate (hundreds of nanometers). Another is the effect of humidity in the meniscus between the tip and the substrate and possible degradative oxidation with this method. Yet another possibility is the combined effect of localized joule heating and crosslinking. However, more studies are needed using different experimental conditions in order to verify these possibilities.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>( I_A ) [( \text{Å}^2 \text{amu} )]</th>
<th>( I_B ) [( \text{Å}^2 \text{amu} )]</th>
<th>( I_C ) [( \text{Å}^2 \text{amu} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3-D-CLK</td>
<td>( 2.14 \times 10^5 )</td>
<td>( 6.31 \times 10^5 )</td>
<td>( 7.39 \times 10^5 )</td>
</tr>
<tr>
<td>G3-D</td>
<td>( 0.779 \times 10^6 )</td>
<td>( 1.08 \times 10^6 )</td>
<td>( 1.15 \times 10^6 )</td>
</tr>
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In conclusion, we have performed experimental and theoretical investigations of conjugated polymer nanoparticles brought upon by the intramolecular crosslinking of dendrimeric precursors using both chemical and in situ electrochemical methods. Both methods have shown variations in size and rigidity of the dendrimer nanoparticles, and regardless of crosslinking methods, the height of the crosslinked dendrimer was found to be higher than its uncrosslinked form. Finally, the models presented confirm both the size and rigidity of the organic nanoparticles, which can be fine-tuned by choosing the right conditions for either crosslinking method. Further studies are underway to investigate their current–voltage characteristics by current sensing AFM.

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Figure 5. AFM images (5 μm × 5μm) of G3-D dendrimers A) before and B) after electrochemical crosslinking using tapping mode (topographical imaging) with a scan rate of 1.49 lines s⁻¹.

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