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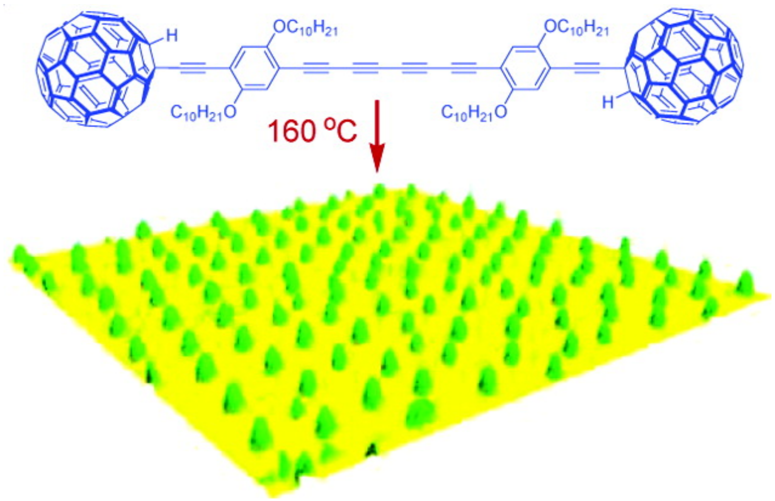

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COMMUNICATIONS

Preparation of Fullerene−Polyyne Nanospheres via Thermally Induced Solid-State Polymerization

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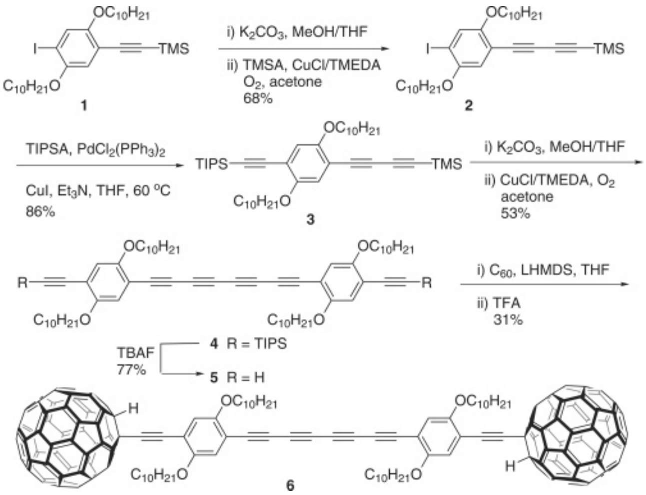
Buckminsterfullerene (C_{60}) is a fascinating building block for various nanoscale structures and architectures, and covalently linking it to a variety of conjugated oligomers/polymers has become an important approach to improve or enhance optoelectronic and photonic properties for diverse polymer composite systems.[1] For this reason, numerous C_{60}-containing conjugated oligomers and polymers have been synthesized and characterized in order to seek potential applications in areas, such as thin-film organic solar cells,[1c,2] nonlinear optical (NLO) and optical limiting materials,[3] to name a few. The fullerene−oligomer approach has been known to be particularly beneficial for fabrication of such devices as bulk heterojunction organic photovoltaic cells[4] and third-order optical nonlinearity controlled telecommunications apparatus.[5]

Spherical polymer nanoparticles, especially those containing fullerene moieties, are very appealing in manufacturing various nanoscale devices.[6] There are a number of methods that can be used to produce polymer nanospheres, including emulsion polymerization, intramolecular cross-linking, and solid-state polymerization. Compared with other methods, little is known about solid-state polymerization despite the simple preparation and compatibility with various solid substrates which it affords.[7] Conjugated polyynes are ideal candidates for the preparation of polymer nanospheres since they are reactive enough to be polymerized in the solid phase when subjected to heat, UV light, γ-ray irradiation, or pressure.[8] Previously, Hirsh and co-workers have reported making C_{60} nanospheres from emulsion polymerization of a butadiyne-containing lipofullerene.[9] Solid-state polymerization of longer polyynes bearing fullerene groups has, however, never been achieved.

To explore this possibility, a 1,3,5,7-octatetrayne-bridged bis(fullerene) "molecular dumb-bell" **6** was synthesized. This fullerene−tetrayne species, as expected, may lead to the formation of highly extended C_{60}−polyenyne networks or supramolecular assemblies, owing to the unique reactivity of the tetrayne unit in the solid state. The resulting polymers, like many reported fullerene−oligomer/polymer hybrids,[1−6] could serve as active components in various organic photovoltaic and NLO devices.

The synthesis of fullerene−tetrayne **6** is outlined in Scheme 1. Iodoarene **1** was first desilylated with K_2CO_3 and then underwent oxidative coupling with a large excess of trimethylsilylacetylene (TMSA) in the presence of Hay catalyst[10] to afford diyne **2** and a byproduct, bis(trimethylsilyl)butadiyne. Compound **2** could be easily isolated by column chromatography and was then reacted with triisopropylsilylacetylene (TIPSA) under Sonogashira conditions to yield **3**. Selective removal of the TMS group in **3** with K_2CO_3, followed by an oxidative homocoupling reaction, gave tetrayne **4** as a relatively unstable solid. Desilylation of **4** with tetrabutylammonium fluoride (TBAF) afforded terminal alkyne **5**, which was subsequently converted to the final product **6** using an in situ ethynylation method.[11]

Scheme 1



The structure and purity of compound **6** were confirmed by ^1H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry (see Supporting Information). Unlike its precursors, **4** and **5**, fullerene−tetrayne **6** is thermally stable from room temperature up to ca. 150 °C, as is evident from differential scanning calorimetry (DSC) analysis; no melting or phase transition appears in the DSC trace within this range. A broad exothermic peak is observed from 156 to 240 °C, and with a maximum at 211 °C. Apparently, the tetraynes start solid-state polymerization in this temperature range, but the broad peak width suggests that the polymerization occurs in a random manner rather than a regioselective topochemical polymerization. This can be explained by the relatively large sizes of fullerene groups prohibiting a tetrayne unit alignment suitable for topochemical polymerization.[12] The DSC trace remains nearly flat and shows no additional phase transitions from 240 to 350 °C. The enthalpy for the exothermic process (ΔH) is measured to be 77.6 kJ/mol, which is considerably smaller than that of tetrayne **5** (317.7 kJ/mol). It is assumed that a stable polymer was formed within these temperatures; however, the polymerization degree was low due to steric effects. The resulting solids after DSC analysis of **6** were brownish in color and completely insoluble in any organic solvent. MALDI-TOF mass spectrometric analysis was attempted on these solids but failed to give any positive identification. IR analysis, however, shows a dramatically differing vibrational spectrum than that of **6**. A new peak at 1728 cm^{-1} in the IR spectrum of the polymer suggests that the polymerization terminates upon reacting with oxygen to form carbonyl groups. X-ray powder diffraction analysis shows that the resulting polymer solids are amorphous.

The DSC results of **6** are in good agreement with its UV−vis spectroscopic analyses. Figure 1 shows the UV−vis profiles for compound **6** measured in both solution and solid films. In toluene, fullerene−tetrayne **6** shows three distinctive absorption bands at 386, 415, and 454 nm due to the central tetrayne unit, while the higher-energy bands around 318 nm are due to the exterior

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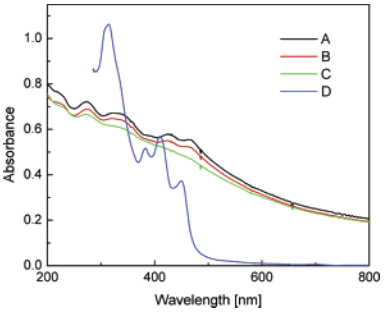

Figure 1. UV−vis spectra for compound **6**: (a) solid film on quartz without heating; (b) solid film after thermal annealing at 135 °C for 30 min; (c) solid film after thermal annealing at 160 °C for 1 h; and (d) in toluene at room temperature.

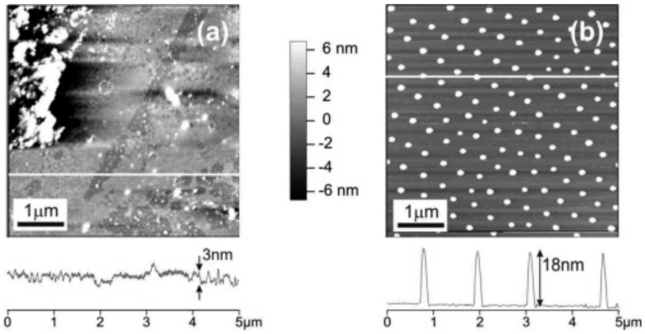

Figure 2. AFM images (5 μm × 5 μm) and corresponding line scans of the thin films of **6**: (a) before thermal annealing, and (b) after thermal annealing at 160 °C for 1 h. White lines indicate where the sections were taken.

phenylacetylene groups. A broad, weak absorption tail ranging from 480 to 600 nm is observed, arising from the contribution of fullerene groups. Solid films of **6** were prepared by drop-casting a toluene solution onto a quartz slide, and UV−vis spectra were measured before and after being heated at different temperatures. The UV−vis spectrum of the film after thermal annealing at 135 °C for 30 min shows no significant changes in comparison to the original film. After heating the film at 160 °C for 1 h, marked distinctions in UV−vis absorption were observed; the three characteristic bands due to the tetrayne unit disappeared completely, while the higher-energy bands below 300 nm and the fullerene absorption tail were barely altered. These results indicate that intermolecular reactions have been limited to the tetrayne moieties.

Finally, the thermally induced polymerization process was examined by atomic force microscopy (AFM). A dilute solution of **6** in toluene (ca. 10^{-4} to 10^{-5} M) was cast on a freshly cleaved mica surface to afford a thin film. The film was initially disordered and amorphous with regions made up of single to several molecular layers, as illustrated in Figure 2a. After thermal annealing of the same film at 160 °C for 1 h, the surface shows strikingly different morphology with highly uniform and ordered nanospheres 15−20 nm high, as seen in Figure 2b. Larger images (up to 90 μm × 90 μm) from different areas of the sample showed similar features, indicating the formation of homogeneously dispersed nanospheres over a relatively large scale.

In some regions, arrays of larger-sized nanospheres (ca. 120 nm in height) were observed, as well. It is likely that the size of the nanosphere is dependent on the thickness of the fullerene−tetrayne film and its dewetting from the substrate. However, we believe that the low degree of polymerization could be a principal reason for the formation of such uniform nanosphere arrays on the surface because no similar spherical nanoparticles were formed when solid films of tetrayne **5** were thermally polymerized under the same experimental conditions.

To our knowledge, this is the first preparation of evenly distributed and uniform-sized fullerene-containing polymer nanospheres via thermally induced solid-state polymerization. In comparison to the previous work on fullerene-based nanoaggregates,[6a,b,f] the transformation from amorphous solid thin films to orderly structured nanosphere arrays is indeed remarkable and exceptional. This method is rather simple, reproducible, and could be useful in manufacturing various oligomer/polymer-based nanodevices.

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Supporting Information Available: Synthetic procedures, ^{1}H and ^{13}C NMR spectra for compounds **2**−**6**, MALDI-TOF mass spectrum, and detailed DSC, IR, and AFM analyses for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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