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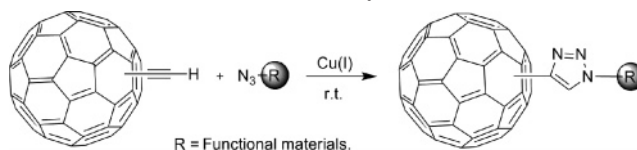Akron, Ohio 44325-3909*

Introduction. Fullerenes are fascinating carbon nanostructures that are not only aesthetically appealing but also have outstanding structural, magnetic, superconducting, electrochemical, and photochemical properties with great potential in both material science and applications.[1,2] However, the poor compatibility of pristine fullerenes with other materials severely limits their derivatization and utilization. Despite the diverse routes to functionalize fullerenes,[1c] only a few are highly efficient and specific.[3] This is especially the case for polymers.[4−6] The often unavoidable multiple addition and the reactive nature of fullerene to various reaction intermediates always leads to a mixture of homopolymer, monoadducts, and multiadducts, which, unlike small molecules, are often difficult to purify. Moreover, the reduced chain end reactivity in polymers (such as azides[6]) might sometimes require drastic reaction conditions (high temperature, long time, etc.), which could lead to potential polymer backbone degradation.[6c] Also, some derivatives are unstable either by themselves (e.g., retro-D−A reaction)[1c] or with singlet oxygen generated by [60] fullerene (e.g., azafulleroid).[7] All of these can complicate the study of the physics of fullerene polymers. Our interest lies in the area of self-assembly in solution including crystallization of the polymer moiety to form a single crystal with two-dimensional arrays of the fullerene on the crystal surface. Thus, as part of our effort to manipulate fullerenes within the polymer paradigm, we wish to develop a strategy to create stable, well-defined fullerene materials under mild reaction conditions.

The concept of "click chemistry" has received enormous attention and has generated a considerable impact in material science since its reinvention in 2001.[8] The idea is to generate materials from a simple set of "click" reactions that are of high efficiency and technical simplicity, as demonstrated by the Cu-(I)-catalyzed [3 + 2] Huisgen cycloaddition reaction between an azide and a terminal alkyne to form a 1,4-substituted 1,2,3-triazole.[9] Taking advantage of this reaction, we should be able to use terminal alkyne-functionalized fullerenes (thus named "Fulleryne" for the sake of simplicity), instead of pristine fullerene, to introduce fullerene into polymers in a "click" fashion (Scheme 1).

To the best of our knowledge, there is no report so far on the use of this reaction to functionalize C_{60} (only one report on the functionalization of single-walled carbon nanotubes via click coupling[10]). The thermal [3 + 2] cycloaddition between azide and the fullerene core at elevated temperatures[11] or the low solubility of fullerene derivatives in polar solvents, which decreases the yield and limits the scope of the click reaction,

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Scheme 1. General Functionalization of Fullerene via "Click" Chemistry

R = Functional materials.

may be the rationale. To circumvent these problems, we need to design Fullerynes that have improved solubility in common solvents and readily react with azide at room temperature. In this communication, we report the design, synthesis, and characterization of such Fullerynes and their click reaction to give narrow polydispersed, stable, and well-defined C_{60}-end capped polystyrenes in high yields.

**Results and Discussion. a. Fulleryne Design and Synthesis.** Both the mechanistic study and experiments on the Huisgen cycloaddition reaction reveal that electron-deficient alkynes enhance the rate of triazole formation and allow for mild reaction conditions.[12] Rubin et al. have demonstrated several stable hydroxyl-functionalized fullerene derivatives as versatile synthons (**3**).[13] Therefore, the terminal alkynes with an adjacent carbonyl group, such as fullerene propiolates, were chosen as a prototype of the Fullerynes. Simple esterification of **3** with propiolic acid gives Fulleryne01 (Scheme 2). Fulleryne01 is a brown powder and has been fully characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, UV−vis, and MALDI−TOF mass spectrometry. Its features include high stability to moisture and air as well as enhanced solubility in common organic solvents, as compared to C_{60}. It is possible to create numerous kinds of Fullerynes, depending on the chemistry to functionalize fullerene and the distinct structures that can be created. The Fullerynes can also be tailored to possess diverse functions, either photo-(in)active or electro(in)active.

Preliminary attempts to improve the preparation of Fulleryne01 according to literature[14] did not give positive results. It was reported that DCC/DMAP-mediated esterification of propiolic acid with phenolic derivatives gives a yield of 20−40%, which is consistent with our result.[14b] The acyl chloride route[14a] resulted in immediate formation of a resinous precipitate upon the addition of propynoyl chloride, and no product could be detected. The low solubility of C_{60} derivatives at molar concentrations made Fisher esterification very inefficient. The attempts using the mixed anhydride route[14b] was plagued by difficulty in purifying fullerene carbonochloridate and its redissolution in THF for reaction with sodium prop-2-ynoate. The DCC/DMAP route remains the simplest way to make Fulleryne01. We are continuing work to improve the yields as well as seeking new Fullerynes. We are optimistic about finding Fullerynes that have high reactivity yet could be easily available in large quantities.
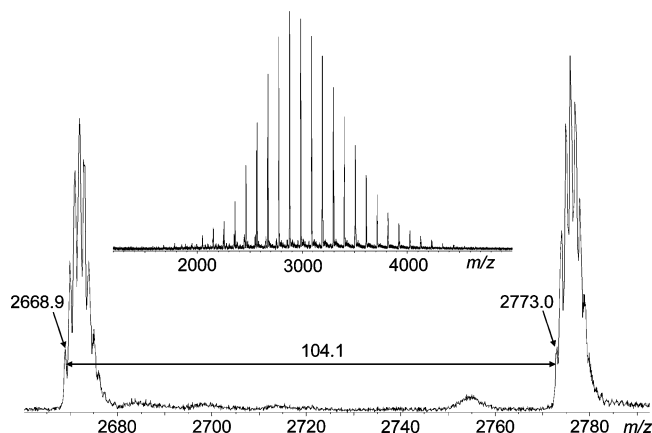
b. Functionalization Using "Click Chemistry." The synthesis of azido-functionalized materials, ranging from small molecules to macromolecules[8,15] and nanoparticles to various surfaces,[16] is well-established. As a straightforward example to demonstrate the concept, an azido-functionalized polystyrene, prepared via ATRP and subsequent nucleophilic substitution[15] (Scheme 2), was chosen as the model. Since polymers are known for their decreased end-group reactivity, the result should also serve as a criterion for evaluating the efficiency of the reaction.

The click reaction was performed at room temperature with CuBr/PMDETA as the catalyst in toluene (Scheme 2).[15] It was
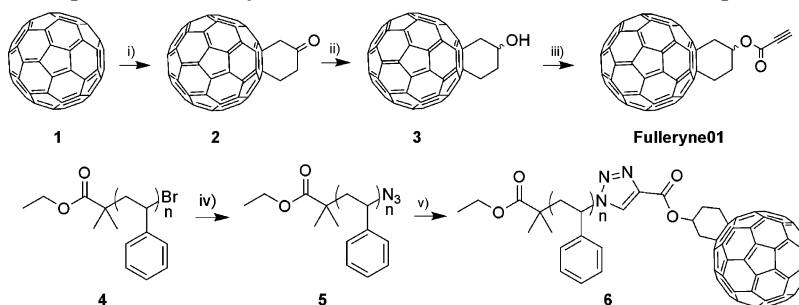
^{a} (i) 2-Trimethylsiloxy-1,3-butadiene, toluene, reflux, 59%; (ii) DIBAL-H, rt, 93%; (iii) propiolic acid, DCC, DMAP, rt, 17%; (iv) NaN₃, DMF, rt, >99%; (v) Fulleryne01, CuBr, PMDETA, toluene, rt, 95%.

Figure 1. MALDI-TOF mass spectra for PS−C$_{60}$ (**6**, 2K).

Figure 2. Overlay of SEC traces of PS−N₃ (**5**, gray line) and the PS−C$_{60}$ (**6**, dark line): (a) M_n = 2000; (b) M_n = 6100; (c) M_n = 10 000 for the polystyrene backbone.

found that there was no [3 + 2] cycloaddition reaction between the PS−N₃ and the fullerene core, even with excess of PS−N₃. This is evidence that there is only monoaddition to the Fulleryne01. The purification was readily performed by passing a short silica gel column to remove the catalyst and excess starting material and then precipitating in MeOH. The triazole product was obtained as a brown powder, readily soluble in common organic solvents such as THF, CH₂Cl₂, etc. The brown solution indicated the covalent linkage of C$_{60}$ with PS (for UV− vis, see Figure S4). The click reaction was successfully carried out on PS−N₃ with three different molecular weights (M_n = 2000, 6100, and 10 000 g/mol).

The success of the cycloaddition was further supported by evidence from ^{1}H NMR, ^{13}C NMR, FTIR, and MALDI-TOF mass spectrometry. The product exhibited the characteristic resonances of protons both in benzylic 1,2,3-triazole (5.1−5.3, 7.6−7.8 ppm) and near the terminal C$_{60}$ unit (2.8−3.0, 3.3− 4.0 ppm) in ^{1}H NMR spectra (Figure S1). It also showed the sp^3 carbons as well as sp^2 carbons of the terminal C$_{60}$ unit (60.2, 64.0, and 135−155 ppm overlapping with aromatic carbons) in ^{13}C NMR spectra (Figure S2). FTIR showed the complete disappearance of the azide (2095 cm^{-1}) and the appearance of a sharp peak at 528 cm^{-1}, which is characteristic for fullerenes (Figure S3). The MALDI-TOF mass spectra showed a very narrow distribution with molecular weight in accordance to the proposed structure, confirming the cleanliness of the reaction and the stability of the resulting fullerene polymers (Figures 1 and S5). Considering the fact that MALDI-TOF mass spectroscopy can detect impurities as low as 1% and the starting materials (homopolystyrene) have a much lower molecular weight and thus are much easier to ionize, the results proved that the samples were free of homopolymer. These results unambiguously establish the structure, uniformity, and purity of the polymer obtained. It was also found that the polymer
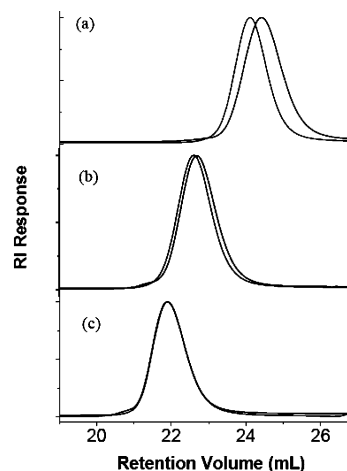
was pretty stable toward singlet oxygen. It can be handled without special caution to exclude oxygen. The ease of reaction and purification, along with the high efficiency in the coupling step, make it particularly useful when the materials to be functionalized are unstable at drastic reaction conditions (e.g., biological molecules), when the products are very difficult to separate (e.g., polymers), or when the materials are hetero- geneous (e.g., surfaces, nanoparticles, etc.).

c. Unusual SEC Observation. To illustrate the basic physics of fullerene polymers, we need model compounds that have 100% well-defined fullerene functionality, well-defined struc- ture, and narrow polydispersity. The fullerene polymers we obtained serve as excellent model compounds. Sometimes, it can show significantly different behavior than those contami- nated by impurities such as homopolymers or multiadducts. Indeed, unusual, interesting phenomena were observed in SEC. As expected, the samples gave a unimodal, symmetric peak with much narrower PDI (1.02 for 2K and 1.01 for 6K and 10K) than the corresponding PS−N₃ (Figure 2). Contrary to literature reports that C$_{60}$-end capped PS fit well with the weights estimated from the parent PS,[4a−d,6b] their retention volume was actually slightly larger than base polymer PS−N₃. The difference is significant for M_w = 2K but less so for M_w = 6K; there is no difference for M_w = 10K, indicating no aggregation in THF and a very small, even negative impact of the C$_{60}$ unit to the overall hydrodynamic volume of the polymer. We speculate that since C$_{60}$ is insoluble in THF, the polystyrene chain tends to wrap around the buckyball in dilute solution. At low M_w, it results in decreasing the hydrodynamic volume down to the size similar to that of C$_{60}$, while at high M_w, the chain size is large enough that the influence of end group becomes insignificant.

Conclusions. In summary, we have successfully applied "click chemistry" (Huisgen [3 + 2] cycloaddition reaction) to the synthesis of fullerene−polymer hybrids. As an example, azido-functionalized polystyrene was reacted with alkyne-functionalized fullerene (Fulleryne01) at room temperature to give well-defined C_{60}-end-capped polystyrene. This reaction is mild and high yielding. The products, free of homopolymer and multiadduct polymer, possess high functionality (∼100%) as well as narrow polydispersity (∼1.01). They are uniquely suitable as model compounds to study the physics of fullerene polymers. Unusual and interesting behaviors were observed in SEC, showing that low-molecular-weight conjugates adopt a more compact conformation than their base polymers in THF solutions. Other results concerning the physics of these model compounds will be discussed in later publications. The synthetic method for the functionalization of fullerene presented here can be further extended to other polymers as well as small molecules.

Supporting Information Available: Detailed experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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