Chemical reactions inside single-walled carbon nano test-tubes†

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We report the application of SWNTs as templates for forming covalent polymeric chains from $C_{60}O$ reacting inside SWNTs; the resulting peapod polymer topology is different from the bulk polymer in that it is linear and unbranched.

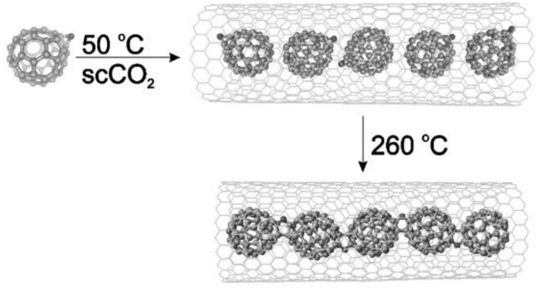
Among the wide range of interesting properties exhibited by single walled carbon nanotubes (SWNTs) is their capacity to encapsulate other species within their quasi one-dimensional cavity.[1] Owing to the confinement offered by the nanotube, the encapsulated materials often form novel crystal packings that are thermodynamically unfavourable in the bulk.[2,3] Here, we exploit and extend this phenomenon by using SWNTs with a narrow diameter distribution as "nano test-tubes" to constrain a chemical reaction and create a new topology of polymeric fullerene oxide that is otherwise impossible to synthesize in the bulk.

Many industrially important polymers show markedly different topologies under different reaction conditions; polyethylene, for example, is synthesised *via* a free radical process, and the resulting material is branched and has lower mechanical strength than linear polyethylene. Linear polyethylene is formed using a specifically designed organometallic catalyst and yields a material with substantially improved structural properties. Rather than using a specific catalyst to control the topology, we aimed to study the effect of one-dimensional confinement on polymerization, with a focus on the change in topology of the polymeric product. We chose as our precursor species the fullerene epoxide, $C_{60}O$. The fullerene epoxide was synthesized from C_{60} using urea hydrogen peroxide and methyl trioxorhenium.[4] It was then purified to $\geqslant$99.9% using high performance liquid chromatography† and characterized by mass spectrometry and UV-Vis spectroscopy. Sample purity was routinely checked before polymerization and encapsulation reactions.

Above 250 °C in the solid state, $C_{60}O$ polymerizes *via* epoxide ring-opening, with a rigid furan-type bridge linking the cages.[5] $C_{60}O$ reacts without side products to form a tangled, branched three-dimensional polymer where the single oxygen atom bonds to any of its twelve nearest neighbours; the interfullerene spacing is 9.97 Å, close to that of C_{60}.[6] To form the fullerene oxide polymer, we heated $C_{60}O$ at 260 °C at 10^{-6} Torr for three days. The polymeric material was suspended in toluene and filtered, and the filtrate was examined by HPLC and mass spectrometry. We found no fullerene or fullerene oxide present in the filtrate, indicating a complete transformation of the monomeric $C_{60}O$ to polymeric $(C_{60}O)_n$. Our selected area electron diffraction (SAED) studies confirm that the fullerene oxide polymer forms a face centered cubic lattice with an interfullerene spacing matching literature values. This polymer has a highly complex and disordered topology, due in part to the large number of equivalent sites on the fullerene cage that are reactive to epoxides.

The walls of SWNTs are chemically stable under the reaction conditions for polymerization of $C_{60}O$, and their interior surface is even more inert than the exterior surface.[7] Within conditions typical for organic reactions, they can act as inert containers for reactive species, analogous to a standard laboratory test-tube. Our full procedure is illustrated in Scheme 1. We mixed a three-fold excess of $C_{60}O$ with opened, purified SWNTs with two main diameters of 13.6 Å and 14.9 Å. The nanotubes were filled with $C_{60}O$ at 50 °C from supercritical CO_2.[8,9] Specifically, we used our optimized procedure, where the pressure of the supercritical cell was cycled daily over a period of six days.[9] There is a strong van der Waals interaction between the $C_{60}O$ and the nanotube, so the $C_{60}O$ readily enters to form "peapod" structures designated as $C_{60}O$@SWNTs; the encapsulation is exothermic by $\sim$3 eV per molecule.[10,11] The filled nanotubes were washed thoroughly and filtered in CS_2 to separate the $C_{60}O$@SWNTs from unencapsulated $C_{60}O$. This gave clean $C_{60}O$@SWNT peapods with a fullerene spacing of 10.0 Å in about 70% yield, as characterized by high resolution transmission electron microscopy (HRTEM)‡ (see Fig. 1a). The filling procedure carried out at 50 °C did not cause $C_{60}O$ to react: no insoluble polymer was observed outside the nanotubes under HRTEM imaging, despite the large excess of $C_{60}O$. Also, the fullerenes inside the SWNTs appeared to be discrete; the only noticeable difference between C_{60} peapods and $C_{60}O$ peapods was that the fullerene oxides degraded more rapidly than fullerenes under electron beam irradiation.

The $C_{60}O$@SWNT peapods were then heated at 260 °C at 10^{-6} Torr for three days to initiate the polymerization of the $C_{60}O$. Fig. 1b shows a HRTEM micrograph of the resulting material. The structure contained in the nanotube still has an interfullerene



Scheme 1

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† Electronic supplementary information (ESI) available: HPLC and MS of $C_{60}O$; SAED and HRTEM images of $(C_{60}O)_n$. See http://www.rsc.org/suppdata/cc/b4/b414247k/

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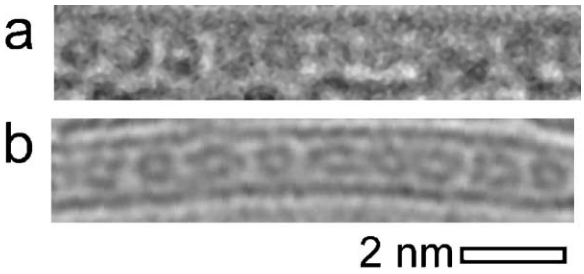

Fig. 1 HRTEM micrograph of (a) unreacted $C_{60}O$ peapods. Note that the cages appear to be separate and circular. (b) A linear $(C_{60}O)_n$ polymer, where the cages become more elongated because of the reaction. In both cases, the interfullerene spacing is 10.0 Å.

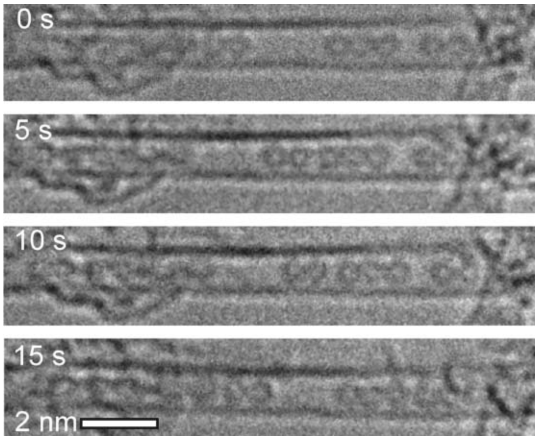

Fig. 2 HRTEM micrographs showing a time series of oligomers $C_{120}O$ and $C_{180}O_2$ translating inside an individual SWNT. Five seconds elapsed between each image.

periodicity of 10.0 Å, indistinguishable from the spacing of the bulk polymer.[6] Most other fullerene polymers have a substantially shorter interfullerene spacing due to abundant C–C bonds.[12] An observation of shorter spacing would be an indication of an uncontrolled polymerization of $C_{60}O$, where adjacent fullerene cages would linked by more than one C–C bond.

In contrast to the unpolymerized fullerene oxide peapods, the fullerene cages are somewhat elongated. The nanotube itself appears unmodified by the reaction. The image in Fig. 1b is consistent with the hypothesis that the individual $C_{60}O$ molecules have polymerized head-to-tail, with the sole role of the nanotube being to constrain the resulting polymer to be linear and unbranched. This observation is reasonable because fullerene epoxide rings do not react with each other, and longer molecules, such as C_{70}, have a small barrier for rotation inside 14.9 Å SWNTs.[13] The linear $(C_{60}O)_n$ polymer has never before been observed.

In order to check our hypothesis more thoroughly, we repeated the procedure with a 65 : 35 mixture of $C_{60}O$ and unfunctionalized C_{60}; the expectation length of the resulting oligomers is about three units because an unfunctionalized C_{60} terminates the polymer. It has been shown in sparsely filled peapods that fullerenes freely translate along the length of the nanotube.[14] If the fullerenes are not covalently bonded, they will collide, then separate under standard HRTEM imaging conditions. Therefore, an observation of fullerenes that remain connected over a period of time is an indication of stable, covalent bonding. Fig. 2 shows a time series of HRTEM micrographs of a particular region of a specimen after the polymerization reaction. Oligomers of two and three units can be seen moving back and forth along the length of the nanotube section over time. This observation strongly confirms the hypothesis of C–O–C chemical bonds between fullerenes; if the material inside the tube had not reacted, then individual units would remain discrete and mobile. Their mobility also demonstrates that the fullerene oxide did not react with the nanotube walls. Additionally, electron beam damage appears to be insignificant under the imaging conditions, as the oligomers do not irreversibly aggregate with each other over the exposure time.

Previously, there have been reports of the degradation and coalescence of unfunctionalized fullerenes encapsulated in SWNTs at temperatures in excess of 800 °C, involving the uncontrollable breaking of C–C bonds on the fullerenes,[15] at temperatures that almost certainly damage the nanotubes. Herein, we have presented a controlled transformation of functionalized fullerenes with a well-defined reactivity, that of epoxide ring opening to form a furan-type bridge. When confined to a one-dimensional cavity, the fullerene oxide reacts to form unbranched, linear polymers. Thus, the topology of the polymer inside the nanotube is substantially improved over the bulk material simply as a consequence of confining the reaction. $C_{60}O$ provides an almost ideal test molecule to study reactions inside nanotubes: it has a well-defined reactivity, its functional group does not hinder encapsulation or rotation inside the nanotube, the reaction produces no side-products, and the transformation is directly observable in HRTEM. However, the drawback of $C_{60}O$ is that the polymerization is difficult to study spectroscopically: the IR modes of the epoxide and furan rings are weak and overlap with strong IR bands and a plasmon background of SWNTs. Raman spectroscopy may be a better alternative for monitoring the polymer evolution, and requires a detailed study of the reaction products within and without SWNTs. A theoretical study on the Menshutkin S_N2 reaction inside SWNTs shows a reduced reaction barrier, as compared to the gas phase, and one similar to low-dielectric solvent.[16] The difference in reactivity of $C_{60}O$ inside a SWNT is not expected to differ greatly from the bulk crystal, but this effect may play a role.

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Notes and references

‡ HRTEM imaging was performed on JEOL 4000EX electron microscope (information limit ~ 1.2 Å) at 100 kV accelerating voltage to minimise the knock-on damage. Typically 1 s exposures were used for imaging. Over 60 micrographs (200 × 200 nm) were taken from different areas of each specimen in order to estimate the SWNT filling factor. Specimens were found to be fairly homogeneous and the yield of 'peapods' was calculated by counting the number of filled nanotubes in each micrograph, and then averaging over the total number of micrographs taken for each specimen.

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