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Polymerisation of 1-iodohexa-1,3,5-triyne and hexa-1,3,5-triyne: a new synthesis of carbon nanotubes at low temperatures

Jaromír Hlavatý,*[a] Ladislav Kavan,[a] Naoto Kasahara[b] and Asao Oya[b]

[a] *J. Heyrovský Institute of Physical Chemistry, Dolejškova 3, CZ 182 13 Prague 8, Czech Republic.*
E-mail: hlavaty@jh-inst.cas.cz
[b] *Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan*

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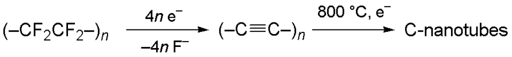
1-Iodohexa-1,3,5-triyne (I) and hexa-1,3,5-triyne (II) spontaneously polymerise in aprotic solution to form a solid carbonaceous product which contains polyyne-like structures and multi-walled carbon nanotubes with outer diameter *ca.* 10–20 nm and length 100–200 nm.

Carbon nanotubes are conventionally produced by high-temperature (T > 1000 °C) catalytic processes. Nanotubes and fullerenes can also be prepared, albeit in low yield, at room temperature by chemical defluorination of perfluorocyclopentene, perfluorodecalin and perfluoronaphthalene.[1] Kawase *et al.*[2] have shown that a totally defluorinated poly(tetrafluoroethylene) (PTFE) can be partly transformed into carbon nanotubes (10–50 nm diameter, 1 μm length) by irradiation with fast electrons (100 kV; 103 C cm^{-2}) at 800 °C. The process assumes the presence of reactive polyyne, which is formed by electrochemical reductive defluorination of PTFE,[2] Scheme 1.



$(-CF_2CF_2-)_n \xrightarrow[-4n\,F^-]{4n\,e^-} (-C\equiv C-)_n \xrightarrow{800\,°C,\ e^-} \text{C-nanotubes}$

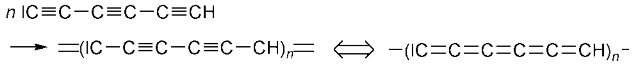
Scheme 1

However, the polyyne, $(-C\equiv C-)_n$ hardly exists in the pure state.[3] The actual precursor of nanotubes in Scheme 1 is, probably, a disordered graphitic carbon containing some chemically bound oligoyne segments with conjugation lengths less than 16 C-atoms.[3,4] If the electron/heat treatment in Scheme 1 was omitted, no nanotubes grew.[2] Also, no defined carbonaceous nanoclusters were found in PTFE defluorinated by alkali metal amalgams.[1]

To avoid the poorly defined precursor in Scheme 1, we have explored whether carbonaceous nanoparticles can be synthesised as in Scheme 1, but from chemically defined low-molecular-weight oligoynes. The reactants of choice seem to be hexatriyne derivatives: butadiyne is almost inert against chemical carbonization,[5] but higher homologues are too reactive to be handled safely.

Hexa-1,3,5-triyne (**II**), was prepared from prop-2-ynylol.[6] 1-Iodohexa-1,3,5-triyne (**I**) was synthesised from hexa-1,3,5-triyne according to a procedure developed by ourselves[5] Briefly, **II** was monolithiated by a stoichiometric amount of MeLi in THF at −30 to −40 °C, and Li was subsequently substituted with iodine.[5,7] Both precursors **I** and **II** are ultimately stable only in solution at low temperatures.

'Poly(iodohexatriyne)' was prepared as follows: a freshly made 0.3–0.4 M solution of **I** in *n*-hexane–diethyl ether (*ca.* 1 : 1 *v/v*; water concentration < 50 ppm; stored under Ar) was vacuum evaporated at room temperature over several minutes, while an insoluble, explosive, brown solid remained. Its composition was not too far from that of the precursor. (Elemental analysis: C 39.65, H 1.23, I 57.20%. Calc. for C_6HI: C 36.04, H 0.50, I 63.46%). The solid was, presumably, produced as a result of radical polymerisation of **I**, which progressed according to a *brutto* scheme (Scheme 2) A more stable, non-explosive material was prepared by slow polymerisation of **I**. This occurred simply after storing the solution under Ar for 1–2 d at room temperature. During this time, a dark brown powder precipitated, and a brown-yellow film deposited on the walls of the reaction vessel. When the reaction progressed, the film tended to peel off and roll into fine tubes. The addition of a small amount of *n*-undecane to the solution impeded the film formation and the product was mostly powder. On the contrary, the film formation was promoted by the addition of THF or ethyl acetate. The product was isolated by filtration, washed with hexane and diethyl ether, dried in vacuum at room temperature and stored under Ar. Elemental analysis evidenced some carbonisation, as the iodine content decreased: C 53.50, H 1.17, I 45.20%. [The difference from 100% mostly corresponds to adsorbed Ar (*vide infra*)]. The loss of iodine was further promoted by illumination with UV light (100 W high-pressure Hg lamp). The photo-assisted polymerisation–carbonisation of **I** gave a product containing: C 57.27, H 1.55, I 38.90%. Infrared spectra of 'poly(iodohexatriyne)' (both powder and film) exhibited comparable features with a characteristic intense band of conjugated sp-bonded carbon atoms (polyyne-like) between 2184–2194 cm^{-1}.



$n\,IC\equiv C-C\equiv C-C\equiv CH \longrightarrow =(IC-C\equiv C-C\equiv C-CH)_n= \Longleftrightarrow -(IC=C=C=C=C=CH)_n-$

Scheme 2

The polymerisation of hexatriyne **II** in *n*-undecane or *n*-hexane (water concentration < 50 ppm) was considerably faster compared to that of iodohexatriyne. It occurred within *ca.* 1 h at room temperature or within 1 d at 0 °C. The reaction accelerated with temperature (from 0–60 °C) and the concentration of **II** (up to 0.8 M). The addition of THF, diethyl ether or benzene promoted the formation of a yellow-brown film at the walls of the reaction vessel. Methanol, on the other hand, blocked any precipitation, and only soluble products were formed. Elemental analysis of a solid 'poly(hexatriyne)' gave: C 88.21, H 3.37%. The sample reversibly lost about 10% of its weight at 250 °C in vacuum, but this was almost completely re-captured if the outgased sample was exposed to Ar (weight increase 9.2%). This roughly accounts for the difference of analytical data from 100%, if we assume that Ar adsorbs from the sample's environment (calculated for C_6H_2: C 97.28, H 2.72%). The 'poly(hexatriyne)' exhibited two IR bands at 2110 and 2188 cm^{-1}, whose intensity was much smaller compared to those of 'poly(iodohexatriyne)'.

A pure 'one-dimensional' polymerisation (Scheme 2) seems to take place only after a fast rise of the concentration of **I**. Slow reactions in the solution are dominated be 'two-dimensional' polymerisation, which occurs *via* cross-linking of oligoyne sections in the precursor and/or in the primary chain-like polymer (*cf.* Scheme 2). The cross-linking of hexatriyne to yield graphene segments is shown in Scheme 3, where R = I, H. There are numerous theoretical[8] and experimental[3] arguments that the two-dimensional polymerisation (Scheme 3) is highly favoured, while it may produce extended graphite-like structures. The graphitisation (Scheme 3) seems to also provide a driving force for the partial splitting off of iodine and hydrogen

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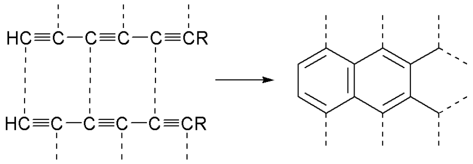

Scheme 3

from the precursor. However, the mechanism of propagation of the extended graphene is unknown.

The presence of iodine in the precursor **I** retards the polymerisation–carbonisation and stabilises the chain-like structure (Scheme 2). Hence, hexatriyne **II** exhibits a larger tendency towards the two-dimensional polymerisation (Scheme 3). Analogously, iodobutadiyne and 1,4-diiodobutadiyne[5] are inert in *n*-hexane (they polymerise only after UV excitation).[5] Butadiyne in *n*-hexane exhibited a very slow spontaneous polymerisation at room temperature in the dark, yielding solely a thin film at the walls, but the film showed a strong IR band at 2246 cm^{-1}. These results match the general conclusion that the stability of sp-bonded all-carbon chains against cross-linking increases when the chains contain bulky substituents at defect sites.[3]

Transmission electron microscopy (TEM) of both 'poly(iodohexatriyne)' and 'poly(hexatriyne)' revealed a presence of multi-walled carbon nanotubes (Fig. 1). The nanotubes were found in all the studied samples except 'poly(hexatriyne)' generated at temperatures $\geqslant$40 °C. (At higher temperatures, the hexatriyne conversion to planar graphene (graphite) seems to prevail). The highest content of nanotubes was found in 'poly(hexatriyne)' polymerised at 0 °C. The nanotubes were not spread statistically in the sample: they formed agglomerates (as in Fig. 1) embedded in a material with an amorphous shape. Hence, the yield of nanotubes cannot be precisely determined. By comparison with many TEM pictures, we estimate the yield of nanotubes to be roughly 1% in good samples. Some products showed also a casual occurrence of spherical onion-like nanoparticles (*cf.* Fig. 1). The nanotubes in 'poly(hexatriyne)' and 'poly(iodohexatriyne)' resemble those generated by reductive defluorination of perfluorocyclopentene.[1] Typically, the nanotubes, are straight, multi-walled, with diameter 10–20 nm and length 100–200 nm, and they are capped by onion-like hemispheres. The presence of curved moieties (onions, nanotube-caps) requires that some five-membered carbon rings are also formed *via* the interchain reaction (Scheme 3). However, the mechanism of pentagon-formation is again unclear. Our nanotubes (grown at low temperature both from hexatriyne and fluorocarbons[1]) are narrower and shorter than those grown from ex-PTFE 'polyyne' by electron bombardment at 800 °C.[2]

Raman spectra of the nanotube-rich 'poly(hexatriyne)' displayed only two broad bands at 1350 and 1600 cm^{-1}, which can be assigned to polycrystalline graphite and/or multi-walled carbon nanotubes. (These two structures are difficult to distinguish by Raman spectroscopy). If we assign the Raman bands at 1350 and 1600 cm^{-1} to the graphite D and G lines, respectively,[4] their intensity ratio (0.43) allows the size of graphite crystals to be estimated at about 10 nm. (Similar-size graphite nanocrystals result also from cross-linking of PTFE-borne 'polyyne'.[3,4]) In accord with TEM, no single-walled carbon nanotubes were detectable in the region of the radial breathing mode (*ca.* 200 cm^{-1}).

In conclusion, hexatriyne derivatives show a pronounced tendency towards conversion into disordered graphene-like nanostructures, *viz* multi-walled carbon nanotubes. The production of nanotubes from hexatriyne seems to be more facile and more efficient, compared to the processes based on defluorination of octafluorocyclopentene and similar precursors.[1] Further effort should concentrate on the understanding and optimisation of the chemical synthesis of nanotubes. This knowledge might also help us to understand the mechanism of production of carbon nanotubes in the common high-temperature catalytic processes.

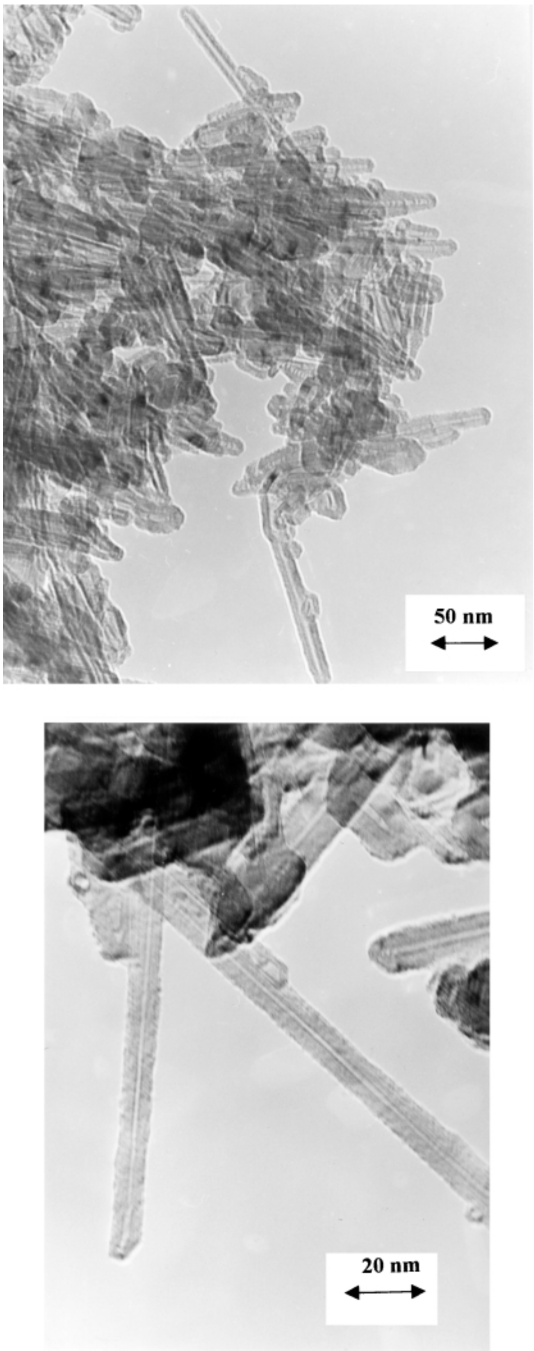

Fig. 1 Transmission electron microscopy of carbonaceous material prepared by spontaneous polymerization of hexatriyne at 0 °C.

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Notes and references

1 L. Kavan and J. Hlavatý, *Carbon*, 1999, **37**, 1863.
2 N. Kawase, A. Yasuda, T. Matsui, C. Yamaguchi and H. Matsui, *Carbon*, 1999, **37**, 522.
3 L. Kavan, *Chem. Rev.*, 1997, **97**, 3061.
4 L. Kavan, F. P. Dousek, P. Janda and J. Weber, *Chem. Mater.*, 1999, **11**, 329.
5 J. Hlavatý, J. Rathouský, A. Zukal and L. Kavan, *Carbon*, in press.
6 L. Brandsma and H. D. Verkruijsse, *Preparative Polar Organic Chemistry*, Springer Verlag, 1987, vol. I.
7 GC-MS, *m/z* (intensity): 201(6), 200 (M$^+$ 100), 128 (25), 100 (5.5), 74 (10), 73 (53), 72 (12), 37 (25), 36 (8). FTIR (*n*-hexane–diethyl ether): υ 625 (m), 2125 (w), 2150 (w), 2190 (w), 3211 (m), 3207 (m) cm^{-1}. UV–VIS λ (toluene): 287, 304, 322, 344 and 392 nm.
8 M. Springborg and L. Kavan, *Chem. Phys.*, 1992, **168**, 249.