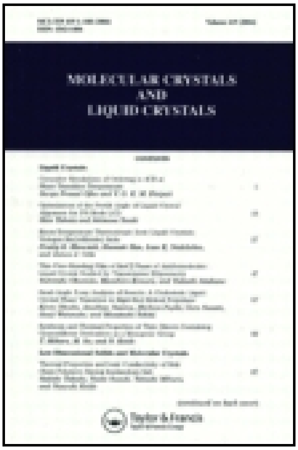


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Nanocarbons made by soft chemistry

Ladislav Kavan [a]

[a] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, Prague 8, CZ-182 23, Czech Republic

Version of record first published: 18 Oct 2010

To cite this article: Ladislav Kavan (2002): Nanocarbons made by soft chemistry, Molecular Crystals and Liquid Crystals, 386:1, 167-172

To link to this article: http://dx.doi.org/10.1080/713738816

Mol. Cryst. Liq. Cryst., Vol. 386, pp. 167–172

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113402

NANOCARBONS MADE BY SOFT CHEMISTRY

Ladislav Kavan
J. Heyrovský Institute of Physical Chemistry,
Academy of Sciences of the Czech Republic, Dolejškova 3,
CZ-182 23 Prague 8, Czech Republic

Elemental carbon is produced by chemical dehalogenation of perfluorinated hydrocarbons at room temperature and pressure. This method allows preparation of unstable carbyne-like materials, which can be subsequently converted to carbon nanotubes. Direct chemical carbonization of 1,3,5-hexatriyne derivatives also leads to nanotubes. Total dehalogenation of perfluorocyclopentene, perfluoronaphthalene and perfluorodecalin produces C_{60} (fullerene) in ca. 0.01–0.1% yield and about 1–2% of carbon nanotubes and onions. Precise thin carbon films were also grown by chemical dehalogenation of various perfluorinated hydrocarbons.

Keywords: carbon nanotubes; fullerenes; perfluorinated hydrocarbons

INTRODUCTION

Carbon materials are usually prepared at high temperatures and/or pressures. However, the carbonization of suitable precursors is thermodynamically favored even at the conditions of "soft chemistry", i.e. at room temperature and pressure. A complete chemical cracking of all carbon-heteroatom bonds in a precursor requires either unstable reactants (e.g. alkali metals) [1–3] or reactive precursors (e.g. oligoynes) [4]. This asks for precisely defined reaction conditions, which make the process delicate and expensive. Hence, the soft-chemical carbonization is advocated (except of addressing of academic problems) for processes, which can benefit from three specific features of chemical carbonization: (1) Production of unstable carbon chains, which are not likely to survive at high temperatures [1,2]. (2) Easy templating of carbon nanostructures by the precursors, allowing tailored syntheses of fullerenes and nanotubes [2,3]. (3) Defined kinetics of certain reactions, yielding precise carbon films [2,3].

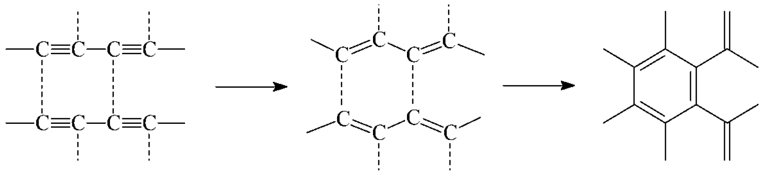
This work was supported by the Grant Agency of the Czech Republic (contract No. 203/99/1015). Thanks are due to Prof. Asao Oya (University of Gunma) for TEM analyses.

CARBON CHAINS MADE BY SOFT CHEMISTRY

Chemical synthesis of all-carbon chains can be demonstrated by a generic conversion of perfluoro-n-alkane into an *sp*-bonded polyyne [1,2,5]:

$$(\text{-CF}_2\text{-CF}_2\text{-})_n + 4ne^- \rightarrow (\text{-C}{\equiv}\text{C-})_n + 4nF^-;\ n = 1,\ 3,\ 10,\ 12,\ \infty \qquad (1)$$

Even though the carbonization is stoichiometrically quantitative (Eq. (1)), the polyyne can hardly be obtained in pure form [5]. Actual products of reaction (1) are mesoscopic sp^2 carbons with short oligoyne sequences ($n < \approx 8$) [1,2]. Polyyne is spontaneously cross-linked to graphene (Eq. (2)):



(2)

The existence of carbon crystals containing solely the *sp*-bonded chains (carbyne) is a subject of debate for more than 40 years [5]. Carbyne nanocrystals (ca. 10 nm in size) were recently reported in shock compressed carbons [6–8]. These studies support the idea that carbyne is a realistic concept of crystalline carbon, in spite of notorious lack of convincing X-ray or other structural evidence made on macroscopic single crystal.

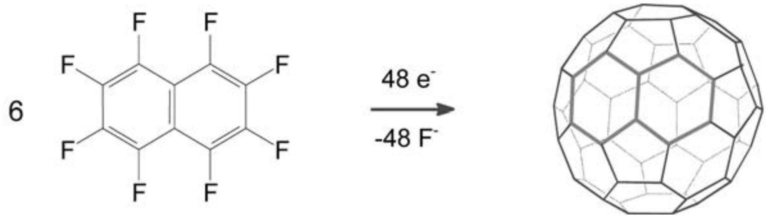
CONVERSION OF CARBON CHAINS INTO NANOTUBES

Whereas the cross-linking of *sp*-chains into graphene (Eq. (2)) is undesired for the synthesis of carbyne, it may also lead to interesting nanocarbons. The production of nanotubes by cross-linking of polyyne (Eq. (2)) was first reported by Kawase *et al.* [9]. The polyyne was generated from poly (tetrafluoroethylene) (PTFE) by dehalogenation (Eq. (1); $n = \infty$). Subsequently, the nanotube formation was promoted by irradiation with a 100 keV-electron beam at 600–800°C. The nanotubes, prepared in this way, had diameters about 10–50 nm and length ca. 1 μm [9].

We have employed a similar strategy, but instead of using the poorly defined *ex*-PTFE polyyne (Eqs. (1, 2)), we started from pure low-molecular weight oligoynes, such as 1,3,5-hexatriyne derivatives [4]. In this case, the nanotubes were obtained at room or sub-room temperatures without the electron-beam activation. The nanotubes, obtained by spontaneous polymerization/carbonization of 1,3,5-hexatriyne and 1-iodo-1,3,5-hexatriyne, were straight, multi-walled, with diameter of 10–20 nm, length of 100–200 nm, and capped by onion-like hemispheres [4].

DIRECT SYNTHESIS OF FULLERENES AND NANOTUBES

Small amounts of fullerene C_{60}, onions and nanotubes were prepared *via* total dehalogenation of gaseous perfluoronaphthalene ($C_{10}F_8$), perfluorodecalin ($C_{10}F_{18}$)and perfluorocyclopentene (C_5F_8) with liquid amalgams of alkali metals [3]. A model conversion of perfluoronaphthalene (Eq. (3)):



(3)

commemorates the former theoretical prediction [10] and experimental demonstration [11] that the gas-phase condensation of C_{60} may start from naphthalenoctyl radicals C_{10}. Assembling of fullerene C_{60} from twelve C_5 radicals seems to be also possible [3,10]. The defluorination of $C_{10}F_8$ (Eq. (3)), $C_{10}F_{18}$ and C_5F_8 gives fullerene C_{60} in ca. 0.01 to 0.1% of the total carbon produced. The best yield of C_{60} was 0.36% in one batch of C_5F_8 dehalogenated by Li-amalgam [3]. Fullerene C_{60} was detected in toluene extracts by HPLC, UV-Vis spectra and mass spectroscopy. Sometimes, also C_{70} was detected in these carbons.

The defluorination of $C_{10}F_8$, $C_{10}F_{18}$ and C_5F_8 gives also some other interesting nanocarbons. Figure I displays an electron micrograph of carbon material prepared from C_5F_8. The picture shows onion-like particles and capped multiwalled tubes, typically 15 nm in diameter and about 50–200 nm long. Whereas the tubes from C_5F_8 were straight (Fig. I), the tubes from $C_{10}F_{18}$ and $C_{10}F_8$ were curly and substantially longer. According to electron microscopy, the concentration of nanotubes was estimated to be 1–2% of the total amount of carbon produced. This yield is not yet competitive to that in high-temperature catalytic transformation of graphite, hydrocarbons or CO (HiPco process) [12]. However, our reaction was the first evidence that nanotubes can be prepared by a non-catalytic "soft chemical" process at room temperature [3].

Recently, small amounts of nanotubes and onions were prepared by anodic oxidation of acetylene at −40°C [13]. Although the chemical

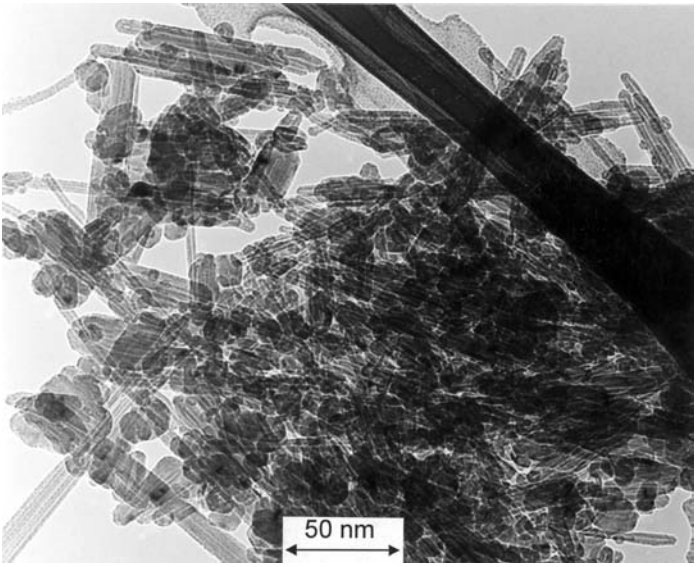


FIGURE I Transmission electron micrograph of nanocarbon made by a total dehalogenation of perfluorocyclopentene by Li-amalgam at 25°C.

synthesis of nanocarbons is interesting from academic points of view, further investigation is needed to optimize the conditions, and to decide, eventually, whether or not this strategy is suitable for large-scale production.

CHEMICAL DEPOSITION OF CARBON FILMS

If a purified vapor of perfluorinated hydrocarbon (see Table I) contacts the surface of liquid amalgam of Li or Na, a spontaneous film-forming carbonization process sets in [2,3]. The film contains carbon in a stoichiometric mixture with the corresponding by-product, i.e. LiF or NaF (cf. Eqs (1, 3)). The growth of film manifests itself by spectacular interference colors, which change periodically during early stages of the reaction. The colors are very regular, because the film grows at an ideally flat surface of liquid amalgam and its thickness is self-controlled by the actual reaction kinetics. The film thickness, δ can be monitored *in-situ* by the interference fringes in UV-Vis reflectance spectra (for $\delta\upsilon <\approx 2\,\mu m$, υ is the refractive index) [3]. Except for perfloro-2-butyne (*vide infra*), the carbonaceous film grows linearly with time on the $Li_{(Hg)}$ surface:

TABLE I Rate Constants of the Reaction with Li/Na Amalgams at 25°C (Eqs. (4, 5)). Data from Ref. [3] Upgraded with Newly Obtained Results

Precursor	K_{Li} [nm.s^{-1}]	K_{Na} [nm.s$^{-1/2}$]
Perfluorohexane	0.03	–
Perfluorocyclobutane	0.2	2.9
Perfluorocyclohexane	0.002	–
Perfluorodecalin	0.5	5
Perfluorocyclopentene	7	9.5
Perfluorobenzene	0.06	–
Perfluoronaphthalene	0.15	13
Perfluorobenzonitrile	5	–
Perfluoropyridine	1	–
Perfluoro-2-butyne	(see text)	9

$$\delta\upsilon = K_{Li}\ t \tag{4}$$

However, the growth followed square-root kinetics on the $Na_{(Hg)}$ surface:

$$\delta\upsilon = K_{Na}\ t^{1/2} \tag{5}$$

The rate constants K_{Li} and K_{Na} are summarized in Table I for various perfluorinated precursors tested.

Apparently, the film thicknesses can be controlled with nanometer-precision simply by adjusting of the reaction time. The different reaction kinetics for Li and Na amalgams corresponds to different mechanism of the rate-limiting process (see Refs. [2,3] for more detailed discussion). In the case of $Na_{(Hg)}$ the transport of Na^+ ions through the carbonaceous film is the slowest process. This charge-transport follows the square-root kinetics, which is dictated by the low Na^+ conductivity of the film [3].

The transport of Li^+ is sufficiently fast, hence, it does not obstruct the intrinsic rate of chemical carbonization at the interface of C_xF_y and the growing film [3]. Consequently, in the case of Li-amalgam, the overall kinetics becomes controlled by the rate of interfacial carbonization, which is independent of the reaction time [2]. Hence, the carbonaceous film grows linearly with time at the $Li_{(Hg)}$ surface. This rule is violated only in the case of perfluoro-2-butyne, which shows $K_{Li} = 120\,nm.s^{-1/2}$ (Note that this reaction is described by Eq. (5), not by Eq. (4)). The interpretation is straightforward: The rate of chemical carbonization of perfluoro-2-butyne is so fast, that the overall reaction becomes limited by the Li^+ transport in the growing film, as in the case of Na^+ transport. Consequently, the carbonaceous film from perfluoro-2-butyne and Li-amalgam grows linearly with square root of the reaction time. The films can be extracted by water to remove LiF (NaF) nanocrystals, which are interspersed in the carbonaceous skeleton.

REFERENCES

[1] Kavan, L. (1997). *Chem. Rev.*, ***97***, 3061.
[2] Kavan, L. (2001). *Tanso*, ***196***, 22.
[3] Kavan, L. & Hlavatý, J. (1999). *Carbon*, ***37***, 1863.
[4] Hlavatý, J., Kavan, L., Kasahara, N., & Oya, A. (2000). *Chem. Commun.*, 737.
[5] Heimann, R. B., Evsyukov, S. E., & Kavan, L. (1999). *Carbyne and Carbynoid Structures*, Kluwer Academic Publ.: Dordrecht.
[6] Donnet, J. B., Fousson, E., Samirant, M., Wang, T. K., Pontier, M., & Eckhardt, A. (2000). *Compt. Rend. Acad. Sci. Ser. IIC*, ***3***, 359.
[7] Yamada, K. & Tanabe, Y. (2001). *Carbon*, ***39***, 1677.
[8] Yamada, K., Tanabe, Y., & Sawaoka, A. B. (2000). *Phil. Mag. A*, ***80***, 1811.
[9] Kawase, N., Yasuda, A., & Matsui, T. (1998). *Carbon*, ***36***, 1864.
[10] Goeres A. & Sedlmayr, E. (1991). *Chem. Phys. Lett.*, ***184***, 310.
[11] Taylor, R., Langley, G. J., Kroto, H. W., & Walton, D. R. M. (1993). *Nature*, ***366***, 728.
[12] Bronikowski, M. J., Willis, P. A., Colbert, D. T., Smith, K. A., & Smalley, R. E. (2001). *J. Vac. Sci. Technol. A*, ***19***, 1800.
[13] Matveev, A. T., Golberg, D., Novikov, V. P., Klimkovich, L. L., & Bando, Y. (2001). *Carbon*, ***39***, 155.