JOURNAL OF MATERIALS SCIENCE 31 (1996) 5557–5571

Review

Carbynes: advances in the field of linear carbon chain compounds

Yu. P. KUDRYAVTSEV‡, R. B. HEIMANN*, S. E. EVSYUKOV**,†
‡ *A.N. Nesmeyanov Institute of Organoelement Compounds, The Russian Academy of Sciences, Moscow 117813, Russia,* * *Department of Mineralogy, Freiberg University of Mining and Technology, D 09596 Freiberg, Federal Republic of Germany, and*
** *Max-Planck Institute for Polymer Research, D55128 Mainz, Federal Republic of Germany*

Synthetic approaches to preparing carbyne, a linear carbon allotrope, including the chemical and physical methods are briefly considered. Modern structural models of carbyne, some of its properties, and the prospects for its practical applications are discussed.

1. Introduction

For a long time it has been held that the only carbon allotropes existing in nature were graphite (2H) and diamond (cubic) with their structural variants, i.e., rhombohedral 3R-graphite and hexagonal diamond (lonsdaleite). The graphites are characterized by sp^2-hybridization of the carbon bonds and the diamonds by sp^3-hybridization. Apparently, the "missing link" was an allotrope with pure sp-hybridization, and there were early attempts to synthesize such a material [1, 2]. In addition to the allotropic forms with pure bond hybridization states there was an ever increasing body of transitional forms of carbon [3] whose structures approach those of graphite, i.e., amorphous and quasi-amorphous carbons such as carbon blacks, soot, cokes, glassy carbon etc. However, the sp-form was still missing and it was considered odd by many researchers that the element with the richest chemistry of all should be limited to just two allotropes.

In 1959–60 systematic investigations of the oxidative coupling of bis(ethynyl)arylenes were carried out at the Soviet Academy of Sciences' A.N. Nesmeyanov Institute of Organoelement Compounds. "Oxidative dehydropolycondensation" [4] led to polymers whose repeating unit retains the structure of the original diacetylene but without the terminal hydrogen atoms. Since acetylene may be regarded as a bifunctional compound having two ≡C–H bonds, it was logical to assume that it can be used as a monomer in this reaction. Further research into this field culminated in the discovery of the elusive third (linear) allotropic form of carbon termed "carbyne" [5, 6]. Carbyne was supposed to occur in two isomeric forms (provided that the end groups are neglected), namely, a conjugated triply bonded form (polyyne, polyethynylene) and a cumulated doubly bonded form (polycumulene, polyethenediylidene). Even though the name seems to conflict with the IUPAC notation for some radicals (cf. Ref. [7] Editor's comment) the time-honoured name will be retained in this review. The discovery was registered (patented) in 1971 with priority dated back to 1960 [8]. In 1968 carbyne was found as a natural mineral [9] and named "chaoite" in honour of the respected American scientist E. C. T. Chao [10].

The recent discovery [11] of a family of spherical closed-cage carbon molecules with a mixed sp^2/(quasi) sp^3-type of hybridization† called fullerenes has added even more excitement to carbon science [13]. It has been recently conjectured that spiral-like and cyclic polyyne oligomers terminated by delocalized electrons at either end can be easily converted with low activation energy into C_{50}–C_{76} fullerenes by a "spiraling and zip-up" mechanism [14, 15].

During the past thirty five years an increasing body of experimental and theoretical work has been published in the scientific literature dealing with the preparation of carbyne and the study of its structure, properties and potential applications. In the present review we have attempted to summarize the most pertinent of these data within the framework of a common concept about carbyne as the third (linear) allotropic modification of carbon. We will concentrate on the synthetic approaches and proposed structural models of carbyne. We consciously exclude more complex carbynoid materials, i.e., hybrids of sp-hybridized structures and sp^2-("layer-chain carbon" [16], graphyne [17]) or sp^3-hybridized ("polyyne-diamond" [18], fullereneynes [19]) structures. Synthetic strategies towards such mixed forms of carbon have been comprehensively reviewed by Diederich and Rubin [20, 21].

Many controversial facts and puzzling dichotomies remain to be solved but the intriguing properties of

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† For instance, the degree of hybridization of carbon atoms in C_{60}, the most in depth studied member of the fullerene family, was reported to be 2.28 [12].

† *Permanent address*: A. N. Nesmeyanov, Institute of Organoelement Compounds, The Russian Academy of Sciences, Moscow 117 813, Russia

carbyne and its widespread potential applications warrant tackling the many challenges ahead.

2. Carbyne in nature

In 1968, a silver-white new mineral was discovered in graphitic gneisses of the Ries Crater (Nördlingen, Bavaria, Germany) [9, 10]. This material was found to consist entirely of carbon, and its hexagonal cell dimensions matched those reported earlier for carbyne by Russian workers. It was concluded that this novel form of natural carbon, chaoite, was generated from graphite by the combined action of high temperature and high pressure, presumably caused by the impact of a meteorite. Soon afterwards this "white" carbon was synthesized by sublimation of pyrolytic graphite in vacuum [22]. Thus proof was given that high pressure is not required to form "white" carbon but that high temperatures suffice. A crystalline carbon form of similar characteristics was also found in the New Urei [23] and Havero [24] ureilites, the stony meteorites which are supposed to be formed from carbonaceous chondrites by collision of asteroid bodies. Subsequently, in-depth analyses of carbonaceous chondrites (Allende and Murchison) revealed a wealth of various carbynoid structures that differed in their electron-diffraction c-axis pattern [25, 26]. From this it was concluded that large portions of interstellar molecular-cloud complexes and circumstellar envelopes of carbon stars may consist of carbyne precursors [27] such as (cyano)polyynes and cumulenes as inferred from radio observations and the degree of optical polarization of the halos of some galaxies and cool carbon stars [28–33]. An even more ambitious suggestion concerns the role of carbyne or its precursor (cyano)polyynes in causing the bulk of interstellar extinction [34], in effect being the "missing dark matter" in the universe. According to the hypothesis by Albinson and Evans [35], the interstellar carbyne species might form in the atmosphere of a white dwarf in a cataclysmic variable system, and be expelled from the system by radiation pressure. In this regard it is interesting to speculate whether interstellar nanometre-sized diamonds [36–39] recovered from meteorites as well as lonsdaleite found in chondritic porous (CP) aggregates and carbonaceous chondrites have been formed, at low pressure and temperature, by radiation-induced cross-linking of such linear short-chain cyanopolyyne clusters.

Meanwhile, carbynes were also reported to be present at impurity levels in natural diamond powders [40] and graphites [41], and chaoite was identified in the rocks of the Popigai impact structure [42].

3. Synthesis of carbyne

A multitude of chemical and physical processes have been reported to yield carbynes. The methods can be divided into the following four groups: (i) polycondensation reactions; (ii) polymer-analogous transformations; (iii) decomposition of various organic substances and; (iv) phase transformations of carbon materials. What follows is a brief description of these synthetic approaches.

3.1. Polycondensation reactions

This group includes several chemical approaches to the synthesis of carbyne by polycondensation of bifunctional monomers via various carbon–carbon coupling reactions which result in the formation of the carbon chain backbone.

3.1.1. Oxidative dehydropolycondensation of acetylene

Passing acetylene through an aqueous ammoniacal solution of a copper(II) salt results in the rapid precipitation of a black powder that explodes on heating in the dry state and on detonation in the wet state [43]. In analogy to the polycondensation of bis(ethynyl)arylenes [4] the reaction can be schematically represented as follows:

$$n\,\mathrm{HC{\equiv}CH} \xrightarrow{\mathrm{Cu^{2+}}} \underset{\mathbf{1}}{\mathrm{H{-}(C{\equiv}C)_{\mathit{x}}{-}H}} + \underset{\mathbf{2}}{\mathrm{H{-}(C{\equiv}C)_{\mathit{y}}{-}Cu}} + \underset{\mathbf{3}}{\mathrm{Cu{-}(C{\equiv}C)_{\mathit{z}}{-}Cu}} \qquad (1)$$

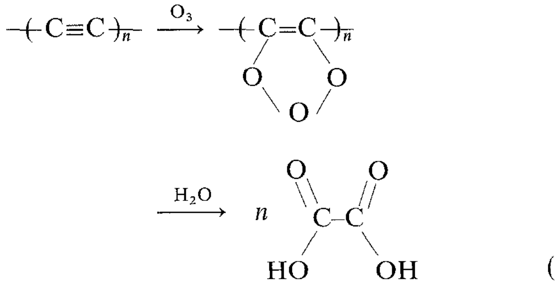
where $x + y + z = n$.

In the presence of an excess of Cu^{2+} ions and fixing the eliminated protons by ammonia, a mixture of polyynes (polyethynylenes, **1**) and Cu(I)polyacetylides (**2** and **3**) of various chain lengths is formed. The terminal copper atoms presumably stabilize the shorter chains due to their complexation with triple bonds of the neighbouring carbon chains [6]. Subsequent oxidation of the products **1**, **2** and **3** resulted in polyynes with doubled molecular weight

$$\mathbf{1} + \mathbf{2} + \mathbf{3} \xrightarrow{\mathrm{Ox}} \mathrm{H{-}(C{\equiv}C)_{\mathit{n}}{-}H} \qquad (2)$$

The oxidants used in this second synthesis step were $FeCl_3$ or $K_3[Fe(CN)_6]$. Copper was removed by refluxing the product of oxidation alternately with dilute HCl and an aqueous solution of NH_3 for several days [44, 45]. The elemental analysis of the copper-free product annealed at 1000 °C in vacuum for several hours showed the carbon content to be 99.9%.

The polyynic nature of bonds in the molecules of the chain-like carbon was substantiated by the results of a study of its oxidation reaction with ozone [45]. Ozonolysis for 30 days resulted in the complete oxidation of the product under formation of oxalic acid thus attesting to the presence of conjugated triple bonds in the chains according to Equation 3.



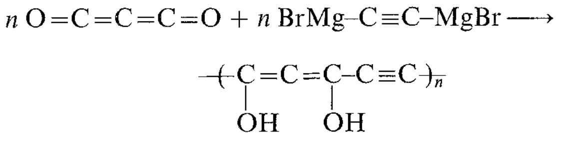
(3)

In 1969 Hay [46] reported on similar oxidative polycondensation of acetylene carried out in pyridine in the presence of copper(I) chloride and *N,N,N',N'*-tetramethylethylenediamine with the use of oxygen as an oxidant. The reaction afforded a finely divided black product containing 62.3% of carbon, whose infrared spectrum indicated the presence of triple $C{\equiv}C$ bonds. The low content of carbon was ascribed to the oxidation of the conjugated triple bond system with oxygen, but no analytical data on contents of copper and nitrogen were given. It should be noted, however, that the products of such a reaction should be washed thoroughly [44,45] to remove the copper impurities whose presence may be surmized from the low content of carbon (82.8%) even in a sample heated to 600 °C [46].

Employing an essentially similar synthetic route, Matsuda *et al.* [47] obtained a polymer with a polyyne structure using butadiyne, $HC{\equiv}C{-}C{\equiv}CH$, as a starting monomer. Noteworthy was the formation of copper-containing poly(metal)ynes when the reaction was carried out under oxygen-free conditions. Surprisingly, the infrared spectrum of a polymer synthesized recently by Kijima *et al.* [48] via oxidative dehydropolycondensation of acetylene using the same procedure did not exhibit any appreciable absorption in the region of stretching vibrations of triple $C{\equiv}C$ bonds.

3.1.2. *Polycondensation of carbon suboxide*

The polycumulene (polyethenediylidene) form of carbyne was synthesized for the first time in 1968 by Sladkov *et al.* [49, 50]. In a first step polycondensation of carbon suboxide (C_3O_2) was carried out with bis(bromomagnesium)acetylide via a Grignard-type reaction to form a polymeric acetylene-allene glycol (**4**) according to Equation 4.



$$n\,O{=}C{=}C{=}C{=}O + n\,BrMg{-}C{\equiv}C{-}MgBr \longrightarrow -\!\!(\underset{OH}{C}{=}C{=}\underset{OH}{C}{-}C{\equiv}C)\!\!-_n \qquad (4)$$

In a second step the glycol **4** was reduced by $SnCl_2$ in an acidic medium (Equation 5):

$$4 \xrightarrow{SnCl_2/HCl} =\!\!(C{=}C)\!\!=_{5n/2} \qquad (5)$$

A transmission electron microscopy study of the annealed product revealed two types of single crystals of carbyne with different unit cell parameters (α- and β-forms) [6, 51].

3.1.3. *Polycondensation of diiodoacetylene*

The dehalogenative polycondensation of various dihaloarylenes, -heteroarylenes, and -alkylenes catalysed by organometallic complexes of transition metals is known to be an efficient method for synthesizing macromolecular compounds, including conjugated polymers [52]. The scope of this reaction has been expanded very recently by Kijima *et al.* [48, 53] to the field of carbyne. Three novel approaches to the synthesis of the polyyne form of carbyne via polycondensation of diiodoacetylene catalysed by nickel complexes have been reported [48] (Equation 6):

$$n\,I{-}C{\equiv}C{-}I \xrightarrow[\text{a), b), or c)}]{[Ni]} -\!\!(C{\equiv}C)\!\!-_n \qquad (6)$$

a). Reductive polycondensation catalysed by a nickel(0) complex. The reaction was performed in dimethylformamide (DMF) at 60 °C under inert atmosphere in the presence of bis(1,5-cyclooctadiene)-nickel(0), 1,5-cyclooctadiene (cod), and a neutral ligand (triphenylphosphine or 2,2'-bipyridyl).

b). Dehalogenative polycondensation catalysed by a nickel(II) complex. According to the experimental procedure the authors referred to reference [54], the Grignard reagent has to be prepared first, which is then treated with a catalyst, (2,2'-bipyridyl)nickel(II) bromide, in tetrahydrofuran (THF) under reflux to form the target polymer.

c). Electroreductive polycondensation catalysed by a nickel complex. The reaction was carried out by cathodic electrolysis of diiodoacetylene at a Pt electrode at − 2.0 V (versus saturated calomel electrode) in DMF or acetonitrile in the presence of a supporting electrolyte and the nickel complex as a catalyst. Various nickel complexes were used in this reaction including NiI_2(dppe), $NiCl_2$(dppe), $NiCl_2$(dppp), $NiCl_2(PPh_3)_2$, and $Ni(cod)_2$, where dppe, dppp, and PPh_3 denote 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, and triphenylphosphine, respectively. Several tetraalkylammonium salts as well as $NaClO_4$ and LiCl were used as a supporting electrolyte.

In all three cases polycondensation yields amorphous, partially cross-linked polyyne structures. The electrochemical method (c) was reported to be most promising for synthesizing longer carbyne chains ($n > 14$ as calculated from Raman spectra) [48]. Electrochemically synthesized carbyne contained ~60% of carbon along with nickel, halogen, nitrogen, and hydrogen and was considered to be *n*-doped with tetraalkylammonium species since the sample showed a negative thermoelectric power. The polymer was found to be air-sensitive and thermally unstable in as much as the infrared absorption band near 2100 cm^{-1}, characteristic for the $-C{\equiv}C-$ bond, gradually decreases on exposure to air and disappears in the spectra of samples heated to 440 °C.

3.1.4. *Polycondensation of lithiumbromoacetylide*

In 1959 Viehe [55] mentioned the formation of a carbonaceous by-product in some reactions of metal-chloroacetylides. On the basis of this observation Lagow *et al.* [15] recently developed a new synthetic approach to produce carbyne via polycondensation of lithiumbromoacetylide, $Li{-}C{\equiv}C{-}Br$, in liquid ammonia or organic solvents at low temperature (Equation 7).

$$n\,\mathrm{Li{-}C{\equiv}C{-}Br} \xrightarrow[\text{liq. NH}_3,\ -56\,^{\circ}\mathrm{C}]{} -\!\!\left(\mathrm{C{\equiv}C}\right)_{n}\!\!- \tag{7}$$

Modifying this synthesis by the introduction of phenyllithium and phenylchloride as endcapping reagents has allowed the preparation of mixtures of stable phenyl-capped polyynes that contained chains of 16, 24, and 28 carbon atoms, according to mass spectra. The polyynic nature of bonds in the products obtained was confirmed by ^{13}C NMR spectra whose characteristic peaks were centred at 60–70 ppm.

3.1.5. *Disproportionation of carbon monoxide*

To check the hypothesis on metastable formation of carbynes in outer space and on earth, Hayatsu *et al.* [26] heated a 1:1 mixture of carbon monoxide and hydrogen at 300–400 °C in the presence of chromite as a catalyst. After reaction, the catalyst was extracted with organic solvents, and the residue was determined to contain 1.16% of carbon, corresponding to 4.7% of the initial carbon in the system. A study of the residue by time-of-flight mass spectrometry revealed various triply bonded linear carbon species. From these results it was inferred that the disproportionation of CO (Equation 8) proceeds faster than hydrogenation in the presence of the chromite catalyst, and that carbyne rather than graphite forms under these conditions.

$$2n\,\mathrm{CO} \xrightarrow[300\text{–}400\,^{\circ}\mathrm{C}]{\text{chromite}} n\,\mathrm{CO_2} + \mathrm{C}_n \tag{8}$$

Low-temperature reactions of this type are thought to be the dominant source of carbynes on earth and in meteorites, and a major source of interstellar carbynes and cyanopolyynes [26].

3.2. Polymer-analogous transformations

The approach to the synthesis of carbyne by polymer-analogous transformations is based on elimination reactions of side substituents (atoms or groups) being performed on linear macromolecules of some carbon-chain polymers. The difference between this method and the polycondensation processes is that the carbon backbone is previously formed by polymerizing relevant monomers, and the main requirement for the formation of carbyne is complete elimination of the side substituents with retention of the linear structure.

3.2.1. *Dehydrohalogenation of polymers*

A convenient way to synthesize carbyne at low temperature is the dehydrohalogenation of some halogen-containing polymers such as poly(vinylidene halides) [56–58], poly(1,2-dihaloethylene) [57, 59, 60], poly (1,1,2- and 1,2,3-trichlorobutadiene) [57, 61] as well as chlorinated poly(vinyl chloride) (PVC) [62, 63]. Chemical [56–61], photo- [62, 63] and electrochemical [64], as well as ion-assisted [65–67] procedures have been developed to perform the dehydrohalogenation reaction and the chemical methods are known to be the most convenient and accessible.

Complete chemical dehydrohalogenation of halogen-containing polymers can be accomplished using only strong bases. Alcoholic solutions of alkalies are known to be widely used as dehydrohalogenating agents. However, in order to completely eliminate the hydrogen halides, the reaction should be carried out at elevated temperatures [68], which may cause a number of side reactions. To circumvent this problem, specific alkali-based dehydrohalogenating systems were developed using various polar organic co-solvents (e.g., THF [56, 57, 60, 61], acetone [69]). Adding polar co-solvents to the alcoholic alkali solutions allows the adjustment of solubility parameters of the reacting medium and polymeric substrate [69], thereby making it possible to perform the reaction efficiently under mild conditions (at room temperature and below).

The dehydrohalogenation reaction is schematically represented in Equation 9 with poly(vinylidene halide) as an example:

$$-\!\!\left(\mathrm{CH_2{-}CX_2}\right)_{n}\!\!- \xrightarrow[-\,n\mathrm{HX}]{\mathrm{B}^-} -\!\!\left(\mathrm{CH{=}CX}\right)_{n}\!\!- \xrightarrow[-\,n\mathrm{HX}]{\mathrm{B}^-} =\!\!\left(\mathrm{C}\right)_{2n}\!\!= \tag{9}$$

where X = Br, Cl, F; and B^- is a base.

The vibrational infrared (IR [56,70] and Raman [71]) and electron (Auger and electron energy loss EELS [56,72,73]) spectra of the products of this reaction were interpreted in terms of the cumulene structure of carbyne formed. To explain this conclusion an ionic mechanism of hydrogen halide elimination was suggested which includes splitting-off a proton from the original polymeric chain to leave a lone pair of electrons followed by elimination of the halogen ion as a result of the redistribution of electronic density [56, 60]. Analogously, the dehydrobromination of poly(1,2-dibromoethylene) prepared by bromination of polyacetylene obtained by dehydrochlorination of PVC, has been reported to produce the cumulene form of carbyne as well [60]. In contrast to this, Akagi *et al.* [59], studying the dehydrochlorination of stereospecifically chlorinated polyacetylene under the action of a strong organic base, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), concluded from the infrared, ultraviolet, and Raman spectroscopical data that the polyyne form of carbyne was formed. A mechanism involving the two-step trans-elimination of HCl was proposed based on these results. According to the Raman spectra, the length of the $(-\mathrm{C{\equiv}C}-)_n$ polyyne chains formed was evaluated to be 12–65 C≡C units. On studying dehydrochlorination of chlorinated PVC and poly(vinylidene chloride) induced by KrF excimer laser irradiation, Shimoyama *et al.* obtained similar results with n up to 8 [62] and Yabe has reported the extension of the technique to n values of 30 [74]. It should be noted, however, that the exact identification of the nature of the chemical bonds in carbyne requires a detailed study of its electronic and atomic structure.

Cathodic electrolysis of a solution of poly(vinylidene fluoride) (PVDF) in DMF containing tetrabutylammonium perchlorate, and tert-butyl alcohol as a mediator has recently been reported [64] to produce n-doped conjugated polymers consisting of 76% of poly(fluoroacetylene) and 24% of carbyne moieties (Equation 10):

$$-\!\!(\mathrm{CH_2{-}CF_2})_{\overline{n}} \xrightarrow[\mathrm{Bu_4NClO_4,\,DMF,\,20\,^\circ C}]{\bar{e},\,\mathrm{Pt},\,t\text{-}\mathrm{BuO}^-} -\!\![(\mathrm{CH{=}CF})_{\overline{0.76}} -\!\!(\mathrm{C{\equiv}C})_{\overline{0.24}}]_{\overline{n}} \qquad (10)$$

In fact, the mediator, i.e., t-BuOH, is electrochemically reduced to the t-BuO$^-$ anion that nucleophilically attacks PVDF to yield elimination products.

On irradiating PVDF with high energy heavy ions (O, Kr, and Xe), X-rays, or electrons, LeMoël *et al.* also observed the dehydrofluorination process [65–67]. The most intensive dehydrofluorination to form the cumulenic carbyne structure was observed on irradiating PVDF by oxygen ions [67], which was corroborated by X-ray photoelectron and IR spectroscopy. The degree of hydrofluorination increases with the irradiation dose, the fluence of the ion, and the energy loss in the polymer. A four-centre mechanism has been proposed for the radiation-induced dehydrofluorination process that includes weakening of the C–H bonds caused by their excitation upon irradiation, and the desorption of the HF molecules facilitated by hydrogen-like bonds existing between the hydrogen and fluorine atoms in the original polymer backbone [66].

While carbynes formed by dehydrohalogenation appear to be completely amorphous, annealing of approximately 50 nm thin films at 400 °C was shown to result in partial crystallization forming a hexagonal crystal lattice with $a = 0.870$ nm [72].

3.2.2. Dehydrogenation of polyacetylene

In 1992, carbyne was obtained by the interaction of polyacetylene with metallic potassium under high pressure conditions up to 4 GPa at 800 °C [7, 76]. Under these conditions complete dehydrogenation takes place to form potassium hydride and a carbon matrix intercalated with potassium. The $(\mathrm{CK_{0.7}})_n$ intercalation compound obtained reacts vigorously with water and mineral acids. The reaction products were brown platy crystals of hexagonal habit (about 1 mm across and up to 1 μm thick). The process can be described by Equation 11:

$$\begin{array}{rl} -\!\!(\mathrm{CH{=}CH})_{\overline{n}} + 3.4n\,\mathrm{K} \xrightarrow[800\,^\circ\mathrm{C}]{4\,\mathrm{GPa}} & (\mathrm{CK_{0.7}})_{2n} + 2n\,\mathrm{KH} \\ & \downarrow \mathrm{HCl} \\ & =\!\!(\mathrm{C})_{\overline{\overline{2n}}} \quad + 1.4n\,\mathrm{KCl} \end{array} \qquad (11)$$

The new class of materials was called carbyne intercalation compounds (CIC's). Their very interesting electronic properties warrant further in-depth investigations [77, 78].

3.2.3. Defluorination of poly(tetrafluoroethylene)

Reductive defluorination of perfluorinated hydrocarbons, first introduced by Tammann [2] and in [79], is being systematically explored as a method for preparing carbyne by a Czech group [79–83]. Chemical [79] and electrochemical [79, 80] defluorination of various perfluoroalkanes and polymers have been reported to produce carbyne, and the most promising approach employs reductive defluorination of poly(tetrafluoro-ethylene) (PTFE) by the action of alkali metal amalgams, M(Hg), where M = Li, Na, K. This reaction, being in fact equivalent to a discharge of a short-circuited M(Hg)|C–MF|C,PTFE galvanic cell [79, 80], is considered to bring about the formation of the polyyne form of carbyne (Equation 12) as inferred from Raman measurements [79, 82, 83].

$$-\!\!(\mathrm{CF_2{-}CF_2})_{\overline{n}} \xrightarrow{4n\bar{e}} -\!\!(\mathrm{C{\equiv}C})_{\overline{n}} + 4n\mathrm{F}^- \qquad (12)$$

The reaction product, C–MF, is composed of nanosized alkali metal fluoride crystals interspersed between the carbyne chains. The alkali metal fluoride appears to provide an important stabilizing function by propping open the interchain distance between adjacent polyyne chains thus preventing cross-linking and collapse of the structure towards graphite [81] (cf. [75, 84, 85]) or graphene [82]. This ability increases in the order Li < Na < K. As pointed out by Kavan *et al.* [79, 82] the carbynoid material obtained contains two MF molecules in close vicinity of each C atom in the chain. They thus assume that this ideal steric chain stabilization is responsible for the best reproducible carbyne yield obtained so far as measured from the unusually high ratio of intensities of the Raman shift 2000 cm^{-1} and the band between 1000–1700 cm^{-1}. The former is highly indicative of the C≡C stretching mode of a linear polyyne chain with a $D_{\infty h}$ point symmetry group [83], the latter appears to belong to amorphous carbon [86]. The material thus prepared is unstable: its degradation being observed under the action of air or water. The carbyne structure collapses completely after washing out the MF salt to form amorphous carbon.

3.3. Pyrolytic methods

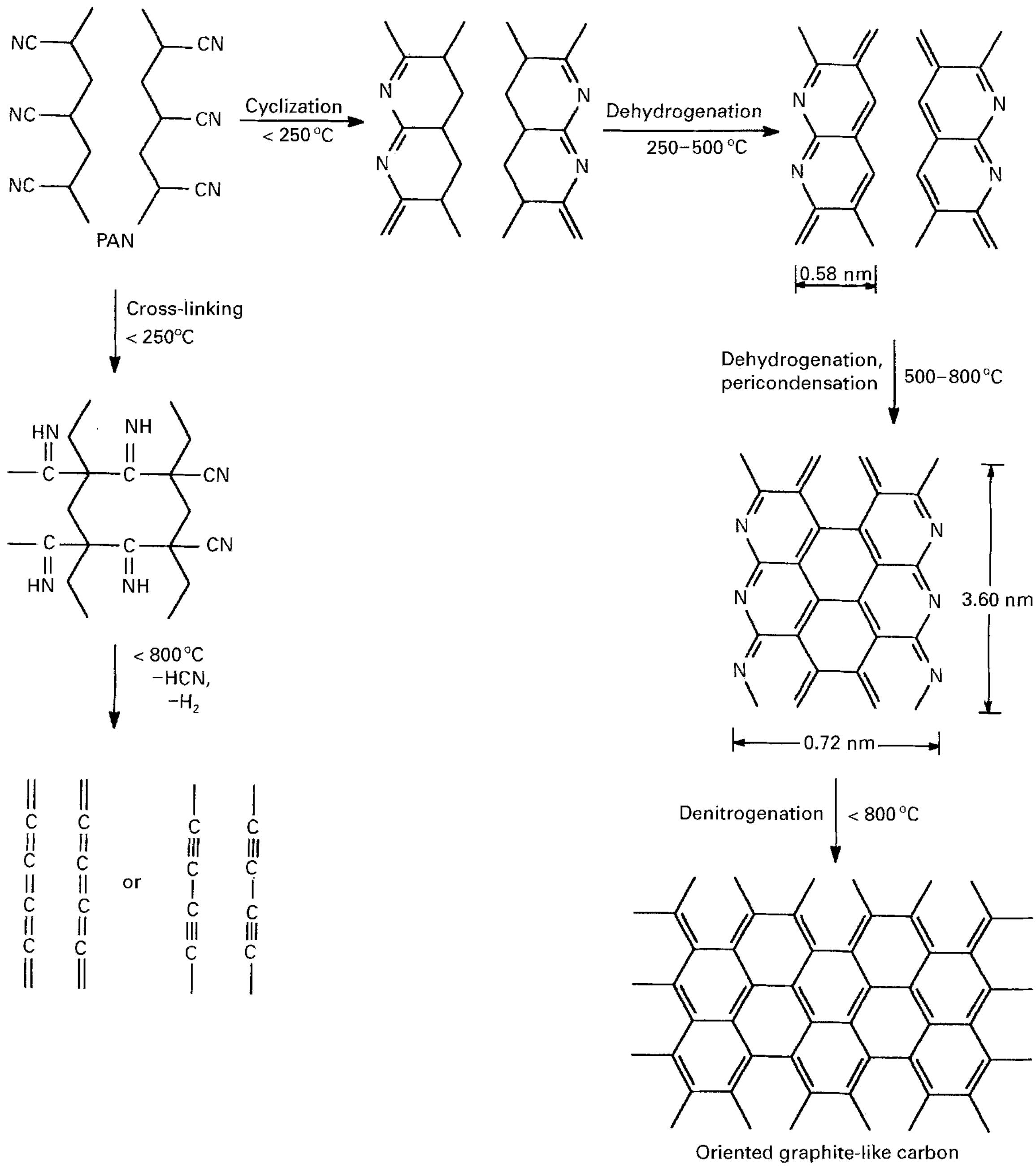
3.3.1. Decomposition of organic compounds

The decomposition of various organic compounds, mostly hydrocarbons, followed by the deposition of carbon species on a substrate is widely used for preparing carbon films and coatings (chemical vapour deposition, (CVD) methods) [87]. Depending on the deposition conditions, all known phases, including metastable ones, can be formed in these processes. The formation of carbyne was also reportedly observed in the carbon CVD processes [88–103]. Various procedures including laser- [88–92] and plasma-assisted [93–97] CVD techniques have been employed. Generally, the formation of carbyne is facilitated by a low concentration of carbon-containing reagents, moderate temperatures, and by quenching linear carbon species being formed with inert gas. The process of the carbyne formation was shown to neither depend on the nature of the organic starting material nor its bond type [95, 96].

Microcrystals of carbyne were also found in the products of dynamic decomposition of adamantane under shock-loading conditions [104].

3.3.2. Pyrolysis of organic polymers

In 1970 Kasatochkin and Kargin [105] assumed that the pyrolysis of oriented poly(acrylonitrile) (PAN) fibres may, under proper conditions, result in the formation of carbyne according to Equation 13:



(13)

This assumption was then confirmed experimentally by calculating the function of the radial electron density distribution in the PAN-based carbon fibres on the basis of X-ray analysis data [106]. Subsequently, crystalline microinclusions of carbyne were isolated from carbonized PAN fibres by the selective oxidation method [107, 108]. The unit cell parameters of the crystals were found to be $a = 0.892$ nm and $c = 1.536$ nm [107]. Recently, the presence of the chain-like species in the carbon fibres has been confirmed by X-ray photoelectron spectroscopy (XPS) data [109]. It should be noted that in some CVD studies utilizing the PAN-based carbon fibres as a substrate for the deposition of carbon formation of carbyne was also observed [88, 92]. In these cases the carbyne species being present in original carbon fibres might serve as nuclei for epitaxial growth of the carbyne crystals.

Whittaker and Tooper [110] have found microcrystals of carbyne in glassy carbons which are produced by the pyrolysis of organic (polymeric) precursors, and the formation of carbynes has also been reported in studies on pyrolysis of poly(diphenylacetylene) [111], poly(toluene-α,α,α-triyl)[†††] [111], and the high-pressure pyrolysis of polyadamantane [40].

[†††] The authors have called their polymer poly(phenylcarbyne) [111]. This name, however may be misleading in terms of the present review (cf. Introduction).

3.4. Phase transformations of carbon materials

The phase transformations of carbon materials subjected to the action of high temperature, high pressure, or ion-beam irradiation are being extensively studied by materials scientists because these processes open up wide opportunities for preparing various forms of carbon including carbynes.

3.4.1. Vaporization of carbon

The vaporization of carbon with subsequent condensation of the vapour on a cooled substrate is widely employed to obtain carbon films of various structures for a plethora of technical applications. An abundance of linear chain-like carbon molecules in a hot carbon vapour, first predicted theoretically [112] and later confirmed experimentally [113–115], makes evident that the formation of the carbyne phases is possible by deposition of carbon vapour under proper conditions. Apparently, when vaporizing graphitic carbons, the formation of the carbyne chains occurs in accordance with a low-energy "cracking" mechanism of the graphite sheets involving only the shifting of electrons and small displacement of carbon atoms [84, 85, 116]. If the polymerization and subsequent crystallization of the carbon vapour on the substrate are sufficiently slow, and thus allowing for heterogeneous nucleation, the carbyne forms prevail. On the other hand, the metastable carbyne phases being formed should be rapidly quenched in order to avoid their high-temperature annealing that would result in graphite-like structures. Various experimental methods of vaporization (sublimation) of condensed carbon (such as graphite, amorphous and glassy carbon) have been reported to produce carbynes. These methods include high-energy laser irradiation [117–125], resistive heating [118, 122, 125–127], and electrical arc discharge [118, 128–133]. Introducing cyanogen and hexafluoroethane as a source of CN and CF_3 radicals, respectively, into a process of the laser-induced vaporization of graphite, Lagow *et al.* [15] have recently synthesized cyano- or trifluoromethyl-capped soluble long-chain polyynes, $(-C{\equiv}C-)_n$, with average $n = 150$ as inferred from the mass spectra.

Whilst the processes mentioned above proceed through the gaseous and liquid states, Fedoseev *et al.* [134] observed the formation of carbyne during laser heating of graphite, followed by rapid quenching with liquid nitrogen, and also during high-pressure sintering or pulse radiant heating of diamond powders at 1200 °C and 2000 °C, respectively [135, 136]. The phase transformations of carbon when sintering diamonds were assumed to proceed through the metallic carbon state [135]. Sokolowski *et al.* [137] reported on the solid-state transformation of graphite into carbyne induced by UV laser irradiation. No signs of vaporization or melting were observed, and the results were explained by one-photon excitation and recombination of electrons in irradiated graphite [137] (cf. [84, 85, 116]).

Microcrystals of carbyne were found by Kimstach *et al.* [138, 139] in iron-carbon alloys (austenitic cast iron and eutectoid steel), and Whittaker *et al.* [140] had mentioned the formation of carbyne when crystallizing a solution of carbon in molten zirconium.

3.4.2. Shock transformations of carbon materials

The phase transformation of pyrolytic graphite into carbyne under shock-compression conditions was reported for the first time in 1976 by Litvinova and Cherkinskaya [141]. Subsequently, various carbyne polytypes were obtained by shock-induced transformations of graphite mixed with metal powders (Fe,Cu) [142], amorphous and glassy carbon [143, 144], carbon black [145], diamond [146], and diamond/amorphous carbon mixture [147]. A solid–liquid–vapour–solid sequence of phase transformations [142, 145] has been proposed as a mechanism of the formation of carbyne. According to this model, carbon powders are melted at high temperatures and high pressures produced by explosive shock. The liquid phase thus formed vaporizes explosively due to its adiabatic expansion during the rarefaction process under the action of high post-shock temperature. Then, the carbyne species are formed in the vapour–solid transition (cf. 3.3.1 and 3.4.1) along with graphite, and the formation of liquid carbon droplets occurs concurrently followed by their solidification. To explain different morphologies of the shock-produced carbyne (chaoite) particles, a solid–solid transition mechanism was also invoked [147].

3.4.3. Ion-assisted sputtering of carbon

Ion-assisted condensation of carbyne to prepare single crystal films occurs by an epitaxial growth mechanism based on surface activation by incident radiation [75, 148–150]. Centres thus formed are surface complexes of point defect densities comparable to those formed during annealing of radiative monodefects. Mass-spectrometric studies have shown [151, 152] that the cluster concentration during ion sputtering varies periodically with cluster size with a period $n = 2$ in agreement with theoretical predictions [112]. The condensing carbon vapour flow obtained by sputtering a graphite sample with a beam of fast ions ($E = 5$ keV) consists of carbon chains with $1 < n < 8$ [151]. The Ar^+ ion beam irradiating the growing carbyne film had an energy of 150 eV corresponding to the maximum cross-section for neutralization of the Ar^+ ions at the carbon chain-like clusters. Carbon vapour was condensed at the (100) surface of a KBr single crystal for which efficient ion-assisted desorption of the halogen occurs at $E_{Ar} = 150$ eV accompanied by formation of charged centres for oriented condensation. This situation ensures low temperatures (50 °C) thus preventing formation of interchain crosslinks and collapse of the carbyne structure thereby allowing preparation of oriented carbyne films [75].

4. Structural models of carbyne

"Carbynes" are structures consisting of (straight [8] or kinked [84, 85]) carbon chains held together by van der Waals forces to form a crystal. Theoretically, linear carbon chains with conjugated triple (polyyne-type) and/or cumulated double (polycumulene) intrachain bonds are assembled in a hexagonal array without any interchain chemical σ-bonds ("pencil-in-box" model). In real samples, however, cross-linking defects with various periodicities as well as kinks may occur resulting in a layered lattice arrangement [75]. Hence the definition above can be extended by stating that carbynes are "partially cross-linked 3D-polymers having more or less regular layered structure and are predominantly composed of extensive fragments of linearly polymerized carbon". In this spirit, graphite and diamond are, respectively, limiting conformations of network and chain structures that are regularly periodically cross-linked by three- (graphite) and four-function (diamond) branching points. Indeed, the graphite plane can be viewed as composed of 2D-cross-linked polyyne [116] or polycumulene [84, 85] chains whereas the diamond structure consists of a 3D-array of an equal number of screw axes of opposite chirality, i.e., helically twisted carbon chains.

Correspondingly, in the first carbyne sample that was structurally investigated two kinds of crystals were found by TEM and electron diffraction that were named α- and β-carbynes and were tentatively ascribed to the polyyne and cumulene forms, respectively [153]. The occurrence of these isomers was explained by assuming carbon chains of different lengths parallel to the hexagonal c-axes; α-carbyne was supposed to contain a polymeric carbon chain whose 2-atomic units of 0.256 nm length was repeated six times. Interplanar spacings obtained from X-ray patterns of carbyne powder and natural carbon, i.e., chaoite showed good agreement under the assumption that there were two hexagonal crystalline modifications present with the cell parameters $a_\alpha = 0.892$ nm, $c_\alpha = 1.536$ nm and $a_\beta = 0.824$ nm, $c_\beta = 0.768$ nm, respectively. Investigations of the thermal transformation of carbyne under pressure confirmed the occurrence of those two modifications [153]. Linear carbon chain polymers with triple C≡C bonds were not transformed to diamond under static pressures equivalent to those of catalytic synthesis and direct transformation from graphite. However, the disappearance of diffraction lines characteristic of the α-modification and the occurrence of new lines corresponding to the interplanar spacings of the β-modification suggested a pressure-induced transformation of α-carbyne with lower density (2.71 g cm^{-3}) to the more stable β-form with higher density (3.17 g cm^{-3} [84, 85]).

Later several new polytypic forms of carbyne or carbyne superstructures were reported (see, for example [84, 85, 132, 133, 140, 154]). Considering the existence of a variety of the carbyne crystalline polytypes, one can assume that the use of crystallographically derived terms, namely, α- and β-carbynes, for describing the type of chemical bonds in carbynes [56, 71] may turn out to be incorrect. Heimann *et al.* [84, 85] suggested a structural model that related the c-axes lengths of the observed carbyne forms to the number of carbon atoms in the chain for both polyyne and polycumulene isomers. To account for the deviation of observed and calculated c-axes parameters it was assumed that straight line parts of carbon chains alternate with regular defects, i.e., kinks (zigzags). Confirmation of the hitherto hypothetical kinks came from several sources. Firstly, numerical calculations of the phonon spectrum, i.e., the fundamental vibrational frequencies for a model polycumulene carbon chain with regular kinks between straight fragments of four carbon atoms were compared to experimentally observed infrared spectra of carbyne, and good agreement was found [70]. Secondly, a study of the electronic structure of carbyne by Auger electron (AES) and electron energy loss spectroscopy (EELS) revealed the continuity of the energy spectrum within the valence band, which attests to a large chain length on one hand, and a band width corresponding to short chains on the other hand, thus confirming the presence of periodically repeated linear fragments in the carbyne structure [72, 73, 155]. Finally, based on electron density distribution data (Fig. 1) a spatial structural model of the carbyne crystal lattice was derived [75] that showed vacancies in every second carbyne layer conforming to a $3^{1/2} \times 3^{1/2}$ superlattice. According to this model, the unit cell of carbyne consists of parallel van-der-Waals-bonded carbon chains with kinks thus resulting in a double-layered structure. In the lower layer the chains are closely packed and located at the corners (1 and 2) and at the centre (3) of a hexagon whereas in the upper layer the central chain is missing thus forming a vacancy in which two impurity atoms are located (Fig. 2). The impurity atoms were found only in the microcrystals and are absent in the bulk of the oriented films that were prepared by ion-assisted condensation of carbon vapour [75]. This model provides an important key to the understanding of the stability of carbyne, i.e., the configuration in which a generally unstable aggregate of linear carbon chains can be stabilized. Even though the impurity atoms are not a mandatory component of the carbyne

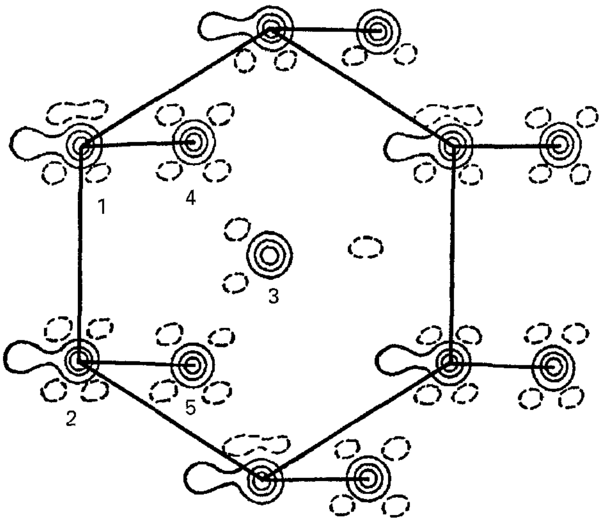


Figure 1 Map of the distribution of electrical potential in the carbyne unit cell [75].

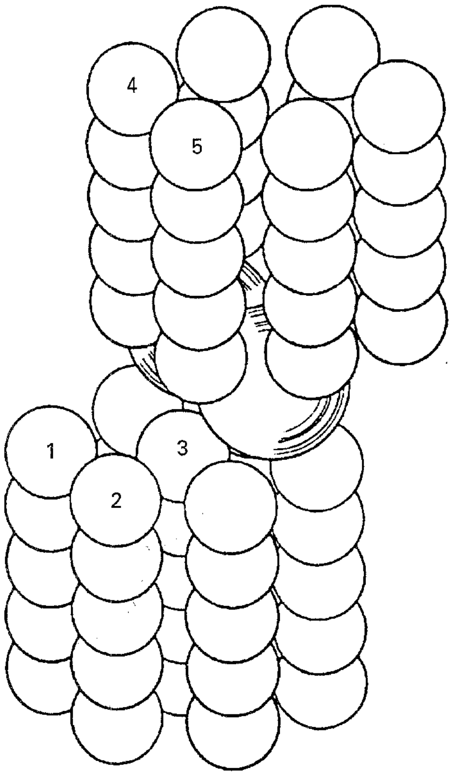


Figure 2 Spatial model of the carbyne crystal lattice [75].

crystal lattice they exert a pronounced steric ordering and stabilization effect of the chains. They may even play the role of a catalyst in the crystallization process of the carbyne. It should be admitted, however, that all crystallographic studies of carbynes published to date dealt with microcrystals existing mostly as minor inclusions in amorphous powders or films and were performed by using electron diffraction techniques. Therefore, because of the small size of single crystals with a small field of coherent dispersion obtained so far, rigorous X-ray structural data are still unavailable.

Recent first-principle Hohenberg–Kohnian [156] electron density function calculation on two interacting parallel polyyne chains [157] predicted a minimum total energy for cross-linked chains with zigzag structures. Such structures saturate existing dangling bonds. However, the energy barrier against crosslinking was found to be rather high (ca. 1 eV per carbon atom) thus explaining the markedly sluggish crosslinking rate under ambient conditions.

Udod *et al.* [77] synthesized a carbyne intercalation compound with sodium (CIC–Na) using a chemical transport reaction of amorphous carbyne with sodium metal in vacuum. A structural model of the intercalation compound has been proposed on the basis of experimental electron diffraction data. The size of the lattice vacancies suggests two sodium atoms to be located in these vacancies that occur in alternating layers of the normal carbyne structure (Fig. 2). The same situation evidently occurs in the case of CIC–Na but here sodium atoms occupy all vacancies in every layer of the carbyne single crystal (Fig. 3). It is highly relevant to mention here the role alkali metal fluoride molecules play in the stabilization of "electrochemical carbon", i.e., C–MF composities as purported by Kavan *et al.* [79, 83].

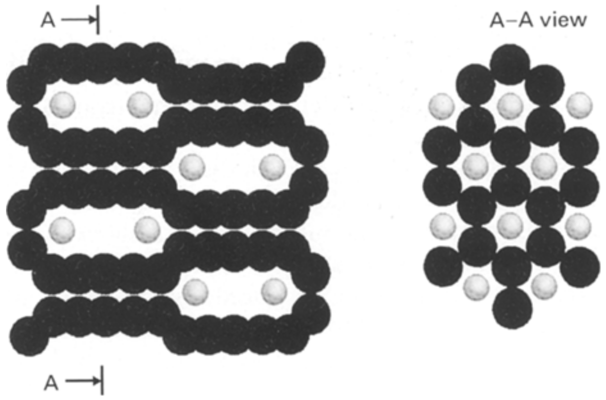


Figure 3 Proposed structure of the (Na)CIC single crystal [77]. Black and light circles denote carbon and sodium atoms, respectively.

Ongoing solid-state ^{13}C cross-polarized magic angle spinning-nuclear magnetic resonance (CPMAS-NMR) spectroscopy studies of carbyne produced by dehydro-halogenation of poly(vinylidene halide)s show a broad chemical shift between 170–20 ppm [158] whose Gaussian deconvolution yielded individual contributions centred at 125 ppm (sp^2) [159], 93 ppm (sp), and 48 ppm (sp^3) [160]. The first one may be related to a kink site, and the last one to a local diamond-like conformation owing to extensive crosslinking. The broadness of these peaks can be related to the presence of paramagnetic species [161] that were also observed by electron spin resonance (ESR) spectroscopy [162].

5. Criticism against carbyne

During its 35-year history, the concept of a linear carbon allotrope with *sp*-type hybridization of carbon bonds had been repeatedly subjected to harsh criticism. The most frequently launched arguments are concerned with the notorious instability of short-chain polyynes and cumulenes, which led Baeyer [1] to postulate the impossibility of preparing "chain-like carbon", i.e., the elusive linear allotrope. It should be noted, however, that Lagow *et al.* [15] have reported recently on the surprising stability of end-capped polyynes to at least 130 °C. Furthermore, carbynes should not be regarded in the narrow framework of classical organic chemistry just mechanistically as "wisps" of non-interacting chain-like carbon molecules (polyynes or cumulenes). Similarly, it would be utterly meaningless to consider graphite and diamond as aggregates to benzene and adamantane molecules, respectively, and to look for direct analogies in properties.

Smith and Buseck [163] cast doubt on the existence of carbynes, supposing that the concept of linear allotropes to be originated from misidentification of sheet silicates. Using energy-dispersive X-ray spectrometry, they interpreted electron diffraction patterns of some samples of natural [9, 10] and shock-produced [143] chaoite, carbon (VIII) from glacier spherule material [164], and the Allende carbyne [25] as, respectively, nontronite + quartz, muscovite, talc, and kaolinite

[163]. Rietmeijer [165] suggested recently that carbynes may not be pure carbon allotropes but crystalline C–(H–O–N) carbons, having based his conclusion on rather tentative arguments, predominantly on a recalculation of the diffraction data reported earlier by different authors. However, both these allegations can be dismissed by considering the fact that carbyne particles formed by the interaction of a shock wave with a graphite-metal mixture in the presence of a high-temperature pulse produced by discharge of a capacitor were found to be free of any contaminating elements [142]. Likewise, pyrolytic graphite with an impurity content of about 6 ppm was used in the preparation of pure carbyne by various techniques [140]. The apparent incompatibility of a layered morphology of carbyne exhibiting layers perpendicular to the sixfold symmetry axis with carbon chains running parallel to it [163, 165] can be accounted for by the layered lattice model [75] based on kinked carbon chains [84, 85].

Nagornyi *et al.* [166] supposed that the hexagonal diffraction pattern observed from some carbyne microcrystals might originate from double scattering of electrons in graphite twins with specific twinning angles. Thus, calculations with the rational angles of 27°48′ and 15°10′ gave diffraction patterns similar to those of α-carbyne and carbon (VI), respectively. However, the real diffraction pattern of carbyne exhibits only a small proportion of spots being close to the positions calculated for a twin of the graphite crystal. Furthermore, basic reflections of graphite from the (1 0 0) and (2 0 0) planes ($d_{100} = 0.212$ nm and $d_{200} = 0.106$ nm, respectively) are absent in the electron diffraction pattern of carbyne [108]. Finally, it is quite impossible to explain by twinning of graphite the existence of a number of crystalline polytypes with different values of the *a* parameter of the hexagonal cell ranging from 0.824–0.940 nm [84, 85].

Thus, all the critical allegations are not convincing enough to reject the concept of linear carbon allotropes, but demonstrate only the need of further in-depth investigation.

6. Properties of carbyne

6.1. Chemical properties

Crystalline carbyne has been reported to exhibit a remarkable inertness towards various oxidizing agents. Only the reaction with ozone for a month (see 3.1.1) results in complete degradation of carbyne [45]. With respect to a boiling 1:1 mixture of nitric and sulfuric acids as well as other chemical agents carbyne displays a high chemical inertness approaching that of diamond [45]. Whereas carbyne can be fluorinated in a wide temperature range to give fluorocarbons of various stoichiometry [167–169], it reacts with chlorine only at temperatures above 800 °C with simultaneous degradation of the original polymer and the formation of polychlorides of undetermined structure. No hydrogenation of a suspension of carbyne in alcohol at 200 °C and 20 MPa was observed over Raney nickel or using homogeneous hydrogenation catalysts [170].

These statements are at variance with more recent findings of cathodic over-reduction (n-doping) and interchain crosslinking ("ageing") of C–MF composite [79] that seem to attest to the inherent instability of carbyne and its derivatives because of their high π-electron density [171, 172]. On the other hand, one should emphasize that the structures and properties of crystalline carbynes and amorphous C–MF composites may be completely different, and carbyne occurring as a natural mineral (chaoite) has survived for at least 60 million years [9, 10]. This glaring discrepancy is just one of the many puzzling riddles required to be solved to arrive at a consistent level of knowledge about carbyne.

6.2. Electronic properties

According to EELS data carbyne is a semiconductor with a forbidden gap width of 1–2 eV [72, 73]. These data correspond to those found by Springborg *et al.* [173]. The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) transitional energies are around 3 eV for a carbon chain of ten atoms [174]. The width of the σ-band and π-band determined from Auger electron spectroscopy data were found to be, respectively $W_\sigma = 5$–7 eV and $W_\pi = 5$–6 eV [72, 73, 75]. Plasmon oscillations were detected in carbyne by EELS with a π-plasmon energy $E_\pi = 4.5 \pm 0.5$ eV as opposed to that of graphite of 7.0 eV.

The value of the *g*-factor for carbyne films, determined from (ESR) data, was found to be 2.0044 ± (3) [162]. The *g*-values of graphite and diamond were reported to be, respectively 2.0036 and 2.0027. The concentration of the paramagnetic species is 2.1×10^{17} spin per g. This is one order of magnitude lower than the value of 3.2×10^{18} spin per g reported by Kavan *et al.* [175] for C–LIF. Detailed analyses of the electronic structure of finite and infinite polyyne-type chains revealed a soliton-assisted mechanism of conductivity in pure carbon chains as well as a rich spectrum of polaron and polarexiton states in doped chains [176]. These features may give rise to interesting electronic phenomena such as photoconductivity, one-dimensional conductivity and even ferromagnetic properties [177]. Crosslinking tends to shift the carbyne material from a semiconductor- to a metal-type conductor by a Mott–Hubbard type mechanism with a remarkable increase of conductivity that brings it in the range of the *c*-axis conductivity of graphite [178].

Carbyne displays photoconductivity when irradiated by a light source [179]. The optical width of the forbidden gap, determined from photoconductivity data at a frequency $\omega = 9.3$ GHz is $E_g = 1.48 \pm 0.1$ eV, and is $E'_g = 1.5$–2.2 eV determined from the fundamental absorption edge. The photoelectric work function of carbyne, determined from the photoemission threshold is $\Phi = 4.9$ eV [180]. The temperature dependence of the electric conductivity and the thermoelectromotive force were measured over a wide temperature range [181]. The activation energy of the conductivity is $E_a = 1.0 \pm 0.1$ eV. Electric conductivity is achieved by electron hopping. Thin carbyne layers deposited on a single crystal of n, p-Si form a heterojunction with a high value of the photo-electromotive force (0.6 eV) in the visible range as well as a rather small value of the back current. Those properties are of interest in microelectronics.

6.3. Thermophysical properties

The heat capacity of carbyne exceeds that of graphite at 80 K by a factor of 1.5. According to their heat capacities the three allotropes of carbon form the series: diamond < graphite < carbyne. The temperature dependence of the heat capacity of carbyne follows a linear law [182] whereas those of graphite and diamond conform to a power law. The value of the combustion heat of carbyne was determined to be $Q = 356\,\mathrm{kJ\,mol^{-1}}$ [183] that is considerably less than that of graphite ($393\,\mathrm{kJ\,mol^{-1}}$). It was previously mentioned that carbyne obtained by oxidative dehydropolycondensation of acetylene did not transform into diamond under conditions sufficient to achieve diamond synthesis from graphite [40, 153, 184]. However, in 1989 Sobolev *et al.* [185] reported on the transformation of carbyne into lonsdaleite and cubic diamond at 5.5 GPa and 1400 °C. It has also been found that carbyne obtained from poly(vinylidene halides) (see 3.2.1) transforms into diamond under static pressures of 8 GPa and 1400–1700 °C without the use of a catalyst [57, 186]. The yield at 1700 °C was about 99%. Even lower pressures are required when shock pressures with a strong shear component are applied [58]. In this case pressures < 5 GPa without external heating suffice to produce diamond from carbyne, presumably by a soft shear deformation "umklapp" mode [187].

7. Possible applications

Carbynes open up exciting prospects for the creation of novel materials with unique properties and applications. From carbyne, one-dimensional semiconducting materials could be produced starting from polyacetylene and polydiacetylene whose many extremely interesting properties have been predicted theoretically and confirmed experimentally. The material predominantly has a soliton mechanism of conductivity that is unrivalled with regard to the high mobility of charge carriers. Owing to the double degeneracy of the π-band the spectrum of the soliton states in carbyne is considerably richer than that in polyacetylene and polydiacetylenes. Furthermore, the latter are thermally and chemically unstable and decompose under the action of heat and light. Carbyne on the other hand is a high temperature phase of carbon stable at a temperature of 2500 °C [116]. According to Wang *et al.* [188] and Whittaker [116] it is even stable up to much higher temperatures, i.e., to the (still hypothetical) triple point carbyne–liquid carbon–carbon gas. Since it is distinguished from other carbon materials by its stability with respect to hydrogen, carbyne may be a promising material for application as a first wall compound in devices for controlled thermonuclear fusion.

Carbyne is semiconducting and thus fits as the "missing link" into the series of carbon allotropes: diamond is an insulator, graphite is a conductor. Coupled with the possible use of ion beam technologies for preparing carbon films with specified properties it opens up prospects for the creation of a new materials basis for microelectronics manufactured solely from carbon [75]. The recently discovered ability of carbyne to form intercalation compounds with alkali metals should be particularly emphasized [77]. The specific electronic structure of carbyne will yield very valuable electrophysical properties in such compounds.

Carbyne has revealed a number of properties that are interesting for applications in medicine. Carbyne-coated materials exhibit high thromboresistance and excellent biocompatibility [57, 189–193] in clear contrast to conventional polymeric materials (PTFE, polyesters) being customarily used in medicine. Carbyne-containing polymeric materials for medical purposes are promising for application as implantates in reconstructive surgery [190–192], as well as a surgical suture material [193]. Upon prosthetics of a dog's *vena cava* by an artificial blood vessel made from conventional PTFE material the animal died of thrombosis within several hours or days [194]. Using carbyne-coated fibres thrombosis was not observed within the observation period of five years after operation. The advantages of carbyne-coated suture material include high biocompatibility, low lithogenic activity, no capillary properties, good handling characteristics, persistent colour and ease of manufacturing [193].

8. Future developments

An important feature of carbyne is its ability to transform to diamond at rather weak static (8 GPa) and dynamic (5 GPa) pressures without a catalyst. On going work indicates that the latter involves a low energy path through a soft shear deformation of cross-linked polyyne chains [187]. Interesting industrial applications can be envisaged using this effect.

More mundane applications of carbyne refer to hard wear- and corrosion-resistant coatings of machine parts subjected to environmental degradation in service [123]. Since carbyne films are optically transparent in the visible and infrared ranges, chemically highly resistant, and very hard (> 9 Mohs) a number of applications become immediately apparent, such as antireflection coatings, dielectric mirrors, interference filters, laser waveguides, and canopies and radomes for IR-survaillance aircraft.

The high thermal and excellent mechanical properties of carbyne have led to proposals to utilize carbyne-based materials in outer space. Suggestions range from materials for nose tips of space re-entry vehicles [195] to coatings for polymeric construction materials subjected to the combined action of the impact of micrometeorites and ablation by atomic oxygen [124] as predicted for the manned space station.

Several suggestions to utilize carbyne-related materials in solid-state oxygen sensors, humidity sensors and as a cathode sensitive material for primary lithium cells with a cell potential of 2.4 V were reviewed by Kavan [80].

The discovery of carbyne in carbon fibres prepared by the pyrolysis of polymers [106, 107] may lead to the creation of ultrastrong carbon fibres inasmuch as defect-poor filamentous crystals of carbyne (whiskers) were theoretically predicted to be amongst the strongest of all known materials [196]. Since it is inconsistent with the layered lattice model [75], this prediction might be accomplished only if such crystalline filaments constituted by long, defect-free linear carbon chains directed along the whisker's axis could be synthesized.

Last but not least, the prediction that an *sp*-hybridized carbon macromolecule should exhibit superconductivity at ambient temperature [197] constitutes another challenging target for future developments in the carbyne field [132].

9. Concluding remarks

Notwithstanding the large number of studies on carbynes published in the scientific literature, it should be admitted that no rigorous and unambiguous structural evidence is available currently, and that the number of publications itself does not provide a testimony for the existence of the matter in question. The main problem still remaining to be solved is: whether or not carbynes can be set apart as an independent family of linear carbon allotropes. In other words, do linear allotropes really exist or are the numerous carbyne polytypes reported hitherto just more or less regularly cross-linked carbon materials containing in their complex structures polyyne or cumulene fragments of different lengths? In the latter case carbynes would be in effect mixed forms of carbon, i.e., those based on all three known types of hybridization of carbon being present in these materials in various combinations (cf. Refs. [3, 16–21]). This case, however, appears to be rather unlikely, and the whole body of experimental data accumulated to date is highly stimulating to continue research in this field. The recent growth in publications [15, 48, 64, 79, 83, 131–133] demonstrate growing interest among scientists in the fascinating area of carbynes, and the experimental techniques currently available allow one to expect that the problem will be eventually solved.

Acknowledgements

Two of the authors (Yu. P. K. and S. E. E.) wish to acknowledge financial support by the International Science Foundation (grant no. MDI 000) and the Russian Foundation for Basic Research (grant no. 93-03-4492a). S. E. E. is also indebted to the Alexander von Humboldt Foundation for granting a research fellowship.

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Received 4 December 1995
and accepted 22 March 1996