Synthesis and Use of Reactive Molecular Precursors for the Preparation of Carbon Nanomaterials

Abstract:
The use of reactive molecular carbon precursors is required if the preparation of carbon nanostructures and nanomaterials is to be achieved under conditions that are sufficiently benign to control their nanoscopic morphology and tailor their chemical functionalization. Recently, oligoyne precursors have been explored for this purpose, as they are sufficiently stable to be available in tangible quantities but readily rearrange in reactions that yield other forms of carbon. In this chapter, we briefly discuss available synthetic routes toward higher oligoynes that mostly rely on transition metal-mediated coupling reactions. Thereafter, a comprehensive overview of the use of oligoyne derivatives as precursors for carbon nanostructures and nanomaterials is given. While the non-templated conversion of simple oligoynes into carbonaceous matter exemplifies their potential as metastable carbon precursors, the more recent attempts to use functionalized oligoynes in host–guest complexes, self-assembled aggregates, thin films, colloids or other types of supramolecular structures have paved the way toward a new generation of carbon nanomaterials with predictable nanoscopic morphology and chemical functionalization.

Keywords: oligoyne, reactive molecular precursor, carbon nanomaterials, chemical functionalization, characterization

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1 Introduction

Fullerenes, carbon nanotubes, graphene sheets, porous carbons, carbon nanospheres and carbon nanofibers are just a few representative examples of the many different carbon nanostructures and nanomaterials that have become available [1–5]. The diverse range of accessible properties in combination with the high natural abundance of carbon, low specific weight as well as an exceptional chemical and thermal robustness distinguish carbon nanostructures as attractive components in organic electronic devices, polymer composites or energy storage systems [2–4, 6, 7]. The respective mechanical properties of the different nanostructures as well as their electrical or thermal conductivities are generally the result of the connectivity and hybridization of the constituting carbon atoms. The two main naturally occurring carbon allotropes, diamond and graphite, may serve as a basis to illustrate the broad range of accessible properties on the macroscopic scale. Thus, the carbon atoms in diamond are $sp^3$-hybridized, and their tetrahedral coordination geometry results in a three-dimensional network of covalent bonds. The resulting bulk material is transparent, extremely hard and electrically insulating, but it displays a high thermal conductivity [2, 8–10]. Graphite, on the other hand, is formed from stacks of carbon sheets that comprise a honeycomb lattice of $sp^2$-hybridized carbon atoms. Unlike diamond, the comparably soft graphite has a highly reflecting black appearance and is an electrical (semi)conductor; its properties drastically change with the direction of measurement, reflecting its anisotropic structure [2, 8, 9]. A corresponding variety of properties is typically observed on the nanoscale. However, it remains difficult to prepare pure, well-defined carbon nanomaterials in tangible quantities, since they feature dimensions that are only accessible through demanding, multistep organic syntheses (“bottom-up” approaches) or through delicate physical processing (“top-down” approaches) [11–14]. Typical physical processes used in top-down approaches are mechanical exfoliation, arc discharge or laser ablation of adequate bulk precursors. Bottom-up approaches are generally based on the wet-chemical synthesis of precursor molecules and their subsequent conversion into carbon nanomaterials at elevated temperatures. In this context, hard or soft templates can be used to control the nanoscopic morphology and microstructure of the resulting carbon materials [15–17]. It is important to point out that all chemical functionality is usually lost during the final carbonization of the molecular precursors at elevated temperatures. Thus, a post-synthetic functionalization of the carbon nanostructures is required...
when a defined chemical functionalization is desired. However, this typically results in an inhomogeneous distribution of the chemical functional groups and accompanying structural defects in the carbon nanostructures [18, 19].

The only way to circumvent this issue is the use of alternative molecular precursors that are sufficiently reactive to undergo carbonization under benign conditions, preferably close to room temperature. This would allow for the preservation of (most) chemical functional groups introduced with the precursors throughout the carbonization process. Along these lines, functional molecules containing segments rich in sp-hybridized carbons are an attractive choice. The inherent reactivity of such segments and the absence of other elements that would have to be eliminated in the course of carbonization facilitate a conversion of the sp-carbon-rich precursors into carbon nanostructures with predominantly sp²-hybridized carbons under mild conditions. Moreover, the chemical functional groups that are introduced with the precursors and remain covalently linked throughout the conversion necessarily lead to sp²-hybridized carbon atoms in the produced carbon nanostructures. The deliberate introduction of such sp² carbon “defects” allows for a control over the chemical functionality as well as its distribution in the obtained carbon materials and, consequently, the properties and processability.

In this context, the present chapter aims to give a concise introduction into the chemistry of functional molecules comprising chains of sp-hybridized carbon atoms and will then provide a comprehensive overview over the different strategies for their conversion into defined carbon nanostructures and nanomaterials.

2 Reactivity of Oligoynes

The extended chains of carbon–carbon triple bonds in conjugated oligoynes are thermodynamically unstable and exhibit an inherent reactivity toward a rearrangement to other, more stable carbon allotropes. Accordingly, all different series of oligoyne derivatives R–(C≡C)n–R display a drastically decreasing stability with an increasing number n of triple bonds [20]. This is readily illustrated on the basis of the parent series H–(C≡C)n–H of unsubstituted compounds. Thus, butadiyne may be distilled at low temperatures to furnish the pure compound but begins to polymerize above 0°C [21]. Hexatriyne slowly polymerizes even at temperatures below −50°C, and samples that were exposed to air reportedly exploded spontaneously leading to the formation of “carbonaceous matter” [22]. Similar accounts that describe the rapid decomposition of compounds containing conjugated acetylenes under formation of insoluble black material are abundant, especially in the literature concerning the preparation of higher oligoynes [23, 24]. Whereas the carbon materials produced by the (in most cases unwanted) decomposition of reactive carbon-rich molecules were rarely investigated in more detail, Kroto et al. [25] discussed whether oligoynes were the “small carbon clusters” involved in the formation of fullerenes by the arc discharge method. This hypothesis found strong support in reports by Grösser and Hirsch [26], who isolated a homologous series of dicyanide end-capped oligoynes NC–(C≡C)n–CN as the main product when the vaporization of graphite was carried out in the presence of cyanogen CN₂. Moreover, Cataldo [27] reported the formation of the unsubstituted derivatives H–(C≡C)n–H when an arc discharge experiment was performed with graphite electrodes submerged in organic solvents (Figure 1).

![Figure 1](a) Oligoynes produced by vaporization of graphite in the presence of cyanogen CN₂ and (b) with graphite electrodes submerged in organic solvents such as methanol [26, 27].

Despite this apparent role of carbon-rich molecules that feature extended chains of carbon–carbon triple bonds in the formation of common carbon nanostructures, the deliberate utilization of oligoynes as molecular precursors for carbon-rich materials has rarely been addressed to date. Most investigations have rather aimed at the preparation of stable oligoyme moieties as model compounds toward the linear, fully sp-hybridized carbon allotrope carbyne (C≡C)ₙ [28] or, alternatively, at the use of oligoynes as molecular wires for an efficient charge...
transport [29–31]. To these ends, thermodynamically unstable oligoyne derivatives have been kinetically stabilized by terminal substituents \( R \) with a high steric demand. The latter act in the sense of protecting groups that prevent an intermolecular cross-linking of the triple bonds, and a large number of oligoyne derivatives have been prepared employing this general strategy [20, 32, 33]. However, it needs to be pointed out that even such sterically shielded oligoynes beyond the decaynes become increasingly unstable as neat compounds and easily react in a manner that converts the molecules into carbonaceous matter. Besides the covalent introduction of protective groups, more recent supramolecular approaches relied on the use of rotaxanes in which an oligoyne segment as the guest was stabilized using a macrocyclic host [34–37].

3 Synthetic Approaches toward Oligoynes

Despite the difficulties associated with the stability of oligoynes, several approaches have been developed for their synthesis. Most of these strategies rely on copper-mediated coupling reactions between \( sp \)-hybridized carbons of terminal alkynes. Prominent examples are coupling reactions such as the Glaser [38], Hay [39, 40], Eglinton–Galbraith [41, 42], Sonogashira [43, 44] or Cadiot–Chodkiewicz [45] reactions (Figure 2) [20, 32, 46, 47]. Furthermore, procedures based on the Negishi coupling reaction have been developed that also allow to couple two different alkyne moieties to each other [48–51]. Besides these transition-metal-mediated approaches, the Fritsch–Buttenberg–Wiechell (FBW) rearrangement of 1,1-dibromovinylidene derivatives [52–54] has also been very successfully exploited for the preparation of higher oligoynes [55].

![Figure 2](image-url)

**Figure 2**: Overview of chemical methods that allow for the preparation of oligoynes with extended \( sp \)-hybridized segments. (a) Synthesis of symmetric oligoynes by Glaser coupling, Hay coupling or Eglinton–Galbraith coupling and (b) synthesis of asymmetric oligoynes by Cadiot–Chodkiewicz, Sonogashira, Negishi coupling or FBW rearrangement.

Among the chemical methods, the Glaser coupling represents the oldest coupling method for terminal acetylenes. Although the mechanism of the Glaser reaction is still under debate with regard to the oxidation state of the catalytically active copper species, it is clear that the presence of a copper salt, molecular oxygen and a base are crucial for the reaction to proceed [56]. Often encountered issues with the solubility of copper salts in common organic solvents were resolved by the use of the copper(I) chloride tetramethylethylenediamine (TMEDA) complex according to the Hay coupling conditions [57]. Closely related to Glaser and Hay reactions is a procedure first described by Eglinton and Galbraith [41, 42]. Instead of catalytic amounts of a copper(I) salt, stoichiometric amounts of a copper(II) salt are used for the coupling of the acetylene derivatives, obviating the need for oxygen as the oxidizing agent.
Whereas symmetric oligoynes can be obtained with all of the preceding procedures, the Cadiot–Chodkiewicz coupling allows for the synthesis of asymmetric oligoynes [58]. Here, a copper(I) halogenide, a base, as well as a halogenated and a nonhalogenated acetylene species are used as reactants. However, in spite of the vast number of investigations describing variations of the reaction conditions for the simple coupling of a terminal acetylene with a haloacetylene to obtain unsymmetrical diacetylenes [59, 60], the practical use of the Cadiot–Chodkiewicz coupling has remained limited, in particular, for the synthesis of higher oligoyne homologues. One possible reason is the seemingly inevitable formation of the symmetric side products resulting from homocoupling of the acetylenes and self-coupling of the haloacetylenes that often result in statistic mixtures and render isolation of the pure product difficult [61, 62]. This selectivity problem is mitigated using the established palladium-mediated cross-coupling reactions, such as Sonogashira or Negishi reactions, in which a haloacetylene is coupled to an in situ generated copper or zinc acetylide, respectively, using a palladium(0) complex as the catalytically active species [44, 63]. Despite a limited number of examples to date, it seems as if the extent of homocoupling side reaction products in Negishi couplings is smaller than under Sonogashira conditions [64].

In contrast to all of the previously described metal-mediated transformations that serve to directly build up the oligoyne segment, the FBW route first seeks to synthesize compounds containing one or more 1,1-dibromovinylidene groups that are then subjected to a base-induced rearrangement to yield the final oligoynes [65, 66].

Among the many notable examples of molecules prepared following the above-mentioned wet-chemical procedures are derivatives such as the methyl-substituted Me–(C≡C)₆–Me [67], pentafluorophenyl-substituted Pfp–(C≡C)₆–Pfp [68], tert-butyl-substituted t-Bu–(C≡C)₆–t-Bu [69, 70] or trispropylsilyl-substituted derivatives TIPS–(C≡C)₁₀–TIPS [71]. Hirsch and coworkers [72] investigated the use of Frechet-type dendrons of the third generation to maximize the steric shielding and prepared G₃–(C≡C)₁₀–G₃. Zheng and Gladysz [73] explored the stabilizing effect of organometallic complexes at the termini with derivatives such as the platinum analogues LₙPt–(C≡C)₁₄–PtLₙ (Figure 3).

**Figure 3:** Different series of oligoynes have been synthesized so far as model compounds for the sp-hybridized carbon allotrope carbyne. Notable examples comprise derivatives such as the nitrile-capped series [74], tert-butyl-substituted derivatives [69, 70] or silylated compounds [71, 75].

Despite the increasing challenges encountered with the stability of higher oligoynes, Chalifoux and Tykwinski [76] were able to even prepare a derivative with 44 sp-hybridized carbon atoms (or 22 acetylene units). Their overall synthetic approach relied on the use of the very bulky tris(3,5-di-tert-butylphenyl)methyl (“supertrityl”, Tr*) end-capping groups. Using a variant of the reliable Eglinton–Galbraith homocoupling protocol but adding a silyl-protected tetrayne in excess in the presence of copper acetate and 2,6-lutidine as a base, they obtained an asymmetric Tr*-protected heptayne (Figure 4). After desilylation, they elongated this heptayne applying the same reaction conditions. The obtained undecayne was eventually desilylated in situ in the presence of cesium fluoride, and the symmetric Tr*-protected compound with 22 acetylenes was obtained in a dimerization reaction in the presence of Cu(OAc)₂·H₂O and 2,6-lutidine. The use of 2,6-lutidine as a base was essential, as attempts with other, more nucleophilic bases such as pyridine failed. The obtained products exclusively consisted of acetylenic carbons, apart from the terminal Tr* groups that were crucial to secure the stability of the final oligoyne derivatives.
These efforts toward the preparation of oligoynes of ever-increasing length demonstrate that the chemical synthesis of such reactive derivatives is feasible and delivers quantities that are sufficient to use oligoynes as precursors for carbon materials. At the same time, experiments with the isolated compounds served to further illustrate the reactive nature of such compounds as, for example, the differential scanning calorimetry traces of the trisopropyl-terminated derivatives TIPS-(C≡C)ₙ−TIPS revealed reversible melting for compounds with two to six acetylene units, and only the diyne did not exhibit an irreversible exothermic transition at higher temperatures [71].

Finally, physical methods have been used to prepare oligoynes, such as arc discharge at graphite electrodes in organic solvents, solution-spray flash vacuum pyrolysis of 3,4-dialkynyl-3-cyclobutene-1,2-diones, electrochemical reduction of poly(tetrafluoroethylene) or laser ablation of graphite [27, 77–80]. In an interesting approach, Shinohara and coworkers obtained a mixture of oligoynes [C≡C]ₙ−H of different lengths (n = 4–6) through laser ablation of graphite microparticles from which the pure decayne was isolated by high-performance liquid chromatography. Subsequently, they used double-walled carbon nanotubes (DWCNT) as hosts for the one-dimensional assembly of the decaynes [80]. The inclusion compounds were formed upon dipping of open-ended DWCNTs into a methanol solution containing decayne. Molecules that adhered to the outer surface of the DWCNT were removed by rinsing and drying of the inclusion complexes at 80°C. Thereafter, a thermal annealing step at temperatures of up to 1,000°C was carried out that initiated a “fusion reaction” between the decayne molecules leading to the formation of sp-hybridized carbon chains with more than 50 carbon atoms. While this constitutes an intriguing approach, the possibility to exploit the inherent reactivity of the decayne to carbonize under mild conditions was left unexplored. In general, the presented physical methods cannot be used to prepare oligoynes that can be isolated in sufficient quantities to subsequently use them as precursors for the tailored preparation of carbon nanostructures, in contrast to the wet-chemical approaches described earlier.

## 4 Carbonization of Non-Preorganized Oligoynes

In experiments that were originally aimed at the preparation of the elusive carbon allotrope carbyne (C≡C)ₙ−

Lagow and coworkers [28] reported the unintended use of oligoynes as molecular precursors for carbonaceous materials. Thus, when investigating the stability of the tert-butyl end-capped tetrayne derivative Bu−(C≡C)ₐ−Bu, a minor amount of the sample (2 %) underwent graphitization when exposed to an increased pressure of 60 kbar over extended periods of time. In contrast to these experiments at high pressures, Hlavaty and coworkers [81, 82] explored the reactivity of different hexatriyne derivatives that lacked sterically demanding end-capping groups in organic solutions at or below room temperature. Thus, solutions of the unsubstituted hexatriyne as well as the 1-iodohexatriyne derivative started to rapidly react at 0°C and room temperature, respectively. Interestingly, these nondirected, low-temperature reactions of the molecular precursors furnished a mix of amorphous, carbonaceous materials that, upon closer inspection, featured a few instances of multi-walled carbon nanotubes with diameters of 10–20 nm, lengths of up to 200 nm and attached “onion-like” carbon nanoparticles [81]. The investigations with the corresponding dilithium and dipotassium salts of the parent hexatriyne showed that the latter were even more reactive as a carbonization already occurred in the course of their preparation. The authors showed that the mixed carbonaceous material obtained after hydrolysis contained few
examples of multi-walled carbon nanotubes [82]. An ill-defined carbonaceous material with a graphitic microstructure was also obtained when a TIPS-hexatriyne derivative was deprotected in situ [83]. While these studies represent the first accounts of the deliberate use of oligoynes as reactive carbon precursors, it should be noted that the interpretation of some of the analytical data was ambiguous, the representative nature of the observed carbon nanostructures remained an open question and no explanation for their selective formation was put forward.

In contrast to this spontaneous solution-phase carbonization of simple molecular precursors, Zhao and coworkers [84, 85] investigated the solid-state polymerization of different fullerene-substituted tetrayne derivatives. The precursor molecules were obtained through oxidative coupling of iodoaryl acetylenes with trimethylsilylacetylene under Hay coupling conditions. The iodoarene was thereafter subjected to a Sonogashira coupling reaction with trisopropylsilylacetylene. Subsequently, selective removal of the trimethylsilyl group followed by an oxidative homocoupling under Hay conditions yielded a symmetric tetrayne. Desilylation of the TIPS-substituted tetrayne allowed for a functionalization with C\textsubscript{60} fullerene moieties in an ethynylation reaction using an excess of C\textsubscript{60} and lithium hexamethyldisilazide (Figure 5).

Figure 5: Reagents and conditions: (a) (i) K\textsubscript{2}CO\textsubscript{3}, MeOH/THF, (ii) TMS–C≡C–H, CuCl/TMEDA, O\textsubscript{2}, acetone; (b) TIPS–C≡C–H, PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, CuI, Et\textsubscript{3}N, THF, 60°C; (c) (i) K\textsubscript{2}CO\textsubscript{3}, MeOH/THF, (ii) TMS–C≡C–H, CuCl/TMEDA, O\textsubscript{2}, acetone, (d) TBAF; and (e) (i) C\textsubscript{60}, LHMDS, THF and (ii) TFA. Synthetic scheme illustrating route toward fullerene-substituted tetrayne derivatives [84].

Thin films of the molecular precursors were prepared by drop-casting or spin-coating of toluene solutions on a mica surface, and their reaction was thereafter induced by a mild thermal treatment at a temperature of 160°C. According to the investigations by means of UV/Vis spectroscopy, the tetrayne moieties were consumed in the course of the thermal treatment, as their characteristic absorption pattern disappeared, and the formation of carbon materials with different morphologies was observed by atomic force microscopy (AFM). Notably, an amorphous film of one of the investigated tetrayne derivatives gave rise to homogeneously distributed carbon nanospheres, with a uniform diameter below 20 nm after the thermal treatment (Figure 6) [84]. Although not discussed by the authors, this formation of a well-defined pattern of uniform carbon nanospheres can probably be rationalized by a thermodynamically driven dewetting of the precursor thin film from the substrate under the carbonization conditions.
Further approaches have been reported, wherein carbon materials were prepared from acetylene-containing molecular precursors by pyrolytic treatment at elevated temperatures, and some of these have been reviewed recently [86]. However, such high-temperature methods do not exploit the potential of oligoyne derivatives as molecular precursors for the preparation of carbon materials under mild conditions, which has certainly been illustrated by the preceding examples. In all of the discussed cases, the conversion of the inherently reactive molecular precursors lacked a defined means of supramolecular control that guided the carbonization process toward a predetermined morphology. With the exception of the conversion of one of the tetrayne derivatives reported by Zhao and coworkers, these carbonization processes therefore furnished product mixtures with minor amounts of distinct carbon nanostructures. Obviously, a preorganization of the molecular precursors prior to and potentially throughout the carbonization is necessary to allow for the preparation of defined carbon nanostructures with control over their nanoscopic morphology.

5 Topochemical Polymerization of Oligoynes

The lack of control over the morphology of the obtained carbonaceous materials prevalent in the preceding examples of undirected conversions of oligoynes may, for example, be overcome by conducting the carbonization in single-crystalline specimen, in analogy to the well-understood topochemical polymerization of diacetylene derivatives [87–89]. In the context of an extensive investigation of the topochemical conversion of various linear and cyclic acetylene derivatives, Baughman and Yee [90] were the first to report an attempt to topochemically polymerize a octatetrayne bis(carbamate). However, a detailed analysis of the product structure was impeded by the loss of crystalline order in the course of the polymerization, and only the comparison with reactions of other acetylene derivatives led to the conclusion that the polymerization most likely proceeded in the sense of a 1,4-polyaddition with unclear regioselectivity. Nakashish and coworkers [91] investigated the reactivity of tetrayne, pentayne and hexayne derivatives with different terminal substituents in terms of their solid-state topochemical polymerization. The polymerization of dithiophene- and diquinoline-substituted tetraynes was achieved by thermal annealing of single-crystalline specimen, and the recorded UV/Vis spectra displayed a broad absorption that the authors claimed to be consistent with the product of a controlled 1,2-polymerization [92]. While this notion has often been repeated in the pertinent literature, it should be noted that it had not been substantiated with analytical data and appears to be highly unlikely on the basis of packing and steric considerations. The same authors reported that the reactivity of an investigated bis(tetradecyl)-substituted hexayne was even higher, and its single crystals readily polymerized at ambient temperature in the dark while consecutively changing the color from green to black [93]. In the course of the reaction, the infrared (IR) bands corresponding to the acetylene moieties disappeared, and UV/Vis/near-IR spectroscopy showed several peaks with a maximum absorption at 776 nm. Monitoring of the UV absorption over the course of a couple of days showed that the absorption band increasingly broadened. The authors interpreted the corresponding, ill-defined solid-state $^{13}$C nuclear magnetic resonance spectra in terms of a slow conversion of an initially formed tetrayne-substituted poly(diacetylene) into a butadiyne-bridged poly(diacetylene) ladder polymer. Moreover, the authors later speculated [91] that a subsequent cyclization would result in graphitic ribbons. However, the actual experimental evidence appears to be insufficient to support this conclusion and, again, the proposed pathways are not plausible on the basis of packing considerations.
Without doubt, topochemical reactions offer the ultimate means of control over the preorganization of the molecular precursors. However, the strict geometric requirements of topochemical reactions drastically limit the choice of side groups. Whether an acetylene-substituted poly(diacetylene) furnished by a topochemical polymerization of higher oligoyne derivatives can subsequently actually be carbonized awaits further exploration. Moreover, if one takes into consideration that the resulting graphene ribbons have a significantly higher carbon atom density compared to a corresponding one-dimensional stack of oligoynes with the same number of carbon atoms per side group, the carbonization must inevitably be accompanied by a significant lateral contraction of such an arrangement. It seems unlikely that the concomitant rearrangements on the molecular level can proceed under preservation of the crystal structure. Moreover, such carbonizations in single-crystalline specimen would only yield insoluble material with a limited variation of accessible morphologies.

Despite these constraints, notable examples have been reported, where the topochemical polymerization of diacetylene derivatives has been employed for the preparation of reactive, polymeric precursors for nanostructured carbons [86, 94]. In an elegant approach that relied on a supramolecular host–guest strategy, Goroff and coworkers [95] prepared a highly ordered poly(diododiacetylene) by a spontaneous polymerization of diiodobutadiyne. Thus, the crystallization of diiodobutadiyne led to the formation of crystals in which the molecules were disordered along the main axis of the molecule and a subsequent controlled topochemical polymerization was not successful. However, exploiting the Lewis acidity of diiodobutadiyne allowed to crystallize the latter in an ordered host–guest crystal with \( N, N' \)-biscyanoalkyl oxalamides as Lewis-basic hosts (Figure 7).

![Figure 7: Topochemical polymerization of diiodobutadiyne in host–guest cocrystals with \( N, N' \)-biscyanoalkyl oxalamides triggered by UV irradiation [95].](image)

After the polymerization, the host was successfully removed by sonication as well as rinsing with organic solvents. As a result, the polymer strands immediately aggregated in solution to furnish fibers with diameters of 10–50 nm [96]. The fibers of the obtained poly(diododiacetylene) can be formally regarded as a “carbon subiodide” and, accordingly, constituted a highly reactive precursor material that underwent an explosive conversion into carbonaceous materials by application of an external stimulus such as shock, pressure or irradiation [97]. The investigations by Goroff et al. [98] revealed that a mild carbonization could be achieved either by irradiation of the bulk fibers under release of iodine or by a dehalogenation of suspensions of the fibrous polymers through treatment with a Lewis base at room temperature. The carbonization of the fibrous polymers furnished a one-dimensionally oriented nanostructured carbon material rich in \( sp^2 \)-hybridized carbons under very mild conditions. While constituting an unambiguous demonstration of the potential of reactive carbon-rich precursors toward the preparation of carbon nanostructures with defined morphology, the employed host–guest strategy cannot be straightforwardly transferred to other precursor molecules, rendering approaches based on supramolecular self-assembly worthwhile alternatives.

### 6 Self-Assembly and Carbonization of Functionalized Oligoynes

In order to allow for a defined preorganization of the reactive carbon precursor molecules before carbonization, an approach based on their self-assembly in solution or in the mesophase offers substantially more flexibility in comparison to a topochemical polymerization in single-crystalline specimen. In addition to the potential error correction before a covalent capture of the structures by cross-linking, the flexible nature of the self-assembled aggregates should be able to structurally adapt to the requirements of the carbonization process. The wealth of potentially accessible aggregates can be readily illustrated on the basis of the various examples for which the self-assembly and polymerization of diacetylene-containing molecules have already been successfully demonstrated. Among others, diacetylenes have been polymerized from mono- or multilayered structures [99–104], in molecular arrays organized on surfaces [105–107], as well as in self-assembled vesicles and tubular aggregates [108–114].

Expanding on the well-established strategy to covalently capture self-assembled aggregates by polymerization of incorporated diacetylene moieties, Morin and coworkers [115, 116] recently employed macrocycles with...
multiple diacetylene units and amide groups for the preparation of one-dimensional nanorods and nanotubes from organogels (Figure 8). The synthesis of the macrocycles featuring polymerizable diacetylene units was achieved by using 5-hexyn-1-ol as a commercially available starting material. Coupling with tetradehyde according to Cadiot–Chodkiewicz conditions and conversion of the hydroxyl group to an amine led to an amine-functionalized diacetylene. Subsequent reaction with diiodo-benzoic acid yielded the corresponding amide, which featured a diidoarene group that was used as the key building block in three sequential Sonogashira couplings. These coupling reactions served to construct half of the desired macrocycle that eventually comprised two terminal alkyne groups. In a final coupling step under Eglinton–Galbraith conditions, two such half macrocycles were homocoupled to yield the full macrocycle containing two diacetylene and four acetylene moieties as well as further two diacetylenes in the attached side groups.

Figure 8: Reagents and conditions: (a) (i) Br₂, H₂O, (ii) 1-tetradehyde, CuCl, n-PrNH₂/n-BuNH₂, NH₂OH, Et₂O/H₂O; (b) (i) TrCl, Et₃N, DMAP, CH₂Cl₂ and (ii) NaN₃, DMF; (c) SnCl₂, MeOH; (d) C₆H₅I₂, COOH, EDS, DMAP, CH₂Cl₂; (e) TMS–C≡C–H, PdCl₂(PPh₃)₂, CuI, Et₂N, THF; (f) (i) KOH, THF, MeOH and (ii) C₆H₅I₂C₈H₁₇, PdCl₂(PPh₃)₂, CuI, DIPEA, THF; (g) TIPS–C≡C–H, PdCl₂(PPh₃)₂, CuI, Et₂N, THF; and (h) (i) TBAF, THF and (ii) CuCl, CuCl₂, pyridine. Synthesis of macrocycles with multiple diacetylene units and amide groups as prepared by Morin and coworkers [115].

The obtained molecules were self-assembled into an organogel, and UV irradiation of the aggregated molecules led to the consumption of both the exocyclic and the macrocyclic butadiyne units, as proven by Raman spectroscopy. While indicating the formation of multiple poly(diacetylene) along the axis of the tubular aggregates, the exact nature of the obtained “nanorods” as well as a potential carbonization of the latter by mild thermal treatment remains to be demonstrated [86]. Following a similar approach, carbon-rich monomers featuring multiple diacetylene units were recently polymerized from a gel state and subsequently partly carbonized at temperatures as low as 55°C to furnish micrometer-sized flakes with a multilayered graphitic structure [117]. However, no control over the nanoscopic morphology was obtained in this case.

Demonstrating the usefulness of higher oligoynes as carbon precursors, Ding and Olesik [118] prepared carbon nanospheres in a wet-chemical approach by carbonization of a dispersion of deca-2,4,6,8-tetrayne-1,10-diol in a THF/water mixture. The tetrayne was obtained starting from commercially available propargyl alcohol and 1-iodo-2-(trimethylsilyl)acetylene that were cross-coupled in a Sonogashira-type reaction. Desilylation under alkaline conditions and subsequent homocoupling of the product under Hay conditions yielded the dihydroxyl functional tetrayne (Figure 9).
Figure 9: Reagents and conditions: (a) (PPh$_3$)$_2$PdCl$_2$, CuI, HCC-TMS, (i-Pr)$_2$NH; (b) KOH/H$_2$O, MeOH; and (c) Cu(OAc)$_2$·H$_2$O, air, TMEDA. Preparation of deca-2,4,6,8-tetrayne-1,10-diol based on a sequence of Sonogashira and Hay reaction [118].

The carbonization of the precursor was carried out by heating the mixture to 70°C, and the addition of surfactants efficiently helped to control the size of the obtained water-soluble carbon nanospheres (Figure 10). From parallel observations on solid thin films of the molecules, the authors suggested that the thermal treatment would first lead to a covalent cross-linking by a polymerization of the tetrynes, followed by further carbonization, although the validity of this analogy remained unclear. Most likely, the initially solid particles in the THF/water dispersion melt at the elevated temperature, resulting in an emulsion of liquid tetryne droplets, of which the size can be efficiently controlled with the additional surfactant. In an extension of their approach, the same group investigated the polymerization of a dibutyl-substituted tetryne derivative in an aqueous emulsion polymerization at 80°C with poly(vinyl alcohol) as the emulsifier [119]. Carbon nanospheres of various sizes were successfully prepared by these emulsion polymerizations of reactive precursor molecules, and the morphology of the nanostructures was preserved throughout further processing steps at elevated temperatures. While in these two examples, the oligoynes themselves have, hence, not been used to obtain a controlled nanostructure by means of supramolecular self-assembly, their phase segregation from a polar medium and the interfacial stabilization using surfactants was successfully employed as a soft template to obtain carbon nanostructures. In this context, their initial polymerization at still very benign temperatures served to covalently capture the template nanostructure that thus survived the final carbonization. Investigating the self-assembly and subsequent polymerization of another molecular precursor with a tetryne moiety, Morin and coworkers [120] also obtained carbon nanospheres from an organogel. Whereas also this example thus involved a step in which the reactive molecular precursors were self-assembled, it is important to note that the nanoscopic morphology of the precursor phase was not preserved in the carbonized product.

Figure 10: Schematic depiction of the wet-chemical preparation of carbon nanospheres. (a) A tetryne-diol self-assembled into thin films in a THF/water mixture. (b) Droplets formed by heating and polymerization resulted in the formation of filled carbon spheres [13, 118].

In order to combine the aspect of supramolecular self-assembly into defined nanostructures with the use of similarly reactive molecular precursors, Frauenrath and coworkers [121, 122] have explored the phase segregation of suitable oligoyne amphiphiles in polar media. To this end, glycosylated hexayne derivatives were prepared that resembled typical glycolipid amphiphiles (Figure 11).
Figure 11: Reagents and conditions: (a) AgNO₃, NBS, MeCN; (b) 1,4-bis(trimethylsilyl)buta-1,3-diyne, MeLi · LiBr, ZnCl₂, PdCl₂(dppf) · DCM, THF/toluene; (c) AgF, NBS, MeCN; (d) 1-trisopropylsilyl-6-trimethylsilylhexa-1,3,5-triyne, MeLi · LiBr, ZnCl₂, PdCl₂(dppf) · DCM, THF/toluene; and (e) (i) NaOMe, 1,4-dioxane, MeOH and (ii) Amberlite IR-120 (H⁺).

Synthesis of reactive hexayne amphiphiles based on bromination and Negishi coupling reactions [121].

The preparation of glycosylated hexayne derivatives was achieved by employing a sequence of bromination and sp–sp Negishi coupling reactions (Figure 12). Thus, acetylated 4-pentyn-1-yl glucoside was first converted into the glycosylated triyne. To this end, 1,4-bis(trimethylsilyl)buta-1,3-diyne was used as an acetylenic building block and converted into a zinc acetylide via the monolithiated intermediate. The Pd-catalyzed coupling of this zinc acetylide with the bromoacetylene furnished the corresponding triyne. The latter was converted into the bromotriyne that was found to be highly reactive toward an unusual dimerization in the solid state and, therefore, had to be kept in solution [123]. It was coupled to 1-trisopropylsilyl-6-trimethylsilylhexa-1,3,5-triyne following the same procedure, yielding the glycosylated hexayne. In the final step, complete deacetylation of the glycosyl residue furnished the corresponding glycosylated hexayne amphiphile.

Figure 12: (a) Schematic representation of the wet-chemical preparation of carbon nanocapsules from glycosyl-functionalized amphiphiles containing a reactive carbon-only hexayne segment. (b) Unilamellar vesicles were obtained after self-assembly of the carbon-rich amphiphiles in water and vesicle extrusion through polycarbonate membranes. (c) The carbonization of these vesicles then proceeded under UV irradiation below room temperature, and the formed carbon nanocapsules comprised a graphite-like amorphous carbon with a hydrophilic carbohydrate shell [121].

These carbon-rich amphiphiles reversibly self-assembled in aqueous solution to furnish a mixture of unilamellar and multilamellar bilayer vesicles with a broad size distribution. Subsequent vesicle extrusion through polycarbonate membranes of controlled porosity furnished mostly unilamellar vesicles with a controlled size. In the aggregated state, irradiation by UV light at a temperature of only 1°C was sufficient as a mild external stimulus to induce the carbonization process. The hexayne segments were completely consumed according to UV/Vis and Raman spectroscopy, and further characterization was carried out with the obtained carbon nanocapsules that provided conclusive evidence for an extensive carbonization. A thorough analysis of the nanocapsules suggested that the walls were constituted of “graphite-like amorphous carbon”, which otherwise requires process temperatures above 600°C. At the same time, the carbohydrate shell of the vesicles was retained, as verified by a glucose-binding assay with Concanavalin A. Thus, combining a carbon-only reactive oligoyne segment with a hydrophilic head group served to furnish amphiphilic precursor molecules that allowed for the preparation of functional carbon nanocapsules under very mild conditions.

Along similar lines, choosing an oligoyne amphiphile with a smaller carboxylic acid ester head group allowed for the preparation of carbon nanostructures of a different morphology, that is, carbon nanosheets from a self-assembled monolayer of the precursors at the air–water interface [124].
The employed hexayne amphiphile was prepared following a similar sequence of bromination and Negishi cross-coupling as described before (Figure 13). The synthesis started from commercially available 1-hexynoic acid, and trityl phenol was introduced as a bulky protective group. The Negishi $sp$–$sp$ cross-coupling toward the hexayne derivative was carried out with the zinc acetylide formed from 1-trimethylsilyloctadeca-1,3,5-triyne in order to introduce a lipophilic dodecyl terminus for improved film-forming properties. Subsequent transesterification furnished the amphiphilic hexayne methyl ester. The latter resembled simple fatty acid esters and, therefore, formed self-assembled monolayers upon spreading an organic solution at the air–water interface in a Langmuir trough (Figure 14).

**Figure 13:** Reagents and conditions: (a) 4-tritylphenol, EDCI, DPTS, DCM/toluene; (b) AgNO$_3$, NBS, MeCN; (c) 1,4-bis(trimethylsilyl)buta-1,3-diyne, MeLi · LiBr, ZnCl$_2$, PdCl$_2$(dppf) · DCM, THF/toluene; (d) AgF, NBS, MeCN; then 1-trimethylsilyloctadeca-1,3,5-triyne, MeLi · LiBr, ZnCl$_2$, PdCl$_2$(dppf) · DCM, THF/toluene; and (e) NaOMe, DCM, MeOH. Preparation of methyl ester hexayne amphiphiles starting from 1-hexynoic acid [124].

The self-assembled monolayer featured a dense packing of the hexayne moieties, which consisted of a less than 7 Å thick carbon-only sublayer. Moreover, the investigations showed that multiple of the $sp$-hybridized carbon atoms of adjacent hexayne moieties were at a reactive distance. UV irradiation at room temperature was sufficient to induce the conversion of the monolayer of aggregated molecules into a self-supporting carbon nanosheet with a thickness of 1.9 nm and lateral dimensions on the order of centimeters, that is, under preservation of the monolayer morphology and chemical functionalization. The carbon microstructure that resembled the one of graphene obtained by reduction of graphene oxide featured an $sp^2$-hybridized carbon content of 85%. This is plausible for hexayne precursors in which two of the twelve acetylene carbons remain covalently linked to the substituents and must hence become tetrahedral defects that, due to the structure of the self-assembled precursors, will be homogeneously distributed throughout the carbon nanosheet.

**Figure 14:** Preparation of carbon nanosheets from methyl ester hexayne amphiphiles: (a) structure of the molecular precursor and the compressed monolayer at the air–water interface; (b) Brewster-Angle microscopy image of a ruptured sheet (gray) on water as the sublayer (black); and (c) scanning electron microscopy image of a carbon nanosheet showing the edge of the carbon nanosheet [124].

**7 Conclusions and Outlook**

Molecules rich in $sp$-hybridized carbons represent an attractive platform to access carbon nanomaterials through cross-linking by UV irradiation or other mild stimuli. Although the preparation of (asymmetric) oligynes remains challenging, it is possible to include a wide range of chemical functional groups into the precursor molecules. Hence, the presented approaches employing mild carbonization conditions constitute an interesting alternative to the largely established pyrolytic methods that employ temperatures above 600°C. Exploiting the high reactivity of the precursors allows to control the chemical functionality of the carbon structure through the predefined chemical functional groups in the precursor molecules. Along these lines, promising...
strategies to further improve the stability of oligoynes through host–guest interactions could be accompanied by control of the supramolecular arrangement of the oligoynes. It is important to point out that the self-assembly of the oligoynes into an ordered arrangement is required to achieve a control over the morphology of the carbon nanomaterials. Since the carbonization proceeds under mild conditions, a variety of interfaces can serve as soft templates, which further facilitates the access to carbon nanomaterials, since chemical etching for the removal of a hard template is no longer necessary. In this context, we conceive templating by, for example, covalent organic frameworks, nonspherical colloids and double emulsions to be highly attractive approaches for the preparation of novel carbon nanostructures and nanomaterials from oligoynes precursors.

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