

Synthesis, Structure and Thermal Properties of Copper and Silver Polyynides and Acetylides

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Received: 11 February 2007 / Accepted: 21 May 2007 / Published online: 19 June 2007
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Abstract Polyynes or oligoynes having general formula $H-(C\equiv C)_n-H$ with $n = 1, 2, 3, 4, \dots$, are a class of molecules that has become easily accessible in recent years due to new synthetic approaches. These molecules form copper and silver salts, which have been called, respectively, Cu-polyynides and Ag-polyynides. Here we show the synthesis of these salts and discuss their FT-IR spectra and thermal behaviour, which is studied by Differential Scanning Calorimetry (DSC). These properties are compared to the spectra and thermal behaviour of Cu_2C_2 and Ag_2C_2 . It is shown that Cu_2C_2 can be oxidized to Cu-polyynides thereby losing its original structure and becoming a polymeric coordinative structure. The structural changes make Cu-polyynides no more explosive than the parent Cu_2C_2 . Similarly, Ag-polyynides, which decompose exothermally when heated, are not explosive compared to Ag_2C_2 . The explosive decomposition of Cu_2C_2 occurs at 127 °C (DSC) whereas Ag_2C_2 decomposes explosively at 169 °C under the same conditions. Conversely, Cu-polyynides, when heated in the DSC, show a broad exothermal peak at about 243 °C. Ag-polyynides decompose near 94 °C and the release of energy is sufficiently gradual that no explosion is detected.

Keywords Polyynes · Copper polyynides · Silver polyynides · Copper acetylide · Silver acetylide ·

Thermal analysis · Thermal stability · Decomposition · Polymeric acetylides · Organometallic polymers

1 Introduction

Polyynes synthesis with laser ablation of carbon materials in solution [1, 2] or with the submerged electric carbon arc [3–5] has opened the way to easy access to these exotic molecules in solution. Although polyynes are stable only in solution, they form insoluble complexes with Cu(I) and Ag(I) ions. These copper or silver polyynides can be described by the general formula, $Me-(C\equiv C)_n-Me$ with $n = 1, 2, 3, 4, \dots$ and with $Me = Cu$ or Ag . They are expected to be highly unstable as the free polyyne chains or the parent compounds, dicopper or disilver acetylides. However, little attention has been dedicated to the study of the structure and particularly to the thermal stability of polyynides. The present paper is devoted to the investigation of the thermal stability and the chemical structure of copper and silver polyynides.

The ability of polyynes to form copper derivatives was recognized in earlier works on polyyne synthesis using a submerged carbon arc [3, 5] or the modified Glaser synthesis [6, 7]. These materials were shown to consist of hydrogen-terminated acetylenic carbon chains. Oxidation of dicopper acetylide is thus an important step toward the chemical synthesis of polyynes; this aspect has been pointed out also in our earlier studies on the synthesis of oligoynes and carbonyl structures [8–11].

Although the chemical structures of dicopper acetylide and disilver acetylide have been known for some time, their chemical transformation into metal polyynides and the structure of the resulting polyynides have received little attention. Furthermore, surface enhanced Raman

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spectroscopy (SERS) [12] has been proven to be a powerful tool in the detection and study of polyynes in solution [13–17]. The SERS technique involves just the interaction of metal particles (typically silver colloidal particles) with polyynes. Therefore, the study of the structure of copper and silver polyynides may be of interest as a verification of the SERS effect.

Polyynes are carbon chains, which can be regarded as true one-dimensional systems and carbon nanowires. Quantum confinement effects are expected in such systems and it is thought that such an effect may find application in nanoelectronic and optical devices. Recently, it has been reported that inclusion compounds of polyynes chains, considered as nanowire models, may be synthesized within carbon nanotubes [18, 19] and that such carbon nanowires may be prepared directly from dicopper acetylide [20]. Moreover, long polyynes chains have been stabilized, and even crystallized, using bulky organometallic end groups [21].

The present work describes the synthesis and thermal properties of dicopper acetylide in comparison to dicopper polyynides and about the analogous silver derivatives.

2 Experimental

2.1 Materials and Equipment

All reagents used, including CuCl, CuI, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and AgNO_3 , were obtained from Fluka or Riedel de Haen and used as received. Acetylene was generated from calcium carbide and water. CaC_2 was obtained from Aldrich. The FT-IR spectra were obtained with a Nicolet IR300 spectrometer from Thermo-Electron. The samples were analyzed in the transmittance mode as KBr pellets or using the horizontal attenuated total reflectance (HATR) mode in a ZnSe plate. Differential scanning calorimetry (DSC) was performed with a Linseis calorimeter model L63 on small samples (1 mg or less) sealed in aluminium crucibles. The heating rate was 5 °C/min in static air. HPLC analysis was performed with an Agilent Technology model 1100 liquid chromatograph equipped with a diode-array detector operating under isocratic conditions. A mixture $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 80/20 vol/vol was used as the mobile phase through a C-8 column. Further details for the chromatographic separation of polyynes are reported elsewhere [5].

2.2 Synthesis of Dicopper Acetylide Cu_2C_2 with Very Low Cu^{2+} Content

Copper(I) iodide (CuI, 6.6 g) was dissolved in 30% aqueous ammonia (100 ml) and distilled water (200 ml) in presence of hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$,

5.6 g). A slow stream of acetylene was bubbled in the solution, which was kept in a large Drechsel bottle. Acetylene was generated in a separated flask from CaC_2 and water. A reddish-brown precipitate of dicopper acetylide (Cu_2C_2) was obtained quantitatively and was collected by filtration under reduced pressure to avoid complete drying of the collected precipitate. CAUTION! IT IS MANDATORY TO KEEP THE ACETYLIDE MOISTENED WITH WATER OTHERWISE IT BECOMES EXPLOSIVE WHEN DRIED. We strongly suggest working with only minimal amounts of this material. The acid hydrolysis of this freshly prepared product yields acetylene as the main product. Polyynes were detected by HPLC in trace amounts [F. Cataldo, unpublished data].

2.3 Ageing in Air of Cu_2C_2 Samples: Formation of Cu-polyynides

Small quantities (~0.5–1 mg) of Cu_2C_2 were placed in a series of open aluminium crucibles for DSC. The first sample was heated in the DSC within a few hours of preparation. An explosive decomposition occurred at 127 °C. Another sample, left in air for about one month, decomposed in the DSC at 192 °C and exhibited reduced explosive behavior. Ageing the material in air for one year appears to change the nature of Cu_2C_2 so that it is not explosive. The decomposition by DSC of the year-aged material occurred at 218–238 °C. Acid hydrolysis of this product yields a mixture of polyynes, which have been separated and identified by HPLC [5–7]. If the Cu_2C_2 sample is kept in an hermetically sealed crucible, the material remains explosive but the decomposition exothermal peak is less intense and is shifted at 146 °C.

2.4 Oxidation of Cu_2C_2 with H_2O_2 : Preparation of Cu-polyynides

Cu_2C_2 oxidation can be performed also in aqueous ammonia with hydrogen peroxide. The same products that are obtained after one year ageing in air can also be obtained in few minutes by H_2O_2 oxidation. For example, a freshly prepared Cu_2C_2 sample (~4.0 g) was placed in a conical flask immersed in a water bath and dispersed by stirring with distilled water (200 ml) and 30% ammonia solution (100 ml). While stirring, dilute hydrogen peroxide (~50 ml; 10% in water) was added dropwise to the solution. The H_2O_2 decomposition was evident by the evolution of O_2 . In addition, the Cu_2C_2 turned from reddish to black, indicating the release free Cu^{2+} ions, which turned blue owing to aqueous ammonia. The oxidized Cu_2C_2 was recovered by filtration as a black mass in 0.7 g yield. The oxidized material was no longer explosive in the DSC.

Acid hydrolysis of the product yields a mixture of polyynes that were separated and identified by HPLC [5–7].

2.5 Synthesis of Cu_2C_2 in an Oxidized State in Presence of High Levels of Cu^{2+} Ions: Preparation of Cu-polyynides

We reported above the synthesis of Cu_2C_2 from a Cu(I) salt in presence of a reducing agent so that the acetylide formed was completely in the reduced form. Here we report the preparation of Cu_2C_2 that is oxidized in situ by the presence of Cu(II) ions in solution. Thus, CuCl (2.5 g) was dissolved with of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (5.0 g) in demineralized water (90 ml) and aqueous ammonia (50 ml of 30% solution). An acetylene stream was bubbled into the blue solution producing a dark brown precipitate. About 2 g of wet precipitate were collected by filtration. The thermal behaviour of the product by DSC was identical to the H_2O_2 oxidation product. The acid hydrolysis of this product yielded a mixture of polyynes that were separated and identified by HPLC [5–7].

2.6 Synthesis of Silver Acetylide Ag_2C_2

Silver acetylide was prepared by passing an acetylene stream into a solution containing AgNO_3 (1.25 g) in demineralized water (18 ml) and aqueous ammonia (14 ml of 30% solution). A grey precipitate was collected by filtration; CAUTION! THE PRODUCT IS EXPLOSIVE AND MUST REMAIN HIGHLY MOISTENED WITH WATER. In order to minimize the risks of explosion, we strongly suggest working with minimal amount of this material. The freshly prepared Ag_2C_2 decomposes explosively in the DSC; decomposition occurs at 169 °C. As with other silver salts, Ag_2C_2 is photosensitive and darkens when exposed to direct light. The acid hydrolysis of Ag_2C_2 produces exclusively acetylene. No polyynes were detected by HPLC [F. Cataldo, unpublished data].

2.7 Direct Synthesis of Ag-polyynides

A mixture of polyynes in hexane solution was prepared as follows [6, 7]: CuCl (5.2 g) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (10.3 g) were dissolved in demineralized water (200 ml) in presence of NH_4Cl (7.2 g). CaC_2 (12 g) was decomposed directly in the solution generating acetylene in situ thereby producing polyynes from the oxidized copper acetylide. After complete decomposition of CaC_2 and cooling, n-hexane (50 ml) was added. The Cu-polyynides formed were decomposed by the addition of aqueous HCl (50 ml, 37%) and the free polyynes mixture was collected in n-hexane.

The n-hexane solution of polyynes was shook with aqueous AgNO_3 (1.25 g dissolved in 15 ml demineralized water) and aqueous ammonia solution (15 ml, 30%). The polyynes precipitate from the solution as deep yellow silver polyynides. The silver polyynides were collected by filtration and left moistened with water. The material is photosensitive and darkens to grey on standing. Acid hydrolysis of this product yields a mixture of polyynes that were separated and identified by HPLC [F. Cataldo, unpublished data].

The DSC indicates that the silver polyynides decompose at 92 °C with an exothermal, but not violent, reaction; the decomposition might be mitigated by the presence of water. Another exothermal transition is observed at 250 °C.

2.8 Synthesis of Ag-polyynides by an Exchange Reaction between Cu-polyynides and AgNO_3

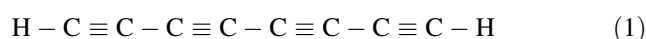
Copper polyynides (1.5 g, wet) prepared as described above were treated with aqueous AgNO_3 (4%) in aqueous ammonia (15%). The dark-brown copper polyynides changed rapidly to grey. Copper ions were released in the ammonia solution as indicated by a deep blue color and were seemingly replaced by silver ions. Acid hydrolysis of this product yields a mixture of polyynes that were separated and identified by HPLC [F. Cataldo, unpublished data].

3 Results and Discussion

3.1 General Aspects about Copper and Silver Acetylides and Polyynides

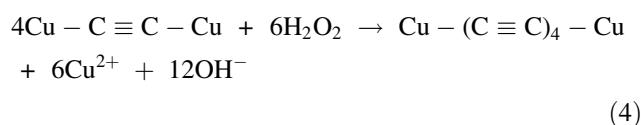
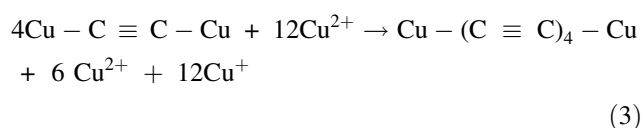
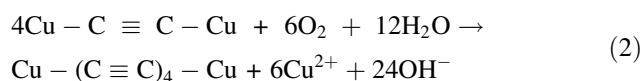
The general properties of dicopper and disilver acetylides are reported in comprehensive reviews and fundamental papers [22–27]. These compounds have been known for a long time [23–25, 27]. Their instability and explosion risk, which is associated to improper handling, have hindered investigation into their thermal properties. Furthermore, easy access to long chain polyynes; e.g., $\text{H}-(\text{C}\equiv\text{C})_n-\text{H}$ with $n = 1, 2, 3, 4, \dots$, has permitted us to obtain directly copper and silver derivatives; i.e., copper and silver polyynides [5], where the terminal acetylenic hydrogen atoms are replaced with Cu or Ag. We will report below the thermal properties of Cu and Ag acetylides and compare them to the polyynides.

Irrespective to the synthetic pathway used, e.g. laser ablation, carbon arc or modified Glaser synthesis, the predominant polyyne chain in the resulting mixtures of chains is always C_8H_2 (1) [5]:



Depending on the synthetic conditions, C_8H_2 may represent up to 80 mol% of the total mixture of polyynes [5–7]; i.e., C_6H_2 , $C_{10}H_2$ and $C_{12}H_2$ the other detectable components. By liquid chromatographic analysis chains up to $C_{18}H_2$ have been detected but their concentration in the polyynes mixture are negligible [5–7]. Therefore, although in the present paper we discuss copper and silver polyynides, we are essentially dealing with the silver and copper derivatives of a mixture of C_8 , C_6 , C_{10} and C_{12} carbon chains with C_8 by far the most important component.

There is also an intriguing and subtle connection between acetylides and polyynides. In particular, dicopper acetylide and dicopper polyynide: for example, dicopper acetylide can be transformed into polyynides under a variety of oxidizing conditions that may be represented schematically as follows:

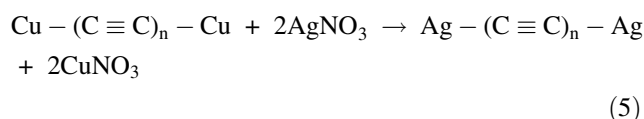


Oxidizing agents such as oxygen from air (2), Cu(II) ions (3), or hydrogen peroxide (4) catalyze the Glaser coupling reaction between acetylide units. These reactions cause the growth of longer chains and release of Cu^{2+} , which in their turn may act as further oxidants. The stoichiometry of (3) is not mandatory because the reaction in air occurs simultaneously to reaction (2). Under these circumstances the Glaser coupling reaction is also known as the Hay coupling reaction [28]. The mechanism of the Glaser coupling reaction is rather complex and has been discussed elsewhere [29].

It has been shown [8–10] that ageing of Cu_2C_2 in the solid state in humid air leads to spontaneous Glaser coupling with the formation of dicopper polyynides. In fact acid hydrolysis of aged Cu_2C_2 permits the collection of a mixture of hydrogen-terminated polyynes [8–10].

When acetylene is passed into a solution of CuCl (or other Cu(I) salt) in aqueous ammonia in the presence of a reducing agent such as NH_2OH or H_2N-NH_2 , dicopper acetylide formation is maximized and polyne formation as by-products is suppressed [8–10]. However, when the reducing agent is absent and/or if oxygen is present, the

formation of Cu_2C_2 is accompanied by a substantial formation of dicopper polyynides [5–7]. The formation of dicopper polyynides can be maximized when acetylene is passed into a solution containing a mixture of Cu^+/Cu^{2+} ions. Under these circumstances dicopper polyynides are formed as a consequence of the in situ oxidation of the acetylide. The formation of polyynes is, instead, negligible when acetylene is passed into an aqueous ammonia solution of $AgNO_3$ without the need of any reducing agent and in presence of air. The key point is that Ag^+ is stable in aqueous solution in contrast to Cu^+ , which is easily oxidized to Cu^{2+} . Thus, the disilver polyynides are more easily prepared by an exchange reaction from dicopper polyynides in aqueous ammonia (5):



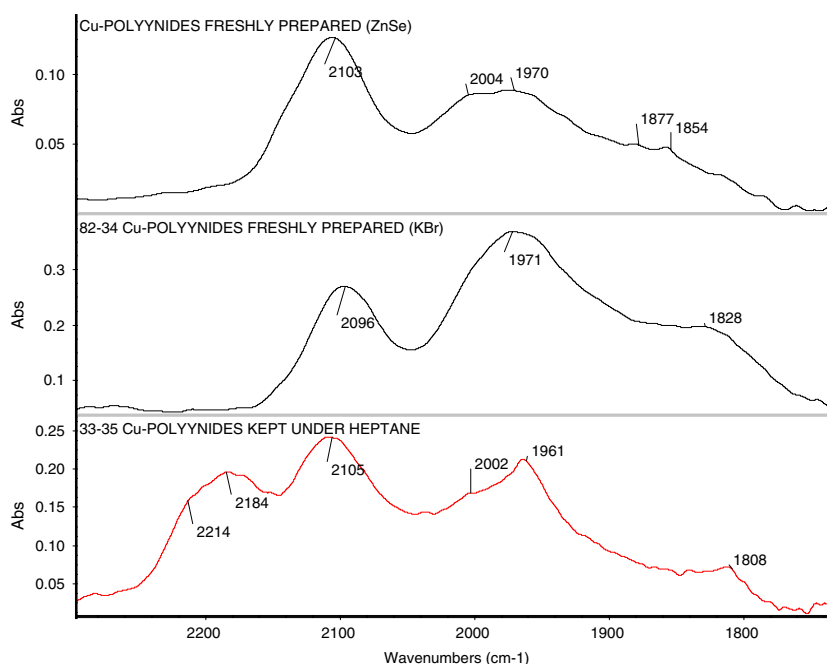
Ag-polyynides can also be prepared by stirring a polyynes mixture in n-hexane with $AgNO_3$ in aqueous ammonia. Similarly, the Ilosvay's reagent; i.e., CuCl in aqueous ammonia, precipitates dicopper polyynides from an n-hexane solution [3–5].

3.2 Infrared Spectra of Cu and Ag Polyynides and their Polymeric Nature

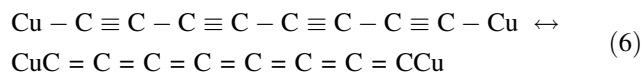
The infrared spectrum of dicopper acetylide is characterized by the complete absence of the typical triple bond stretching band at about 2200 cm^{-1} . This fact has been verified recently [8, 9] but has been known for some time [22]. This absorption band is usually very weak or not detectable for symmetry reasons; i.e., symmetrically disubstituted acetylenes in many cases do not display the triple bond stretching band [30]. On standing in humid air, dicopper acetylide is converted into copper polyynides and gradually shows up a series of bands in the triple bond stretching region [8–10].

The FT-IR spectra (Fig. 1) display the bands due to Cu-polyynides. There are small differences between the spectrum taken in transmittance mode in KBr and that obtained from a sample on a ZnSe plate in reflectance mode. However, both Cu-polyynides spectra are characterized by two main bands; one at about 2100 cm^{-1} and one at 1970 cm^{-1} , which is broader with a shoulder at 2004 cm^{-1} . The shoulder is more pronounced when the spectrum is recorded in reflectance. The band at higher frequency is definitely due to the symmetric $\nu_{C\equiv C}$, while the shoulder at 2004 cm^{-1} has been assigned to the asymmetric triple bond stretching. The triple bonds of metal acetylides are also known to have partial cumulenyl character and

Fig. 1 FT-IR spectra of Cu-polyynides. The top two spectra refer to freshly prepared Cu-polyynides, respectively, recorded in reflectance mode on ZnSe plate and in transmittance mode on KBr pellet. The bottom spectrum is that of aged Cu-polyynides preserved under n-hexane



limiting resonance structures as in (6) where Cu(I) and Cu(II) are simultaneously present [22].



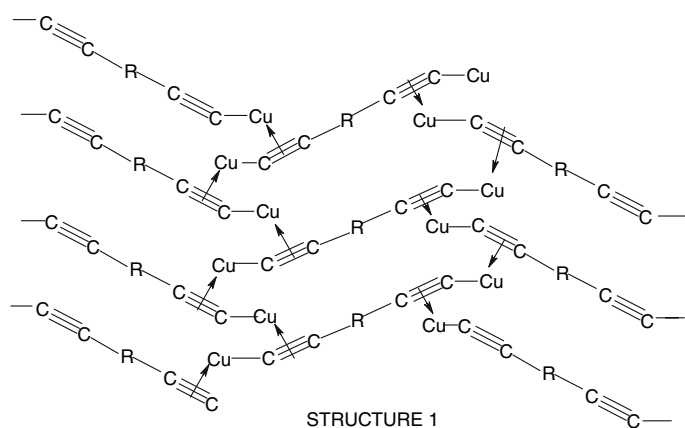
Regarding the cumulenic resonance structure, the formation of copper salts from acetylenic compounds implies a significant shift of the triple bond stretching frequency of the free acetylene group to lower wavenumbers on copper substitution [8–10, 22]. Therefore, the absorption band at 1970 cm^{-1} may be attributed to the cumulenic structure. This shift is due to the reduction of the bond order in the acetylenic groups as indicated in (6) [22].

Aged Cu polyynides show an additional infrared band at 2184 cm^{-1} accompanied by a shoulder at 2214 cm^{-1} (Fig. 1, bottom). This band has been observed in highly oxidized copper-depleted polyynes samples [9, 10] in carbonaceous matter containing carbynoid structures; i.e., a relatively high level of sp-hybridized carbon atoms after an extensive Glaser coupling reaction in solution [11, 31]. A band at 2184 cm^{-1} has also been observed in polyynes chain segments produced with a dehalogenation reaction of chlorinated paraffin [32] and in the carbonaceous products derived from the thermal decomposition of Cu_2C_2 and Cu_2C_4 [9, 10] or diiodoacetylene [33]. All the spectra in Fig. 1 also show a band, or a shoulder, below 1900 cm^{-1} . Fresh Cu-polyynides in reflectance mode show bands at 1877, 1854 and 1820 cm^{-1} ; however, in transmittance only a band at 1828 cm^{-1} is clearly distinguishable. For the aged Cu-polyynides sample, this band is shifted to 1808 cm^{-1} .

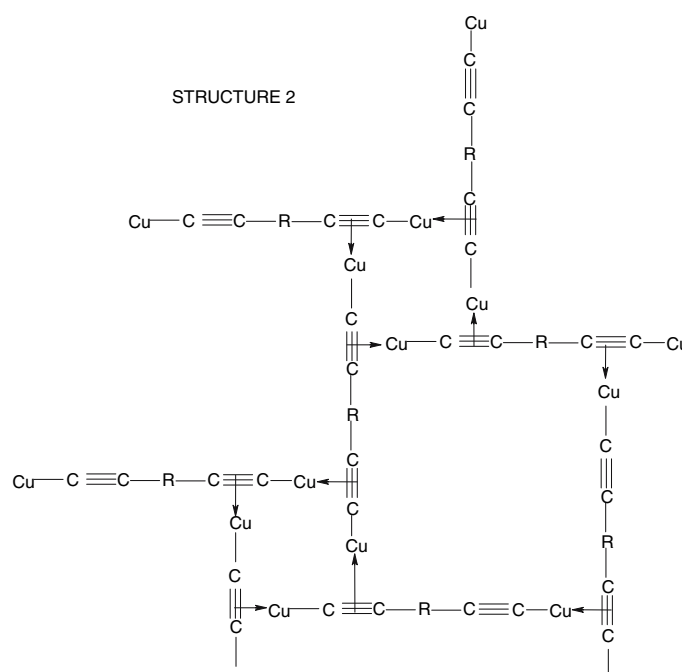
It has been reported that Cu_2C_2 has a crystalline structure similar to CaC_2 , as suggested by X-ray diffractometry [23]. However, no further confirmation of this result has been reported in literature. Whatever the initial structure of Cu_2C_2 , its oxidation to Cu-polyynides implies the growth of polyne chains and the deletion of the original structure. Practically all the copper salts of monosubstituted acetylenes have a polymeric structure [22] where copper atoms are directly linked to carbon atoms at the end of the acetylenic group, but are also coordinately bonded to the triple bonds of adjacent acetylenic groups. Very nice and complex polymeric structures have been determined by X-ray diffraction, for instance, in the case of copper phenylacetylide [22] or gold phenylacetylide [34] and t-butylacetylide [35]. Since polyynes can be viewed as rigid and almost linear carbon rods having reactive heads and tails with copper ions, they should be able to form polymeric structures completely analogous to that obtained for phenylacetylene and t-butylacetylene organometallic complexes.

Scheme 1 (Structure 1) suggests the possible structure of Cu-polyynide using, as reference, the known structure of copper phenylacetylide [22]. The carbon chains are staked together at an angle and the chains are connected to each other through coordination involving the copper end groups. Alternatively, other structures for Cu-polyynides can be proposed. For example, Scheme 2 (Structure 2) can be conceived using the principle of the coordinate interaction between copper atoms and the triple bonds found for gold t-butylacetylide [35]. The infrared absorption bands at $1850\text{--}1800 \text{ cm}^{-1}$ in copper derivatives of acetylenic compounds have been attributed to the formation of π -com-

Scheme 1 Possible chemical structure of Cu-polyynide. This structure has been designed with analogy to the structure of Cu-phenylacetylide. The radical R means any polyynide segment of any length



Scheme 2 Another possible structure of Cu-polyynide. This time the structure has been designed by analogy with that of Au-t-butylacetylide. The radical R means any polyynide segment of any length



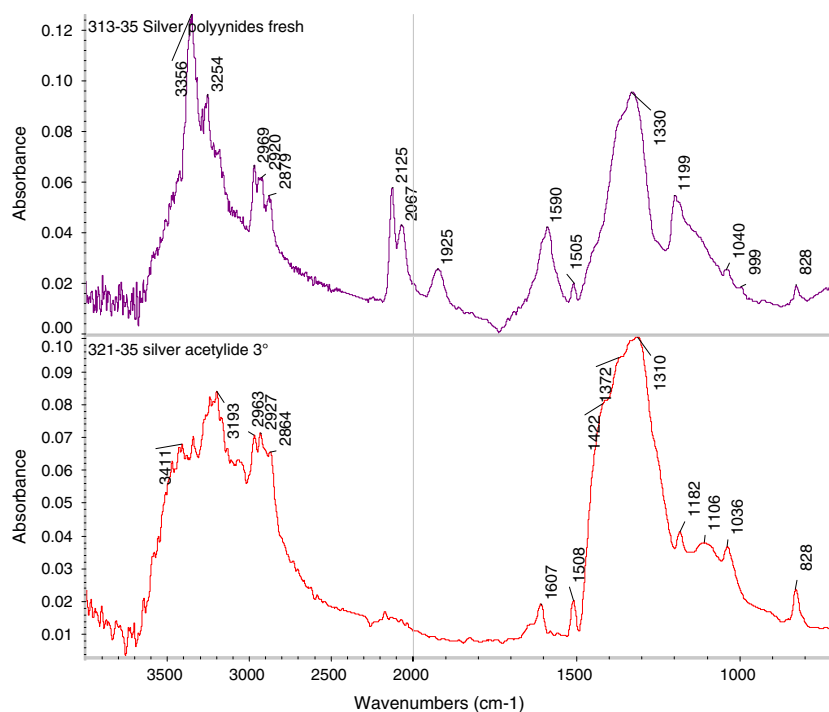
plexes between copper and the acetylenic triple bonds [22]. Therefore, the presence of these infrared bands in Cu-polyynides (Fig. 1) represents experimental evidence for the polymeric nature of these molecules as in copper phenylacetylides and similar compounds [22]. Another indication of the polymeric nature of these materials is the incomplete solubility of the compounds in any common solvent.

Figure 2 shows the FT-IR spectrum of silver acetylide. This compound also does not display a well-defined triple bond stretching band. However, the spectrum of silver polyynides (Fig. 2) shows two bands at 2125 and 2067 cm^{-1} , respectively, due to symmetric and asymmetric $\nu_{\text{C}\equiv\text{C}}$. In this case an additional band appears in the cumulenenic stretching region at 1925 cm^{-1} . Perhaps (6) applies also to silver polyynides and cumulenenic resonance occurs. On this

basis, a polymeric structure for Ag-polyynides is suggested as with Cu-polyynides.

Raman spectroscopy of hydrogen-terminated polyynes in solution reveals a weak band at 2170 cm^{-1} while calculation for the most abundant polyynide, C_8H_2 , suggests two bands at 2182 and 2107 cm^{-1} (13,14). Surface enhanced Raman spectroscopy (SERS) in the presence of colloidal silver particles shows two strong bands at 2040 and 1975 cm^{-1} . It is curious that these two bands, which are detected by Raman SERS, are shifted to lower frequencies (85 and 92 cm^{-1} , respectively) compared to the FT-IR bands of the Ag-polyynides. This confirms that Raman SERS is a physical surface phenomenon effect and should not imply the formation of chemical bonds with the silver particles. Further work on this matter is in progress.

Fig. 2 FT-IR spectra of Ag-polyynides (top) and silver acetylide (bottom)



3.3 Thermal Analysis of Cu-polyynides by DSC; a Comparison with Cu_2C_2

The thermal stability and decomposition temperature of Cu_2C_2 and Ag_2C_2 until now have not been investigated by differential scanning calorimetry (DSC). Moreover, nothing is known about the thermal stability of Cu-polyynides and Ag-polyynides, which are supposed to be as hazardous, more explosive, and unstable as the parent acetylides.

Freshly prepared Cu_2C_2 decomposes explosively at 127 °C (sharp exothermal peak in Fig. 3). The decomposition enthalpy of -1225 J/g is only an approximate, lower limit value because the weight of the sample at the beginning of the DSC test included also an unknown amount of water. If the Cu_2C_2 decomposition occurs in air, the decomposition products are disordered elemental carbon that contains a mixture of sp , sp^2 and sp^3 hybridized carbon atoms, disordered graphite, Cu_2O , and some CuO [10, 24]. The Cu_2C_2 decomposition in vacuum occurs at much higher temperature (265 °C) [24] and the products are highly disordered elemental carbon with a detectable fraction of sp hybridized carbon atoms (carbynoid structures) mixed with other forms of carbon and Cu_2O [10].

One-year storage of a Cu_2C_2 sample in a closed flask under water indicates a minimum of oxidation and hence minimal Glaser-type oxidative coupling in the solid state. The product is well-preserved since the DSC shows only an increase in the decomposition point that appears at 146 °C as a sharp exothermal transition (explosive decomposition), which is identical in shape to that shown in Fig. 3.

In humid air Cu_2C_2 oxidizes gradually leading to a mixture of Cu-polyynides having a polymeric structure comparable to those described in Schemes 1 and 2. The consequence of the oxidation and coupling reaction is the alteration and then the complete disappearance of the original Cu_2C_2 structure as discussed previously. The importance of this fact can be observed in Fig. 4 where the decomposition of an oxidized Cu_2C_2 sample, aged in air for one month, is shown. The decomposition temperature occurs at 192 °C and the exothermal peak appears broadened relative to the sharp transition of Fig. 3, and is accompanied by another even broader exothermal transition at 229 °C. Thus, under these conditions, the decomposition energy is released in two stages and more gradually than in the case of fresh Cu_2C_2 resulting in non-explosive decomposition. An explosion implies a sudden release of energy and matter in a very short time period. These conditions do not apply in the case of the sample reported in Fig. 4, although the approximate energy released exceeds the value for a pure Cu_2C_2 sample; i.e., -2400 J/g .

One-year ageing of Cu_2C_2 in humid air leads to complete oxidation to Cu-polyynides. Figure 5 shows an extremely broad exothermal transition with two peaks at 218 °C and 239 °C. Another broad transition appears at lower temperature (139 °C) and has been attributed to the shorter Cu-polyynides chains. This transition suggests a relatively slow release of the energy.

The oxidation of Cu_2C_2 to Cu-polyynides can be achieved in several minutes by oxidizing Cu_2C_2 with H_2O_2 or with Cu^{2+} ions (see Experimental). As expected the

Fig. 3 DSC of freshly prepared Cu_2C_2 scanned at $5^\circ\text{C}/\text{min}$ in air. Note the sharp exothermal transition at about 127°C , which corresponds to explosive decomposition

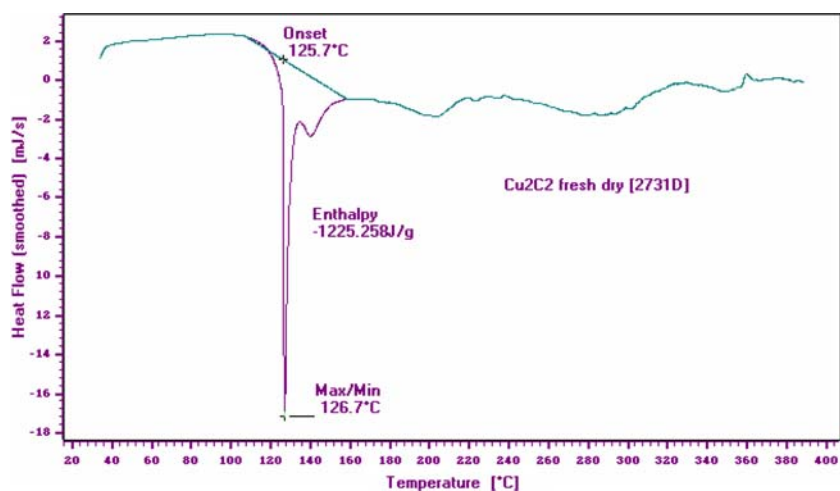


Fig. 4 DSC of aged Cu_2C_2 exposed to humid air for about one month. The exothermal decomposition, which is shifted to higher temperatures (192°C), broadens and is accompanied by an additional transition at 228°C

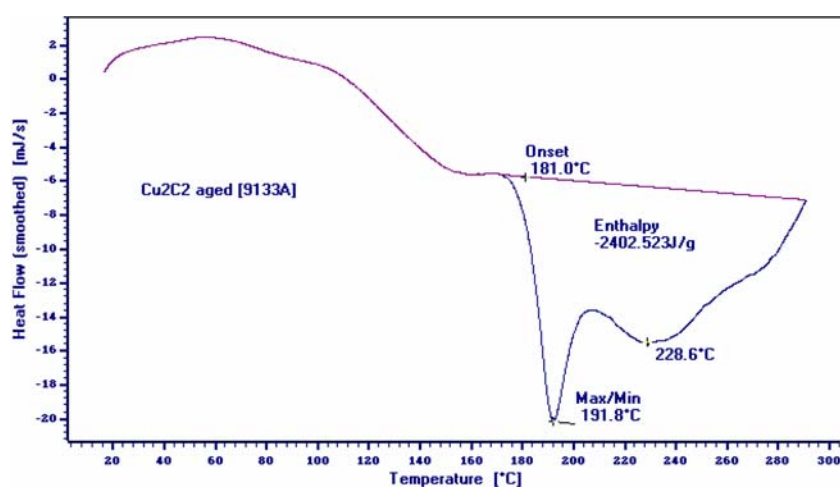
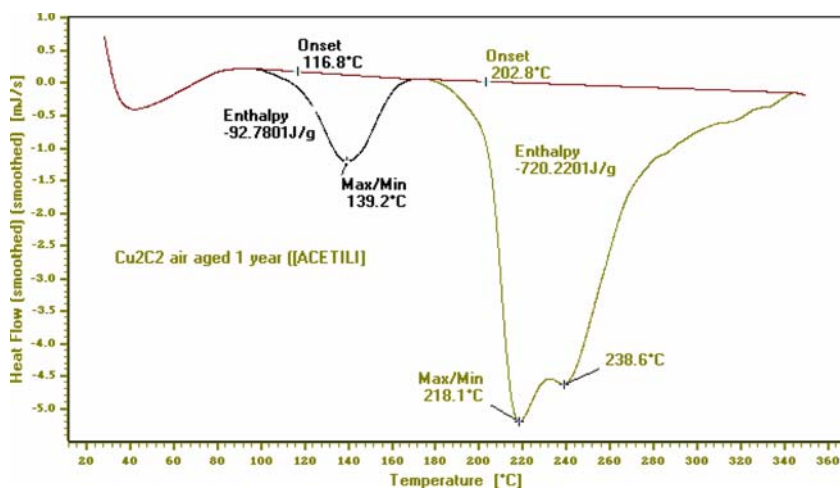


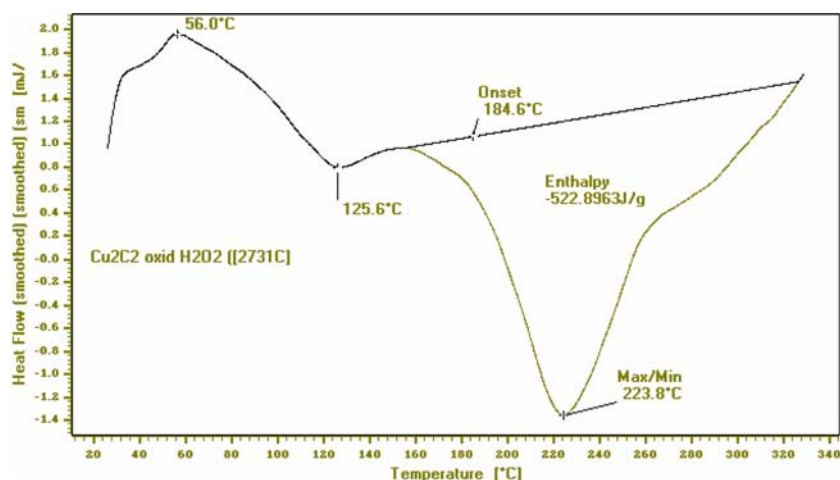
Fig. 5 DSC of Cu_2C_2 after one year of ageing in air. The sample appears to involve inhomogeneous oxidation. Shorter chains show a transition at 139°C (similar to the value found in Fig. 2), while longer polynides chains show the exothermal decomposition at 218°C and 238°C . No explosion was detected



resulting product shows a DSC trace that is very similar to the air-oxidized Cu_2C_2 after one year (compare Fig. 6 with Fig. 5). Figure 6 refers to a sample of Cu_2C_2 oxidized by H_2O_2 ; however, oxidation with Cu^{2+} yields a product with

the same thermal behaviour and a very broad exothermal peak at 224°C with minor sub-features at 126°C . Thus, the DSC, which is consistent with UV, infrared [8–10], Raman, and NMR spectroscopy [11a–11c], and HPLC [5–

Fig. 6 Cu_2C_2 can be oxidized with a treatment with H_2O_2 . This treatment is an accelerated “ageing” and is similar ageing in air for several months. A broad exothermal transition is observed at 224 °C. There is also a transition at about 126 °C, which indicates the presence of less oxidized product



7], demonstrates that Cu_2C_2 is transformed into a mixture of Cu-polyynides.

Cu-polyynides can also be prepared by direct synthesis by treating a hexane solution of a mixture of polyynes with Ilosvay’s reagent [3–5]. The DSC of Cu-polyynides prepared in this manner is shown in Fig. 7. Again, a broad exothermal peak is observed at 243 °C with exothermal sub-features at 108 °C and 183 °C. There is an analogy with the thermal behaviour of the samples reported in Fig. 5 and 6. The slight differences can be attributed to the effects of residual water and solvents in the samples and with differences in the distribution of the Cu-polyynides chains, which vary according to the synthetic route used.

The fact that Cu-polyynides are not explosive in thermal decomposition is consistent with the polymeric structure of these compounds. Relatively long polyne chains, when coordinated by copper in the polymeric structures (Schemes 1 or 2) are stabilized and, therefore, not explosive. Probably the polyynes chains due to their high number of conjugated triple bonds have also a more coordinative ability than that exerted acetylene or diacet-

ylene and this surely contributes to the thermal stability of the resulting materials.

3.4 DSC of Ag-polyynides compared to Ag_2C_2

McCowan [26] has reported that Ag_2C_2 explodes within 5–10 s when heated to 195–200 °C. We have shown by DSC (Fig. 8) that the decomposition of Ag_2C_2 occurs at 169 °C with a sharp exothermal transition. The released heat for Ag_2C_2 is 1070 J/g, which is similar to that for Cu_2C_2 (1225 J/g). The values of released heat should only be taken as indicative values because both Ag_2C_2 and Cu_2C_2 were moistened with water to reduce the risk of explosion in the DSC experiment.

Ag-polyynides are not explosive when heated in the DSC in static air. Figure 9 shows the DSC trace of a sample of Ag-polyynides, which decompose exothermally and surprisingly at a much lower temperature than Ag_2C_2 . Figure 9 also shows a decomposition peak at 94 °C. This peak appears broadened relative to the decomposition of Ag_2C_2 ; therefore, the decomposition energy of Ag-poly-

Fig. 7 Cu-polyynides ageing involves almost complete disappearance of the low temperature transition and a broadening and shift to higher temperature of the exothermal transition, which now appears at 243 °C

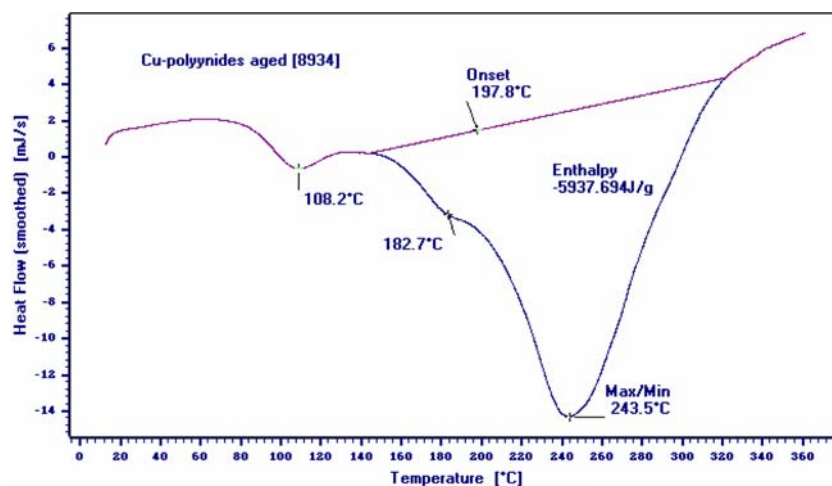


Fig. 8 DSC of pure Ag_2C_2 . Freshly prepared Ag_2C_2 is explosive as it is fresh Cu_2C_2 ; however, exothermal decomposition occurs at 169 °C, hence at higher temperatures than Cu_2C_2 , which decomposes at 127 °C (see Fig. 1)

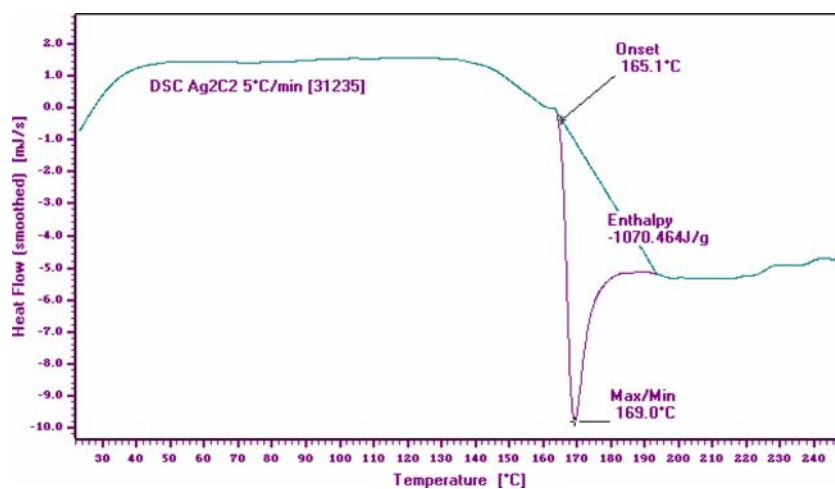
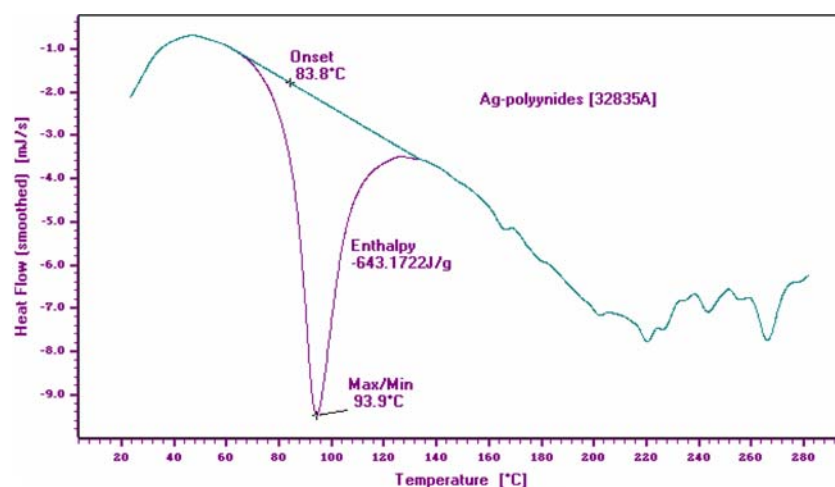


Fig. 9 DSC of Ag-polyynides prepared by treating free polyynes with AgNO_3 in aqueous ammonia



nides is released more gradually than for Ag_2C_2 and the total enthalpy for the former is about half the value.

4 Conclusions

Cu-polyynides and Ag-polyynides can be prepared by stirring a hexane solution of polyynes with an aqueous ammonia solution of a Cu(I) salt or AgNO_3 . Cu-polyynides are also prepared by oxidation of Cu_2C_2 in humid air in the solid state or in aqueous solutions using Cu^{2+} ions or H_2O_2 . The FT-IR spectra and DSC clearly show that Cu-polyynides produced from polyynes are the same as those obtained from Cu_2C_2 oxidation.

Ag-polyynides cannot be easily derived from Ag_2C_2 , which appears somewhat stable toward oxidation but can be prepared by an exchange reaction from Cu-polyynides with an aqueous ammonia solution of AgNO_3 or directly from free polyynes in hexane and AgNO_3 in aqueous ammonia.

A polymeric coordination structure of Cu-polyynides is suggested for the first time on the basis of the FT-IR spectra, thermal behaviour, insolubility in common solvents, and analogy to other well-known polymeric acetylides. An analogous polymeric structure may be suggested for Ag-polyynides.

For the first time the thermal behaviour of Cu_2C_2 and Ag_2C_2 has been studied by DSC. It was found that the explosive decomposition of Cu_2C_2 occurs at 127 °C while Ag_2C_2 decomposes explosively at 169 °C under the same conditions. The amount of heat released from Cu_2C_2 is comparable to that released by Ag_2C_2 .

For the first time it has been ascertained that Cu-polyynides and Ag-polyynides are not explosive, although they decompose exothermally when heated in the DSC. The release of heat is more gradual in these compounds than in the case of the acetylides. The gradual thermal decomposition has been attributed to their polymeric nature of the material. Cu-polyynides show a broad exothermal peak at about 243 °C, which is a much higher temperature

than the parent Cu_2C_2 . On the other hand Ag-polyynides decompose at 94 °C, a much lower temperature than Ag_2C_2 ; and, the released heat is sufficiently gradual that no explosion is detected.

References

- (a) M. Tsuji, S. Kuboyama, T. Matsuzaki, T. Tsuji, *Carbon* **41**, 2141 (2003); (b) M. Tsuji, S. Kuboyama, T. Tsuji, in *Polyynes: Synthesis, Properties and Applications*, ed. by F. Cataldo (Taylor & Francis Publishing House, CRC Press, Boca Raton, Florida, 2005), Chap. 7
- H. Tabata, M. Fuji, S. Hayashi, *Carbon* **44**, 22 (2006)
- (a) F. Cataldo, *Carbon* **42**, 129 (2004). (b) F. Cataldo, *Carbon* **41**, 2671 (2003)
- (a) F. Cataldo, *Tetrahedron Lett.* **45**, 141 (2004). (b) F. Cataldo, *Tetrahedron* **60**, 4265 (2004). (c) F. Cataldo, *Polyhedron* **23**, 1889 (2004). (d) F. Cataldo, Fullerenes, *Nanot. Carbon Nanostruct.* **12**, 603; 619; 633; 765 (2004). (e) F. Cataldo, Fullerenes, *Nanot. Carbon Nanostruct.* **13**, 21 (2005)
- F. Cataldo, *Polyynes: Synthesis, Properties and Applications* (Taylor & Francis Publishing House, CRC Press, Boca Raton, Florida, 2005), Chap. 8, pp. 18 and 20
- F. Cataldo, *Tetrahedron Lett.* **46**, 3665 (2005)
- F. Cataldo, *Carbon* **43**, 2792 (2005)
- F. Cataldo, *Eur. J. Solid State Inorg. Chem.* **35**, 281 (1998)
- F. Cataldo, *Eur. J. Solid State Inorg. Chem.* **35**, 293 (1998)
- F. Cataldo *Polym. Int.* **48**, 15 (1999)
- (a) F. Cataldo, D. Capitani, *Mater. Chem. Phys.* **59**, 225 (1999). (b) F. Cataldo, *Fullerene Sci. Tech.* **9**, 153 (2001). (c) F. Cataldo, *Carbon* **37**, 161 (1999)
- E. Smith, G. Dent, *Modern Raman Spectroscopy: A Practical Approach*, (J. Wiley & Sons, New York 2005), Chap. 5
- A. Lucotti, M. Tomasini, M. Del Zoppo, C. Castiglioni, G. Zerbi, F. Cataldo, C.S. Casari, A. Li Bassi, V. Russo, M. Bogana, C.E. Bottani, *Chem. Phys. Lett.* **417**, 78 (2006)
- C. S. Casari, V. Russo, A. Li Bassi, C.E. Bottani, F. Cataldo, A. Lucotti, M. Tomasini, M. Del Zoppo, C. Castiglioni, G. Zerbi, *Appl. Phys. Lett.* **90**, 13111 (2007)
- S. Hayashi, T. Konishi, *Japan. J. Appl. Phys.* **44**, 5313 (2005)
- H. Tabata, M. Fujii, S. Hayashi, *Chem. Phys. Lett.* **420**, 166 (2006)
- T. Wakabayashi, H. Tabata, T. Doi, H. Nagayama, K. Okuda, R. Umeda, I. Hisaki, M. Sonoda, Y. Tobe, T. Minematsu, K. Hashimoto, S. Hayashi, *Chem. Phys. Lett.* **433**, 296 (2007)
- X. Zhao, Y. Ando, Y. Liu, J. Makoto, T. Suzuki, *Phys. Rev. Lett.* **90**, 187401 (2003)
- D. Nishide, H. Dohi, T. Wakabayashi, E. Nishibori, S. Aoyagi, M. Ishida, S. Kikuchi, R. Kitaura, T. Sugai, M. Sakata, H. Shinohara, *Chem. Phys. Lett.* **428**, 356 (2006)
- K. Judai, J. Nishijo, N. Nishi, *Adv. Mater.* **18**, 2842 (2006)
- S. Szafert, J. Gladysz, *Chem. Rev.* **103**, 4175 (2003)
- (a) H. Bauer, J. Faust, R. Frobose, J. Fussel, U. Krueker, M. Kunz, H.M. Somer, *Gmelin Handbook of Inorganic Chemistry*, 8th Edition, Cu Organocopper Compounds, Part 4, System Number 60, (Springer-Verlag, Berlin, 1987). (b) *Gmelin Handbuch der Anorganischen Chemie, Kupfer, Teil B, Lieferung 2, System- Nummer 60*, (Verlag Chemie, Weinheim, 1961)
- R. Nast, W. Pfab, *Z. Anorg. Allgem. Chem.* **292**, 287 (1957)
- R. Klement, E. Koddermann-Gros, *Z. Anorg. Allgem. Chem.* **254**, 201 (1947)
- W.C. Easterbrook, J.W. Erskine, *J. Appl. Chem. Suppl.* **1**, S53 (1953)
- R. Keim, H. Bergmann, H. Bitterer, A. Bohne-Neuber, V. Haase, B. Haibel, G. Kirschstein, H.K. Kugler, S. Ruprecht, *Gmelins Handbuch der Anorganischen Chemie, Silber, Teil B3, System- Nummer 61*, (Verlag Chemie, Weinheim, 1973)
- J.D. McCowan, *Trans. Faraday Soc.* **59**, 1860 (1965)
- K. Vatsouro, G. Michtchenko, *Reactions Organiques Clasées par Auteurs* (Mir Editions, Moscow, 1981).
- L. Fomina, B. Vasquez, E. Tkatchouk, S. Fomine, *Tetrahedron* **58**, 6741 (2002)
- M. Avram, G.D. Mateescu, *Infrared Spectroscopy Applications in Organic Chemistry*. (Wiley-Interscience, New York, 1972), p. 196–200
- (a) F. Cataldo, *Polym. Int.* **44**, 191 (1997). (b) F. Cataldo, *Eur. J. Solid State Inorg. Chem.* **34**, 53 (1997)
- (a) F. Cataldo, *J. Mater. Sci.* **35**, 2413 (2000). (b) F. Cataldo, *Angew. Makromol. Chem.* **264**, 65 (1999)
- F. Cataldo, *Fullerene Sci. Tech.* **9**, 525 (2001)
- S.J. Shieh, X. Hong, S.M. Peng, C.M. Che, *J. Chem. Soc. Dalton Trans.* 3067 (1994)
- D.M.P. Mingos, J. Yau, S. Menzer, D.J. Williams, *Angew. Chem. Int. Ed. Engl.* **34**, 1894 (1995)