Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Simple Synthesis of α,ω-Diarylpolyynes Part 1: Diphenylpolyynes

Franco Cataldo[a][b]; Ornella Ursini[c]; Giancarlo Angelini[c]; Matteo Tommasini[d]; Carlo Casari[e][f]
[a] Istituto Nazionale di Astrofisica, Osservatorio Astrofisica di Catania, Catania, Italy [b] Lupi Chemical Research, Rome, Italy [c] Institute of Chemical Methodologies, Rome, Italy [d] Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta" and NEMAS, Center for Nanoengineered Materials and Surfaces, Politecnico di Milano, Milano, Italy [e] Dipartimento di Energia and NEMAS - Center for Nanoengineered Materials and Surfaces, Politecnico di Milano, Milano, Italy [f] Center of Nano Science and Technology of ITT@PoliMI, Milano, Italy

To cite this Article Cataldo, Franco , Ursini, Ornella , Angelini, Giancarlo , Tommasini, Matteo and Casari, Carlo(2010) 'Simple Synthesis of α,ω-Diarylpolyynes Part 1: Diphenylpolyynes', Journal of Macromolecular Science, Part A, 47: 8, 739 — 746

To link to this Article: DOI: 10.1080/10601325.2010.491749

URL: http://dx.doi.org/10.1080/10601325.2010.491749

Journal of Macromolecular Science, Part A: Pure and Applied Chemistry (2010) **47**, 739–746
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2010.491749

Simple Synthesis of α, ω-Diarylpolyynes Part 1: Diphenylpolyynes

FRANCO CATALDO[1,2,*], ORNELLA URSINI[3], GIANCARLO ANGELINI[3], MATTEO TOMMASINI[4]
and CARLO CASARI[5,6]

[1]*Istituto Nazionale di Astrofisica, Osservatorio Astrofisica di Catania, Catania, Italy*
[2]*Lupi Chemical Research, Rome, Italy*
[3]*Institute of Chemical Methodologies, CNR, Monterotondo Stazione, Rome, Italy*
[4]*Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta" and NEMAS, Center for Nanoengineered Materials and Surfaces, Politecnico di Milano, Milano, Italy*
[5]*Dipartimento di Energia and NEMAS – Center for Nanoengineered Materials and Surfaces, Politecnico di Milano, Milano, Italy*
[6]*Center of Nano Science and Technology of ITT@PoliMI, Milano, Italy*

Received, Accepted February 2010

A series of α, ω-diphenylpolyynes were synthesized through the Cadiot Chodkiewicz reaction starting from Cu(I)-phenylacetylide and diiodoacetylene. The complete series of diphenylpolyynes Φ-(C≡C)$_n$-Φ with n = 2,3,4 and 5 was obtained and analyzed by electronic absorption spectroscopy, liquid chromatography (HPLC-diode array) and FT-IR spectroscopy. The diphenylpolyynes when treated with nascent hydrogen produced by the action of HCl on Zn dust are changed into a mixture of diphenylpolyenes as shown by UV spectroscopy and HPLC.

Keywords: Diphenylpolyynes, oligoynes, Cadiot-Chodkiewicz reaction, UV spectroscopy, HPLC analysis, FT-IR spectroscopy, hydrogenation

1 Introduction

Polyynes are polyacetylenic carbon chains having the general structure R-(C≡C)$_n$-R' (with R = R' or R≠R' and R = H, alkyl, aryl, CN, organometallic group, etc.) which are of wide interest in the development of new materials and in the synthesis of new medicinal drugs (1). Additionally, polyynes or polyynes derivatives are naturally occurring in natural products, for instance, playing a role as natural antibiotics in plants and fungi (2). Another important topic regarding polyynes is the fact that they are present in space, for instance in the circumstellar medium of late-type carbon-rich stars, and have been quite easily detected by radioastronomy; their synthesis can be achieved in the laboratory scale using a carbon arc under conditions of temperature and pressure somewhat similar to those existing in the circumstellar medium of carbon stars (3–8).

Hydrogen-terminated polyynes and nitrogen-terminated polyynes (monocyanopolyynes and dicyanopolyynes) are stable only in diluted solution, when concentrated or dried hydrogen-terminated polyynes undergo a crosslinking reaction while the nitrogen-terminated polyynes decompose in solution with the dicyanopolyynes more unstable than the monocyanopolyynes (9–12). When the polyyne carbon chains are terminated by bulky end groups they are stabilized (13) and can be crystallized so that their solid state structure has been determined in many cases (14–16). The structural data show a distinct reduction in the bondlength alternation as a function of the polyyne chain length, but this trend appears to saturate before a cumulenic-like structure is achieved (14).

The synthesis of diarylpolyynes and other polyynes was achieved in the middle of the last century through the step synthesis combining the use of NaNH$_2$, Grignard reagent with the Glaser, Hay or Eglington-type coupling reactions (17). Only diacetylenes and triacetylene derivatives were produced (18–20). Long chain polyynes were produced only in 1972 using step synthesis and silylation as a protective method for terminal alkynes in coupling reactions (21–23). This synthetic approach was used more recently for the synthesis of carbon materials (24) and of polyynes chains with bulky substituents (25, 26). The synthesis of longer polyyne chains appear limited by the type of reagents used

---

*Address correspondence to: Franco Cataldo, Lupi Chemical Research, Via Casilina 1626/A, 00133 Rome, Italy. E-mail: franco.cataldo@fastwebnet.it

and by the synthetic approach adopted as pointed out in a recent review (27). However, the application of innovative synthetic approaches permits us to achieve quite amazing results such as in the case of the synthesis of pentafluorophenyl and triisopropylsilyl end-capped polyynes up to an octayne chain which was developed based on the use of a Fritsch-Buttenberg-Wiechell rearrangement as the key step (28–30). Other novel synthetic approaches in the synthesis of substituted acetylenes have involved the reaction of acetylene gas with aryl iodides (31) and under palladium–copper catalysis which correspond to the Sonogashira reaction conditions (32).

In the synthesis of polyynes, our preference for simple synthetic approaches has led to the development of the submerged carbon arc synthesis or the use of the Glaser reaction using calcium carbide (1). The present work is dedicated to a simplified, one-pot synthesis, and characterization of α, ω-diphenylpolyynes produced through a synthetic route which involves the use of diiodoacetylene as synthon and the Cadiot-Chodkiewicz reaction conditions.

2 Experimental

2.1 Materials and Equipment

Phenylacetylene was obtained from Aldrich or Fluka together with all other solvents and reagents mentioned in the present work. Diiodoacetylene was prepared according to the method reported previously (33). The UV absorption spectra were recorded on a Shimadzu UV2450 and the FT-IR spectra on a Nicolet IR300 spectrometer from Thermo-Fisher Corp. The HPLC analysis was performed on an Agilent Technologies 1100 station equipped with a diode array detector and a C8 column. FT-IR spectra were recorded in transmittance mode on an IR300 spectrometer from Thermo-Fisher Corp. on a thin film of diphenylpolyynes mixture grown on the surface of a KBr plate by evaporating their decalin solution.

2.2 Synthesis of Copper Phenylacetylide

Cu(I) chloride (1.0 g) was dissolved in 30 mL of aqueous ammonia (30%) together with 0.5 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$). To this solution, phenylacetylene (1.0 ml) was added under stirring. A brilliant yellow precipitate of copper(I) phenylacetylide was collected by filtration in quantitative yield (1.45 g).

2.3 Coupling Reaction to a Mixture of Diphenylpolyynes

Diiodoacetylene (I-C≡C-I) as white needles (Warning! Acetylene diiodide is an irritant and poisonous) was stirred with decalin. About 5.0 g of I-C≡C-I was dissolved/suspended in 90 mL of decalin and transferred into a 500 mL round bottomed flask and stirred with 100 mL of distilled water. Copper(I) phenylacetylide (1.45 g) was added to the reaction mixture together with 25 mL of tetrahydrofuran, 50 mL aqueous NH_3 30% and 30 ml of N,N',N,N'-tetramethylethylenediamine (TMEDA). The mixture was stirred at room temperature for two days and the decalin layer became deep orange. With a separatory funnel, the organic layer was separated from the aqueous layer. The UV spectroscopy and the HPLC analysis of the diluted decalin solution confirms the formation of a mixture of diphenylpolyynes (see section 3).

2.4 Precipitation of Terminal Acetylenes

The residual terminal acetylenes present in the decalin solution were precipitated by shaking the solution with 4.0 g of CuCl dissolved in 100 mL of aqueous NH_3 30% together with 3.0 g of $NH_2OH{\cdot}HCl$.

The formation of a red precipitate was observed and separated by filtration. The diphenylpolyynes decalin solution was then shaken with 200 mL HCl (10%) to neutralize the alkalinity due to the presence of ammonia and TMEDA. After neutralization, the solution changed its color from deep orange to orange. The UV spectroscopy and the HPLC analysis was made on samples of decalin solution diluted with a large excess of pure decalin.

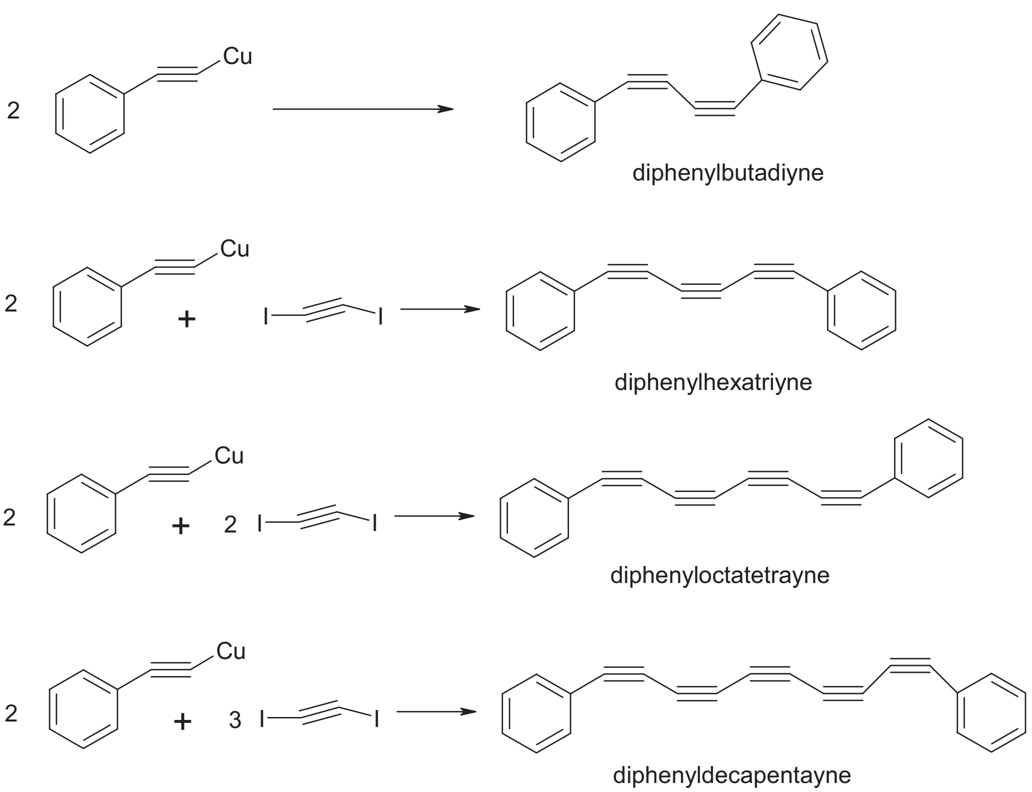
2.5 Hydrogenation of Diphenylpolyynes

A small amount of diphenylpolyynes solution in decalin (section 2.4) was aspired with a Pasteur pipette and five drops were diluted with 50 mL of decalin. To this solution were added 8.0 g of Zn powder and the mixture was shaken in a conical flask with 30 ml of HCl (37%) added in two portions. After the addition of each HCl portion, the conical flask was closed with a rubber stopcock and hand-shaken. The stopcock was opened after appropriate intervals of time to release the excess of H_2 developed by the acid attack of the Zn dust. After this treatment, the decalin solution was decanted from the Zn and aqueous layer and filtered through a paper filter. The effects of hydrogenation were easily checked by the UV spectrum of the solution.

3 Results and Discussion

3.1 The Cadiot-Chodkiewicz Synthesis of Diphenylpolyynes

The Cadiot-Chodkiewicz reaction (34) applied to the specific synthesis of diphenylpolyynes is illustrated in Scheme 1. The reaction involves the coupling of a copper(I) salt of an acetylene, in our case copper phenylacetylide, with a halide of another acetylenic hydrocarbon. Specifically, we have used diiodoacetylene which is not easily accessible (33) and is also poisonous and an irritant, but it is extremely versatile since it permits the synthesis of a mixture



Sch. 1. The synthesis of diphenylpolyynes using diiodoacetylene.

of diphenylpolyynes in one shot avoiding the complex step syntheses used by previous investigators as discussed in the Introduction. Another feature of the reaction route shown in Scheme 1 is that during stirring of the reagents an exchange reaction should occur between iodine and copper present in the mixture so that diiodoacetylene is converted into a copper salt according to the following scheme:

$$\text{I-C}{\equiv}\text{C-I} + 2\text{Cu}^+ \rightarrow \text{Cu-C}{\equiv}\text{C-I} + \text{CuI}$$

The formation of in the reaction mixture Cu-C≡C-I can be only postulated as a labile intermediate which can lead to long polyyne chains such that of diphenyldecapentyne (DPDPY) or lower homologues. Without such an intermediate, it becomes difficult to justify the formation of DPDPY.

The electronic absorption spectrum of the mixture of diphenylpolyynes obtained with our synthetic approach is shown in Figure 1. By overlapping the diphenylpolyynes spectra taken from the HPLC analysis of the reaction mixture, as shown in Figure 2, it can be observed that the peak at about 309 nm can be attributed to the $\Phi\text{-}(C{\equiv}C)_2\text{-}\Phi$ since the other compounds $\Phi\text{-}(C{\equiv}C)_3\text{-}\Phi$ and $\Phi\text{-}(C{\equiv}C)_4\text{-}\Phi$ are minor contributors and necessarily more diluted at this wavelength. Instead the concentration of $\Phi\text{-}(C{\equiv}C)_3\text{-}\Phi$ can be read at 369 nm, that of $\Phi\text{-}(C{\equiv}C)_4\text{-}\Phi$ at 399 and finally, $\Phi\text{-}(C{\equiv}C)_5\text{-}\Phi$ 433 nm. By using the molar extinction coefficients for these molecules reported by Gillam et al. (40) and Perkampus (41) a concentration of 3×10^{-5}, $1\text{x}10^{-5}$, 3×10^{-6} and 8.3×10^{-7}mol/L can be derived for $\Phi\text{-}(C{\equiv}C)_2\text{-}\Phi$, $\Phi\text{-}(C{\equiv}C)_3\text{-}\Phi$, $\Phi\text{-}(C{\equiv}C)_4\text{-}\Phi$ and $\Phi\text{-}(C{\equiv}C)_5\text{-}\Phi$, respectively.

3.2 HPLC Analysis of the Diphenylpolyynes Mixture

In order to separate the mixture of the diphenylpolyynes synthesized with the Cadiot-Chodkiewicz reaction, about

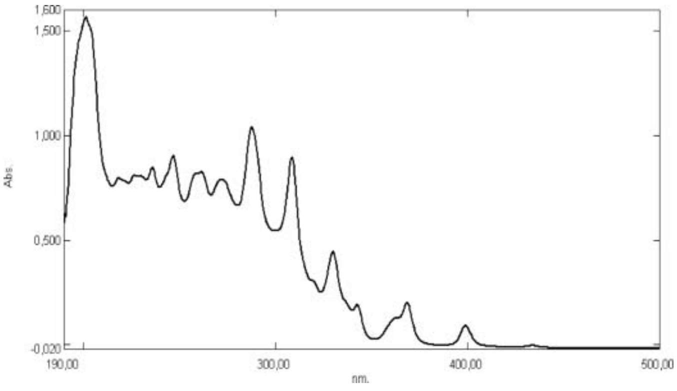


Fig. 1. Electronic absorption spectrum of diphenylpolyynes mixture in decalin.

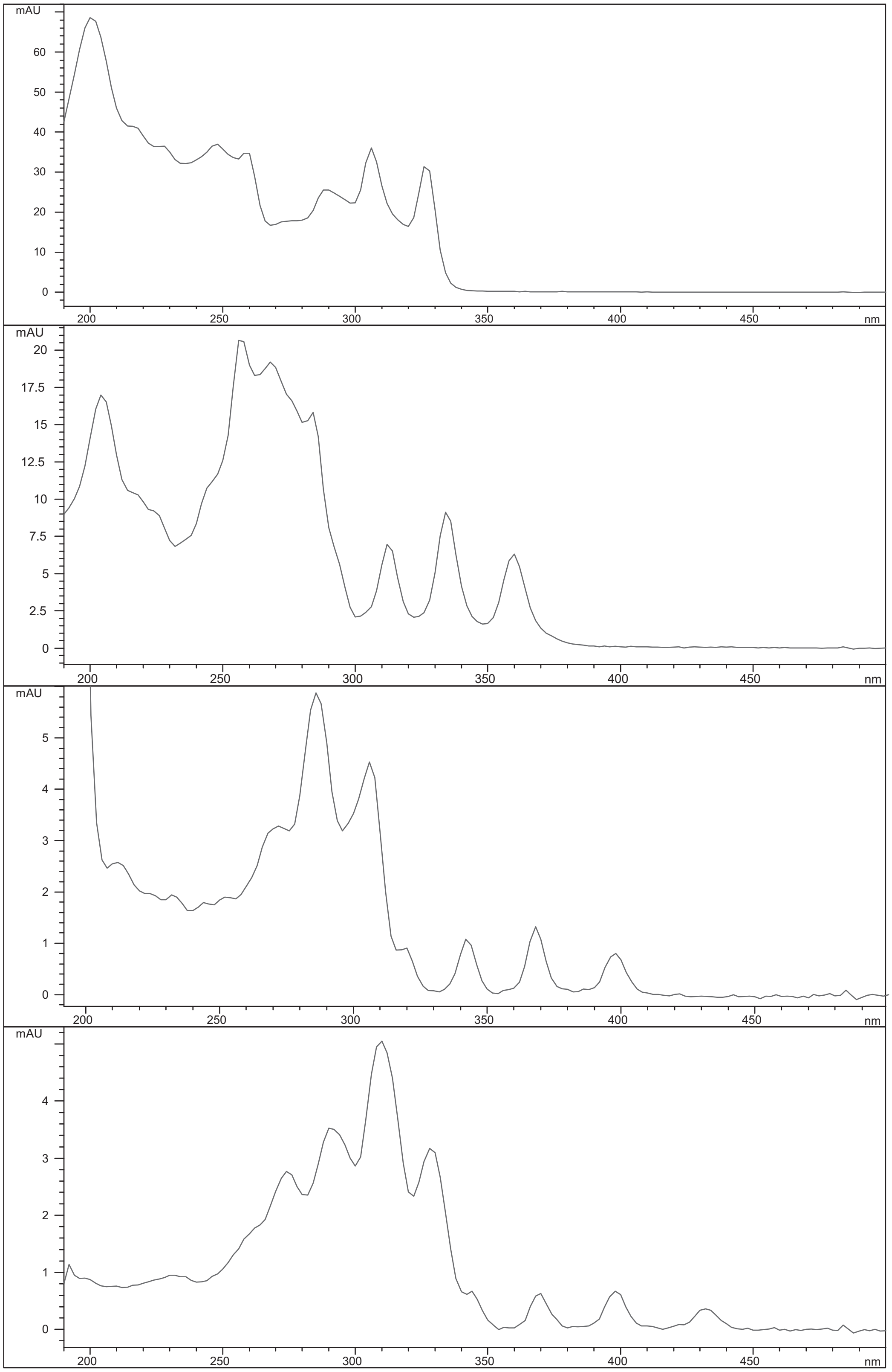


Fig. 2. The electronic absorption spectra of the diphenylpolyynes recorded with the HPLC-diode array. The spectra of $\Phi\text{-}(C{\equiv}C)_n\text{-}\Phi$ with $n = 2, 3, 4$ and 5 are shown from top to bottom, respectively.

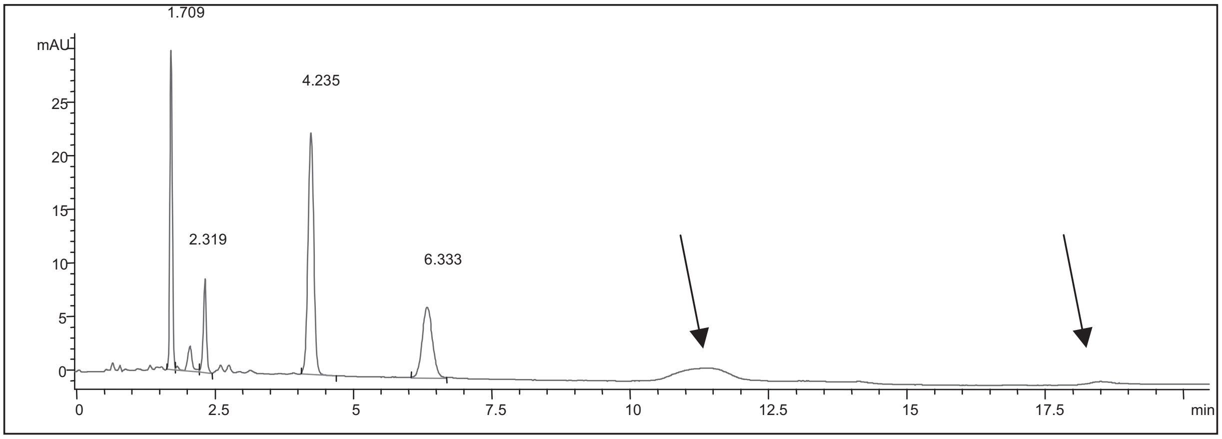


Fig. 3. HPLC analysis at 225 nm of the diphenylpolyynes mixture. Φ-(C≡C)$_2$-Φ shows a retention time of 4.23 min, Φ-(C≡C)$_3$-Φ elutes at 6.33 min, Φ-(C≡C)$_4$-Φ at about 11.25 min (indicated by an arrow) and Φ-(C≡C)$_5$-Φ at about 18 min, again indicated by an arrow.

10 microL of highly diluted decalin solution were injected in the HPLC C8 column using acetonitrile/water 80/20 vol/vol as mobile phase at a flow rate of 1.5 ml/min. Figure 3 shows the results of the separation: the peak with a retention time of 4.23 min displays the spectrum of Φ-(C≡C)$_2$-Φ (spectrum at the top of Figure 2), Φ-(C≡C)$_3$-Φ elutes at 6.33 min (second spectrum from top in Figure 2), Φ-(C≡C)$_4$-Φ is detected at about 11.25 min (third spectrum from top of Figure 2) and Φ-(C≡C)$_5$-Φ at about 18 min (spectrum at the bottom of Figure 2). The spectra of the polyynes were easily recognized from reference data (35, 36). By looking at the peaks of Figure 3, it can be observed that the diphenylpolyynes, having low molecular weight (with n = 2 and 3), display a normal "triangular" peak in the chromatogram. Instead, the higher molecular weight diphenylpolyynes, those having 4 and 5 triple bonds, have a very long retention time in the column and show a very broad and irregular peak in the HPLC chromatogram which suggests that they have poor solubility in the mobile phase. We infer that, if chains longer than n = 5 are present, we cannot detect them with the analytical technique and set-up adopted. The concentration of the various polyynes can be easily estimated also from the absorption spectra recorded with the HPLC-DAD and shown in Figure 2. Again, using the molar extinction coefficients given by previous investigators (35,36) a concentration of 1.2×10^{-5}, 2.9×10^{-6}, 9.0×10^{-7} and 3.2×10^{-7}mol/L can be derived for Φ-(C≡C)$_2$-Φ, Φ-(C≡C)$_3$-Φ, Φ-(C≡C)$_4$-Φ and Φ-(C≡C)$_5$-Φ, respectively (the relative concentration of the polyyne chains in the mixture is as follows: Φ-(C≡C)$_2$-Φ, 74.4%; Φ-(C≡C)$_3$-Φ, 18.0%; Φ-(C≡C)$_4$-Φ, 5.6% and Φ-(C≡C)$_5$-Φ, 2.0%). Compared with the concentration estimated in section 3.1, this demonstrates an overestimation of the diphenylpolyynes concentrations obtained by analyzing directly the UV spectrum of Figure 1. Such overestimation is derived from the inevitable overlap of the absorption spectra of all the polyynes present in the mixture. An additional consideration regards the fact that Φ-(C≡C)$_4$-Φ and Φ-(C≡C)$_5$-Φ elute in a irregular way as already discussed. This fact may affect the precision of the determination of the concentration of these two molecules through the HPLC.

The chromatogram of Figure 3 also shows three other peaks which deserve some comment. The peak at 1.71 min is due to a small amount of phenylacetylene which was not removed completely by the purification of the reaction mixture with Cu(I) treatment. The peak at 1.71 min has been assigned to phenylacetylene on the basis of the retention time of a pure standard and on the basis of its electronic absorption spectrum which corresponds completely to that of phenylacetylene. Other two minor peaks, respectively at 2.05 and 2.32 min are due to impurities present in the decalin used as solvent.

3.3 FT-IR Spectroscopy of Diphenylpolyynes

As reported in Figure 4, phenylacetylene is characterized by the strong ≡C-H stretching band at 3294 cm^{-1} and by a weak C≡C stretching at 2111 cm^{-1} (37). The crude and purified decalin solution of diphenylpolyynes was used to record the FT-IR spectrum of these molecules. In Figure 4, pure decalin shows a very simple infrared spectrum with two cycloaliphatic stretching bands at 2921 and 2850 cm^{-1} and a wide range of transparency at the other wavenumbers. Thus, by putting a drop of decalin solution of diphenylpolyynes on the ZnSe crystal, it is possible to record directly the major features of the FT-IR spectrum of the solute. In Figure 4, it can be observed that the ≡C-H stretching band of phenylacetyene completely disappeared in the FT-IR spectrum of diphenylpolyynes

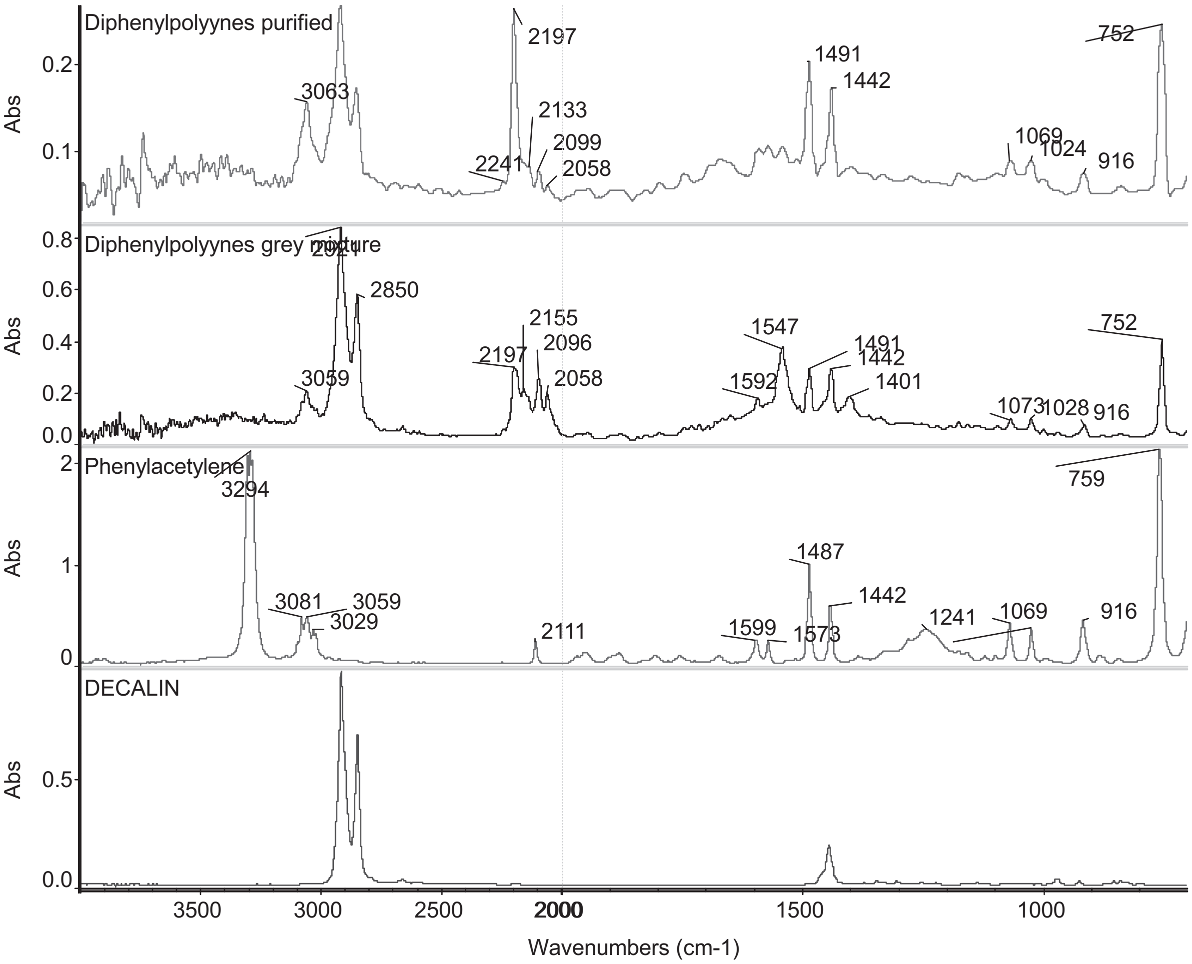


Fig. 4. FT-IR spectra in reflectance mode (on ZnSe Crystal): Purified spectrum of diphenylpolyynes mixture (top); diphenylpolyynes grey mixture (second spectrum from top); reference spectrum of phenylacetylene (second from bottom); reference decalin spectrum (bottom).

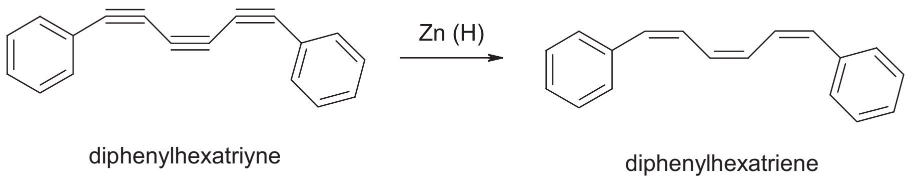
obtained from the chemical synthesis. This is a clear demonstration that phenylacetylene has been consumed in the reaction and now is under the form of terminal groups of the diphenylpolyynes chains. Moreover, the weak C≡C stretching at 2111 cm^{-1} of phenylacetylene is now replaced in the crude diphenylpolyynes spectrum by a series of bands at 2197, 2155, 2096 and 2058 cm^{-1}. We observe that the purification of the reaction mixture enhances the band at 2197 cm^{-1} over the other C≡C stretching bands (Fig. 4).

On standing in a closed flask, the diphenylpolyynes are relatively stable for a very long time although they release a black precipitate very slowly. The FT-IR spectrum of the acetone washed and dried precipitate is shown in Figure 5. It is characterized by a broad $\nu_{C\equiv C}$ band at 2124 cm^{-1} and somewhat resembles the IR spectra of the carbonaceous matter containing carbynoid structures which was already reported (38). Therefore, the diphenylpolyynes undergo a slow crosslinking reaction in solution probably caused by the action of light.

3.4 Hydrogenation of Diphenylpolyynes

The hydrogenation of a mixture of polyynes with the nascent hydrogen generated by the action of hydrochloric acid on zinc dust leads to a mixture of ene-ynes as final products (1). Therefore, also in this case, the ene-yne derivatives of diphenylpolyynes were expected. Instead we obtained a mixture of polyenes and other products (Sch. 2).

Figure 6 shows the electronic absorption spectrum of the hydrogenated mixture: the spectrum corresponds to that of diphenylbutadiene which have maxima of absorption just at 206, 236, 320, 337 and 366 nm (36). Additionally, $\Phi\text{-}(C\equiv C)_2\text{-}\Phi$ has a retention time of 4.24 min and its hydrogenated derivative $\Phi\text{-}(CH = CH)_2\text{-}\Phi$ elutes at 3.77 min (Fig. 7). On the other hand, the higher acetylenic homologue $\Phi\text{-}(C\equiv C)_3\text{-}\Phi$ elutes at 6.33 min and $\Phi\text{-}(CH{=}CH)_3\text{-}\Phi$ is detected at 4.52 min with the spectrum identical to that of diphenylhexatriene. No traces of ene-ynes have been detected at all. Instead, various other products were detected including a naphthalene derivative eluting at 2.321 min.



Sch. 2. The hydrogenation of diphenylpolyynes with Zn/HCl (nascent H) leads to diphenylpolyenes.

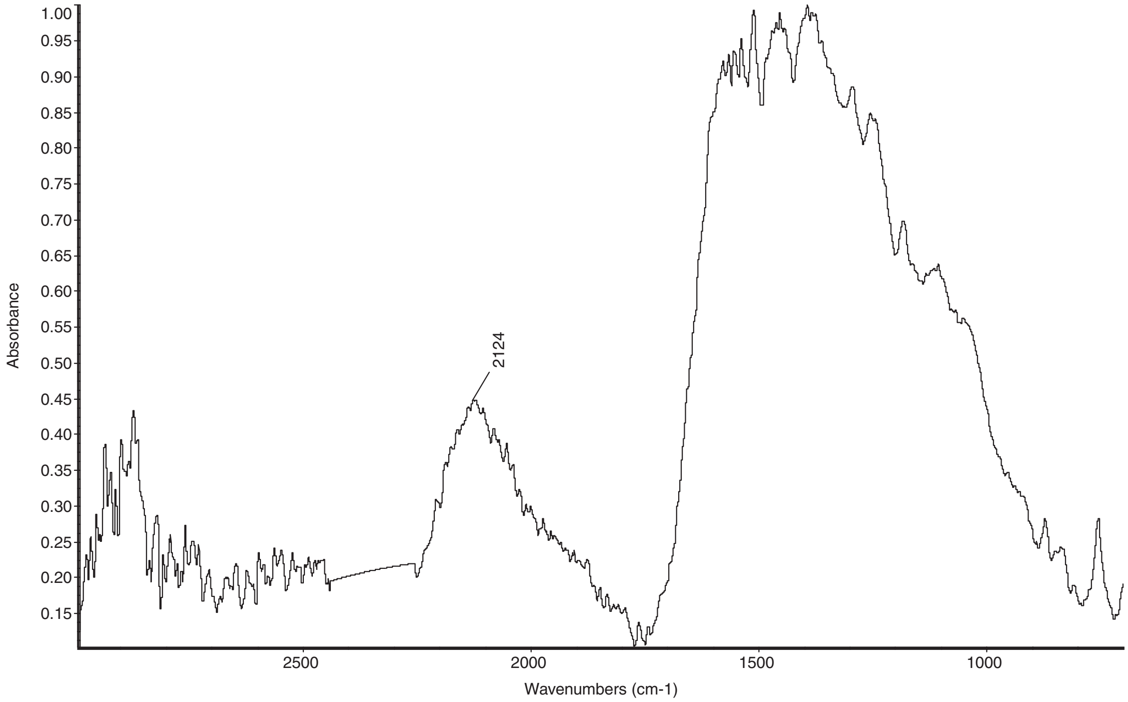


Fig. 5. FT-IR spectrum of the black product precipitated from a diphenylpolyynes solution. Note the broad triple bond stretching band at 2124 cm^{-1}.

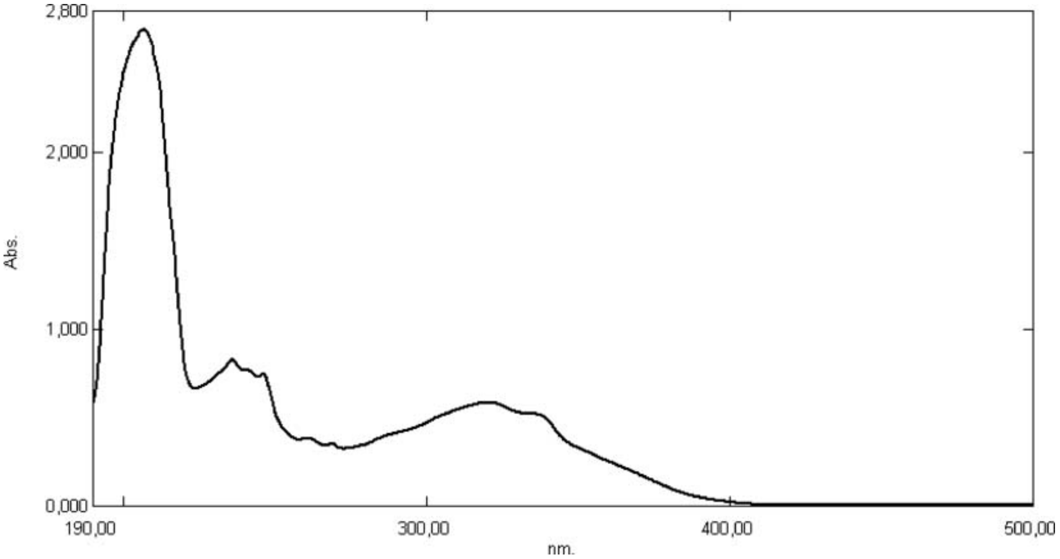


Fig. 6. Electronic absorption spectrum of diphenylpolyynes after hydrogenation. The spectrum shows the formation of diphenylpolyenes.

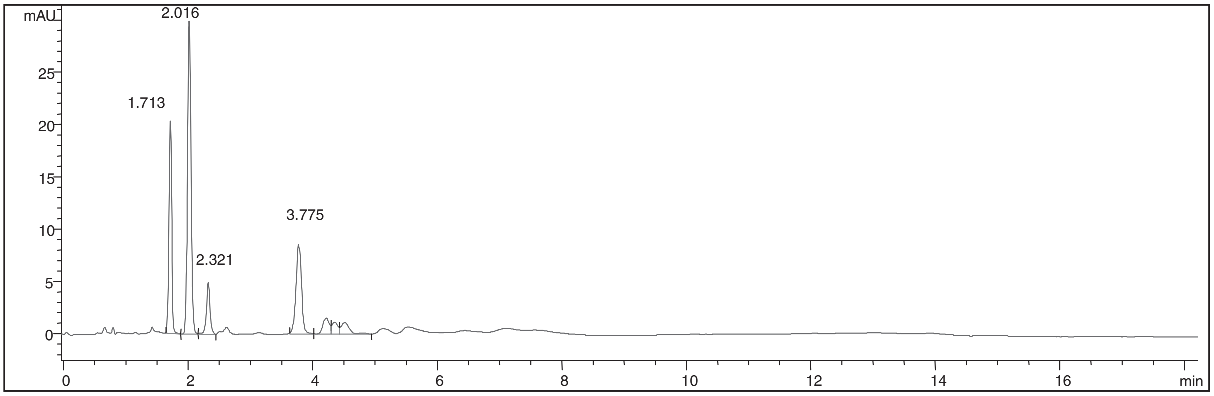


Fig. 7. HPLC analysis of the diphenylpolyynes mixture after hydrogenation with nascent hydrogen.

4 Conclusions

The Cadiot-Chodkiewicz reaction was applied in the synthesis of a mixture of diphenylpolyynes in decalin. The diphenylpolyynes series $\Phi\text{-}(C\equiv C)_n\text{-}\Phi$ with $n = 2,3,4$ and 5 were obtained in one shot and were separated and characterized by HPLC-diode array, by electronic absorption spectroscopy and by FT-IR spectroscopy. The diphenylpolyynes were hydrogenated with nascent hydrogen and the main products were the diphenylpolyenes.

Acknowledgments

Franco Cataldo acknowledges that part of this research has been supported by the Italian Space Agency contract number I/015/07/0 (Studi di Esplorazione del Sistema Solare).

References

1. Cataldo, F. (Ed.) *Polyynes: Synthesis, Properties and Applications*. CRC Press: Boca Raton, FL, 2005.
2. Bohlmann, F., Burkhardt, T. and Zdero, C. *Naturally Occurring Acetylenes.* Academic Press: London, 1973.
3. Heath, J.R., Zhang, Q., O'Brien, S.C., Curl, R.F., Kroto, H.W. and Smalley, R.E. (1987) *J. Am. Chem. Soc.,* 109, 359.
4. Cataldo, F. (2007) *Fullerenes Nanotub. Carbon Nanostruct.,* 15, 291.
5. Cataldo, F., Ursini, O. and Angelini, G. (2007) *J. Electroanal. Chem.,* 602, 82.
6. Cataldo, F. (2006) *Int. J. Astrobiol.,* 5, 37.
7. Cataldo, F. (2006) *Origin of Life Evol. Biosph.,* 36, 467.
8. Cataldo, F. (2004) *Int. J. Astrobiol.* 3, 237.
9. Lucotti A., Casari C.S., Tommasini M., Li Bassi A., Fazzi D., Russo V., Del Zoppo M., Castiglioni C., Cataldo F., Bottani C.E. and Zerbi, G. (2009) *Chem. Phys. Lett.,* 478, 45.
10. Heymann, D. (2005) *Carbon*, 43, 2235.
11. Cataldo, F. (2006) *Polym. Deg. Stab.,* 91, 317.
12. Cataldo, F. (2006) *Fullerenes Nanotub. Carbon Nanostruct.,* 14, 1.
13. Casari, C.S., Russo, V., Li Bassi, A., Bottani, C.E., Cataldo, F., Lucotti, A., Tommasini Zoppo, M., Castiglioni, C. and Zerbi, G. (2007) *Appl. Phys. Lett.,* 90, 13111.
14. Szafert, S. and Gladysz, J.A. (2003) *Chem. Rev.*, 103, 4175.
15. Chalifoux, W.A., McDonald, R., Ferguson, M.J. and Tykwinski, R.R. (2009) *Angew. Chem. Int. Ed,* 48, 7915.
16. Lucotti, A., Tommasini, M., Fazzi, D., Del Zoppo, M., Chalifoux, W.A., Ferguson, M.J., Zerbi, G. and Tykwinski, R.R. (2009) *J. Am. Chem. Soc.,* 131(12), 4239.
17. Bohlmann, F. (1953) *Angew. Chem.* 65, 385.
18. Armitage, J.B., Jones, E.R.H. and Whiting, M.C. (1952) *J. Chem. Soc.,* 1952, 1993.
19. Armitage, J.B., Cook, C.L., Jones, E.R.H. and Whiting, M.C. (1952) *J. Chem. Soc.,* 1952, 2010.
20. Armitage, J.B., Entwistle, N., Jones, E.R.H. and Whiting, M.C. (1954) *J. Chem. Soc.,* 1954, 147.
21. Eastmond, R. and Walton, D.R.M. (1972) *Tetrahedron*, 28, 4591.
22. Eastmond, R., Johnson, T.R. and Walton, D.R.M. (1972) *Tetrahedron*, 28, 4601.
23. Johnson, T.R. and Walton, D.R.M. (1972) *Tetrahedron*, 28, 5221.
24. Hlavatý, J., Kavan, L. and Kubišta, J. (2002) *Carbon,* 40, 345.
25. Gibtner, Th., Hampel, F., Gisselbrecht, J.P. and Hirsch, A. (2002) *Chem. Eur. J.*, 8, 408.
26. Zheng, Q., Bohling, J.C., Peters, T.B., Frisch, A.C., Hampel, F. and Gladysz, J.A. (2006) *Chem. Eur. J.,* 12, 6486.
27. Chalifoux, W.A. and Tykwinski, R.R. (2009) *Comptes Rendus Chimie*, 12, 341.
28. Tykwinski, R.R., Kendall, J. and McDonald, R. (2009) *Synlett*, 13, 2068.
29. Azyat, K., Jahnke, E., Rankin, T. and Tykwinski, R.R. (2007) *J. Chem. Soc. Dalton Trans.*, 2007, 4495.
30. Eisler, S., Slepkov, A.D., Elliott, E., Luu, T., McDonald, R., Hegmann, F.A. and Tykwinski, R.R. (2005) *J. Am. Chem. Soc.,* 127, 2666.
31. Pal, M. and Kundu, N.G. (1996) *J. Chem. Soc., Perkin Trans. 1*, 1996, 449.
32. Zhang, W., Wu, H., Liu, Z., Zhong, P., Zhang, L., Huang, X. and Cheng, J. (2006) *J. Chem. Soc. Chem. Commun.,* 2006, 4826.
33. Cataldo, F. (2001) *Fullerene Sci. Technol.,* 9, 525.
34. Vatsourò, K., Michtchenko, G. *Réactions Organiques Classées Par Auteurs.* Editions Mir: Moscow, p. 130-131, 1981.
35. Gillam, A.E., Stern, E.S. and Jones, E.R.H. *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*. Edward Arnold Publishers: London, 1954, p. 78.
36. Perkampus, H.H. *UV-VIS Atlas of Organic Compounds.* Wiley-VCH: Weinheim, 1992, p. D10/17 and D10/36.
37. Lin-Vien, D., Colthup, N.B., Fateley, W.G. and Grasselli, J.G. *The Handbook of Infrared and Raman Charateristic Frequencies of Organic Molecules*. Academic Press: San Diego, 1991, Chapter 7.
38. Heimann, R.B., Evsyukov, S.E. and Kavan, L. *Carbyne and Carbynoid Structures*. Kluwer Academic Publishers: Dordrecht, 1999.