EXECUTIVE SUMMARY OF THE THESIS

Investigation of polyynes in polymeric electrospun nanofibers

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY – INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

AUTHOR: Andrea Taini

ADVISOR: Carlo S. Casari

CO-ADVISOR: Simone Melesi

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1. Introduction

Carbon Atomic Wires (CAWs) are linear chains made of sp-hybridized carbon atoms. They have gained increasing attention due to their superlative mechanical, thermal and electrical properties, which are predicted to be higher than other studied carbon allotropes, like graphene or carbon nanotubes. CAWs properties are modelled from a theoretical infinite wire model (*carbyne*), which can possess two structures: an alternating sequence of single and triple C-C bonds (*polyyne*) or a repetition of double bonds (*cumulene*) [1]. Real carbon wires are finite chains terminated by various heteroatoms or chemical groups: the simplest termination is hydrogen capping, but several chains capped by bulky endgroups have been successfully synthesized. Endgroup effects are crucial in determining real CAWs' electronic and vibrational properties. Moreover, they influence carbon wires stability since bulky groups hinder crosslinking effects that cause chain degradations.

CAWs production can be achieved by different chemical reaction routes or by exploiting physical processes (ablation methods). Among the latter, Pulsed Laser Ablation in Liquid (PLAL) is one of the most used techniques to produce hydrogenated polyynes with different chain lengths, in a simple and scalable way; the main drawback is the low polyyne concentration obtainable (around 10^{-6} mol/L) [1, 2]. Polyynes stabilization has been achieved by embedding them in polymeric matrices; moreover, the introduction of metallic nanoparticles (e.g., silver or gold) in these nanocomposites, or in solution, has allowed the exploitation of Surface Enhanced Raman Spectroscopy (SERS) as an effective method to detect polyynes with low concentrations [2, 3].

A fascinating technique to produce polymeric nanomaterials is electrospinning. It possesses huge versatility, having been studied for biomedical, textile, energy, and filtration applications [4]. Its working principle is rather simple: a liquid polymeric solution is electrified by the application of a high potential difference between the needle of

a syringe (containing the solutions) and a conductive collector. Thus, the electric field elongates the liquid droplet, creating submicrometric fibers that are collected on a proper substrate placed on the collector. Electrospun nanofibers morphology depends on several parameters, usually grouped in solution, process and environmental contributions [4].

The aim of this work was to find suitable detection methods for low concentrated polyynes embedded in electrospun polymeric nanofibers; chains with different terminations were investigated. Since the low concentration of polyynes makes them non-detectable by Raman spectroscopy, characterization was performed with the help of silver nanoparticles, exploiting SERS effect.

2.   Materials and methods

Each sample in this work is composed by three main components: polyynes (the analytes), silver nanoparticles (the enhancers), and polymer (the matrix).

The investigated polyynes are as halogenated and hydrogenated. Halogenated polyynes have four sp-carbon atoms, terminated by chlorine on one side and by a nitril para-substituted phenyl on the other; these polyynes are called C4Cl for simplicity. They are synthesized by a chemical process, and they are available in powder form. C4Cl possesses good stability in many organic solvents. Solutions were obtained by simple dilution. Acetonitrile (ACN), dimethyl sulfoxide (DMSO), dichloromethane (DCM) and dimethylformamide (DMF) were the exploited solvents.

Hydrogenated polyynes are a mixture solution containing chains with various lengths. These chains are produced by Pulsed Laser Ablation in Liquid (PLAL) exploiting a graphite target immersed in water o ACN. Ablations were achieved by a Nd:YAG pulsed laser (Quantel Q-Smart 850) working at 1064 nm with repetition rate of 10 Hz and 6 ns of pulse duration. Ablations in water were performed for 30 minutes in 1 mL, with an energy pulse of 50 mJ/pulse; ablations in ACN were performed for 15 minutes in 2 mL, with the same energy pulse. The size-separated polyyne (HC8H) was obtained by Reverse-Phase High Performance Liquid Chromatography (RP-HPLC), with a Shimadzu Prominence UFLC instrument. A mixture of polyynes in ACN was first concentrated with a Rotavapor, then filtered and injected in the

HPCL: HC8H was the most abundant polyyne in solution, therefore collected to be investigated.

Silver Nanoparticles (AgNP) were produced following the Lee-Meisel approach; a water colloid of nanoparticles was obtained by reduction of silver nitrate ($AgNO_3$) by sodium citrate. For some specific sample preparations AgNP were also concentrated with a centrifuge, at 8000 rpm for 20 minutes, obtaining a 40 times reduction in volume. Poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA) were chosen as polymer matrices. PMMA was exploited to produce water-resistant nanofibers embedding polyynes. All the other samples were prepared by dissolving PVA in water-AgNP mixtures and subsequently adding polyynes solution (PVA needs temperature around 90°C to be dissolve in water, thus polyyne thermal degradation must be avoided). Films were deposited by drop casting or spin coating. Nanofibers were produced by electrospinning. Solutions were put in Hamilton Gastight syringes; an infusion pump KDS Scientific (model series 200) provided the feed rate (0.3 or 0.5 mL/h for PVA blends, 0.05 mL/h for PMMA), while a potential from 13 to 17 kV was applied with a High Voltage Power Supply (Spellman SL30P300).

Experimental characterizations of samples were performed with three main instruments. UV-Vis analysis of polyynes and AgNP was provided by Shimadzu UV-1800 spectrophotometer.

Nanofibers morphology was observed with a Zeiss Supra 40 Field Emission Scanning Electron Microscope.

SERS measurements in liquid, films and nanofibers were done exploiting a Renishaw inVia Raman microscope, equipped with a 532 nm solid-state laser and a 50x optical objective.

3.   Experimental results

The experimental work has been divided in two main sections: first the investigation of halogenated polyynes, then the detection of hydrogenated ones. Since hydrogenated polyynes produced by PLAL are characterized by low concentrations (around 10^{-6} mol/L), the investigation of halogenated polyynes was conducted at comparable values (around 10^{-5} mol/L) with the aim of finding a suitable system for SERS detection of sp-carbon chains.

3.1. Detection of halogenated polyynes in polymeric nanocomposites

The characterization of C_4Cl polyynes followed several steps. First, carbon chains were studied by SERS in liquid since it was the easiest way to obtain a clear knowledge about position and intensity of their specific signals. A solution of C_4Cl 10^{-5} mol/L in ACN was mixed at different volume ratios with the AgNP colloid. By increasing relative AgNP:C_4Cl volume ratio from 1:2 to 4:1, multiple signals were detected. A peak found at 1600 cm^{-1} was recognized as the Raman response of polyyne's phenyl ring. Other peaks have been found in the characteristic sp-carbon region (1900-2200 cm^{-1}) and they were better investigated with SERS experiment in PVA films, to verify which ones were related to polyynes response.

SERS measurements were performed in films drop casted from PVA aqueous solutions. The polymer was dissolved in several water-AgNP blends; then, halogenated polyynes were integrated by mixing 10% in volume (%vol) of a 10^{-4} mol/L C_4Cl solution in DMSO with 90%vol of the polymeric solution. The final blend had 10% in weight of PVA, 10^{-5} mol/L of C_4Cl and a variable volume fraction of AgNP colloid (33, 50, 66, 90 %vol). This preparation procedure and polyynes concentration were kept constant for all the samples embedding C_4Cl.

SERS spectra of PVA films with polyynes and AgNP (at 33 and 50 %vol) are shown in Figure 1. By comparing each spectrum with a reference sample (obtained from the same solutions without polyynes) it was verified that only the peak at 1975 cm^{-1} clearly indicates the presence of polyynes (together with the one at 1600 cm^{-1}). The other signals in the 1900-2200 cm^{-1} region are probably caused by contaminations trapped during samples preparation, since they are also present in the reference spectra; their intensity is due to SERS enhancement from AgNP.

The investigation in liquid and films was useful to understand the specific SERS response of C_4Cl molecules; the subsequent step was to analyse polyynes embedded in electrospun nanofibers.

To investigate C_4Cl presence inside nanofibers, three different samples architectures were exploited. The purpose was to establish how many configurations were effective for the detection of polyynes. The first preparation consisted in covering electrospun nanofibers with
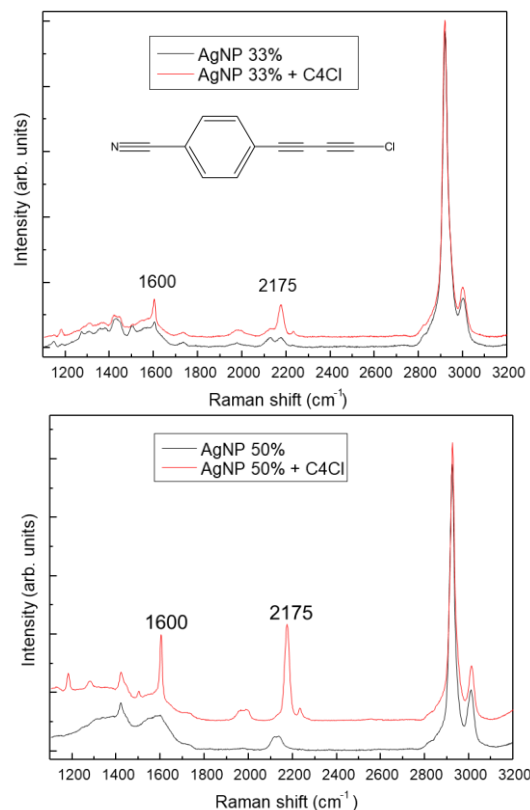

Figure 1 SERS spectra (normalized on PVA peak) of PVA films containing C_4Cl with different AgNP loading, compared with their references. The inset in the upper graph shows C_4Cl molecular structure

the AgNP colloid (*AgNP above* configuration): since PVA is a water-soluble polymer, PMMA nanofibers were used (C_4Cl integration was made by exploiting DMF as a common solvent). The second configuration adopted the reverse approach: PVA nanofibers were electrospun above a substrate covered with silver nanoparticles from colloid evaporation (*AgNP under*). For these two experiments, three different concentrations of AgNP colloid were exploited: undiluted, 10-time dilution and 100-time dilution. The third configuration mimicked what was done for SERS in films; polymeric solutions with polyynes and AgNP at different volume ratios (33, 50, 66 %vol) were electrospun (*AgNP inside*). Figure 3 shows SEM images of some obtained specimens.

Raman spectra were acquired for each sample: unfortunately, results did not bring polyynes detection, since no sample shows a peak at 1600 or 2175 cm^{-1}. Moreover, in the majority of the spectra, contaminations signals around 2120 cm^{-1} were observed, especially in those configurations exploiting higher concentration of AgNP.

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(a)

(b)

Figure 3 SEM images of PVA nanofibers with concentrated AgNP
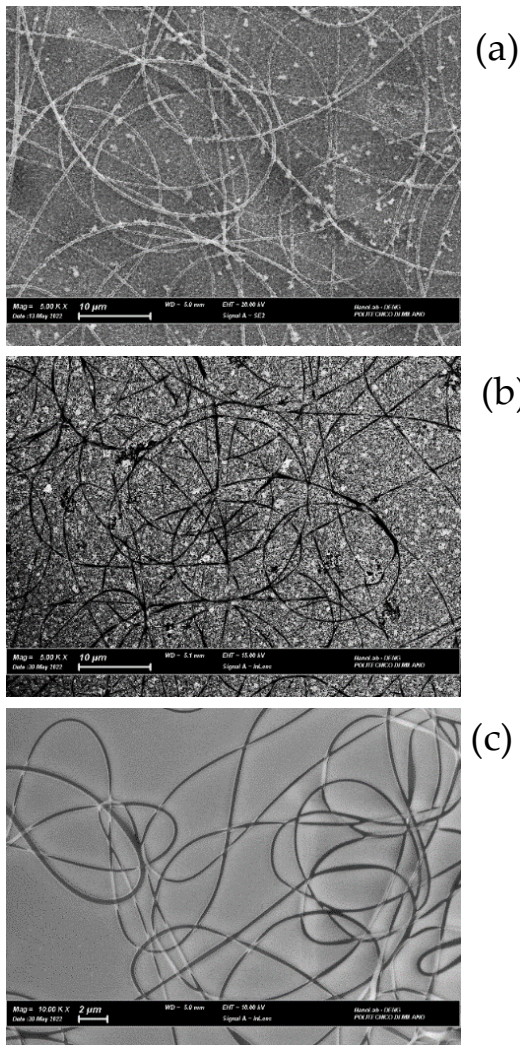

(c)

Figure 4 SEM images of the three configurations exploited for polyynes detection (one example per case): (a) undiluted AgNP above fibers; (b) undiluted AgNP under fibers; (c) 66%vol AgNP inside fibers

Moreover, fibers proved to be more heterogeneous than films regarding nanoparticles dispersion; the overall shape of Raman spectra drastically changed by measuring different spots, showing in some points huge nanoparticles signals that shadowed the polymer response.

To find a suitable method for C_4Cl detection, a side test was performed, exploiting a well-known system for superficial SERS analysis; it consisted in a substrate made of a compact nanofibers arrangement, obtained from electrospinning of PVA dissolved in a concentrated AgNP colloid. These fibers are loaded with a quantity of nanoparticles sufficiently high that can be seen at SEM (Figure 2); that, in principle, allows the detection of very low concentrated analytes deposited on them. Thus, this SERS active
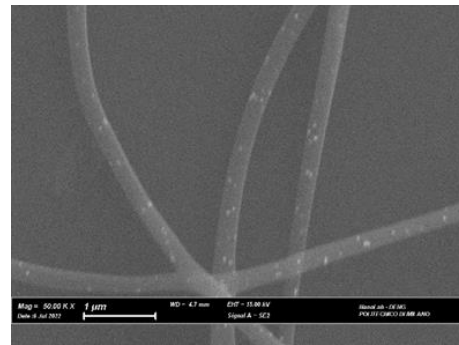
substrate was exploited for superficial investigation of polyynes; SERS signals were observed by depositing few drops of C_4Cl in DCM at 10^{-4} mol/L. Lowering the polyynes concentration, a very weak signal was observed for a 10^{-5} mol/L drop, while nothing was found at 10^{-6} mol/L (Figure 4). Even if the response of the 10^{-5} mol/L polyynes drop is barely distinguishable (and this is the C_4Cl concentration inside all PVA electrospun solutions), a test with polyynes embedded in nanofibers was anyhow performed. Nanofibers electrospun from a solution of PVA, concentrated AgNP and C_4Cl were analysed with Raman spectrometer. However, also this configuration did not show any significant polyyne's SERS signal.

This test concluded the investigation of halogenated polyynes; detection was achieved only in solution and polymeric films, but no result was obtained with polyynes embedded in nanofibers.

The following section describes the investigation of hydrogenated polyynes, showing the major results obtained, which are discussed and compared with C_4Cl behaviour.
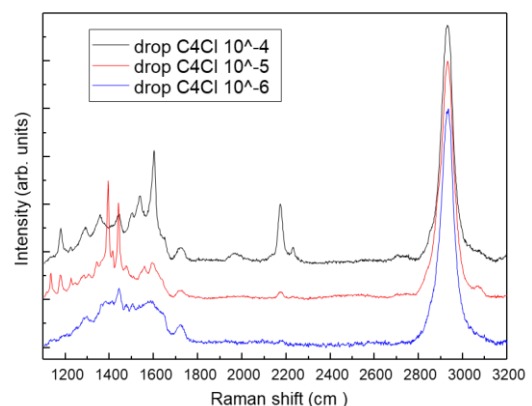

Figure 2 SERS spectra of the superficial C_4Cl polyynes investigation

3.2. Detection of hydrogenated polyynes in polymeric nanocomposites

The detection of hydrogenated polyynes followed similar steps. First, a mixture of polyynes in water was blended with the AgNP colloid at different volume ratios, to perform SERS in liquid. SERS spectra shows a twofold broad response in the 1800-2200 cm^{-1} region, which indicates polyynes response; other studies have verified, indeed, that SERS of polyynes mixtures is characterized by two main broad peaks like the ones observed in this case [3]. The main difference with SERS of C_4Cl is that, here, the most intense signals were found when AgNP:polyynes volume ratio was closer to unity, while for halogenated polyynes the best response was found with the highest ratio (4:1).

Polyynes were embedded in nanofibers starting from mixtures produced by laser ablation in water, since the latter is a common solvent for PVA and AgNP. Polyynes in water were always added to a polymeric-AgNP solution at 50%vol. The first two analysis exploited some nanofibers configurations already tested for C_4Cl investigation: *AgNP under* (undiluted) and *AgNP inside* (at 50%vol). However, also in this case no SERS response was found.

A third trial was made by dissolving PVA in a concentrated solution of AgNP, then adding polyynes in the blend (as was done for C_4Cl in the last described experiment). This configuration proved to be very successful: significant SERS signals were observed in electrospun fibers and in a spin coated film. The evolution in time of SERS spectrum was measured for the nanofiber sample; polyynes signals (the two broad peaks in the 1800-2200 cm^{-1} region) were detected up to more than 60 days (Figure 5).

This result is even more interesting considering that C4Cl analysis was performed with a higher polyynes concentration in the nanofibers. This consideration suggests that hydrogenated polyynes present a stronger interaction with AgNP than halogenated ones. The origin of this behavior could be found in the polyynes endgroup effects; C_4Cl are carbon chains with bulky terminations (chlorine and phenyl group), while hydrogenated polyynes possess the smallest possible capping element. This difference could have played a role in determining the interaction with AgNP and thus in the enhancement effect.
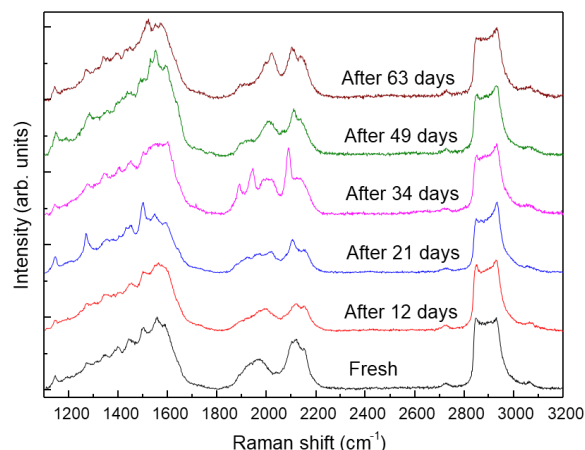

Figure 5 Time evolution of SERS spectra for nanofibers embedding polyynes in water

The subsequent step was to investigate hydrogenated polyynes produced by laser ablation in ACN. Polyynes production yield in ACN has shown to be higher than water; moreover, as an apolar solvent, ACN offers a more stable environment for polyynes [2]. A polyynes mixture in ACN was also the solution injected in HPLC to obtain the size-separated chains (HC_8H).

The main issue related to these experiments was the insolubility of PVA in pure acetonitrile; however, it has been demonstrated that PVA could still be dissolve in water-ACN mixtures up to 42%vol fraction of the organic solvent [5]. In this work, an optimization of electrospinning parameters was performed: nanofibers were electrospun from PVA solution with increasing ACN fractions. Homogeneous fibers with diameter under 0.5 μm were collected up to a 40%vol of acetonitrile. Therefore, a PVA solution containing concentrated AgNP and 40%vol of polyynes in ACN was electrospun and analyzed. SERS spectra reveal once again the presence of polyyne signals (found also in a spin coated film); evolution in time measurements proved the existence of a significant response up to 40 days, even if a decrease in signal intensity was observed (Figure 6).

Moreover, a superficial SERS detection was performed, to compare results with the ones found with C_4Cl polyynes (Figure 4); a drop of a polyynes mixture in ACN, with a concentration of approximately 10^{-6} mol/L, shows higher SERS intensity than the drop of C_4Cl at 10^{-4} mol/L, confirming once gain the better enhancement experienced by hydrogenated chains. The last investigation was conducted by embedding HC_8H polyynes (form HPLC separation) in the nanofibers. Samples preparation was done as in
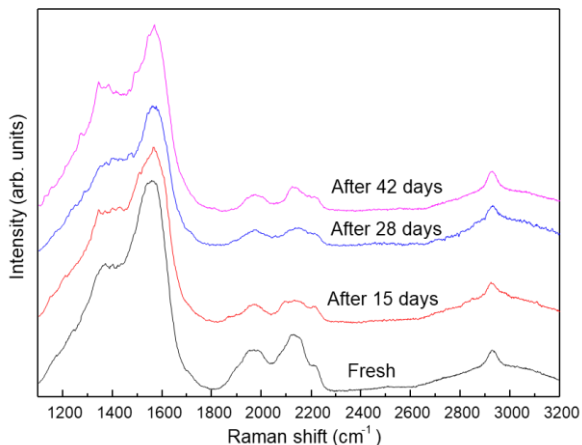
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Figure 6 Time evolution of SERS spectra for nanofibers embedding polyynes in ACN

the previous case (exploiting concentrated AgNP). SERS spectra show a surprising strong polyynic response, characterized by three well-defined sharp peaks (Figure 7). Peaks positions are in good agreement with other SERS measurements of the same polyyne [3]. Signal presence was verified up to 30 days.

In conclusion, electrospun nanofibers with concentrated AgNP showed to be highly effective in detection of embedded hydrogenated polyynes mixtures and size-separated chains.
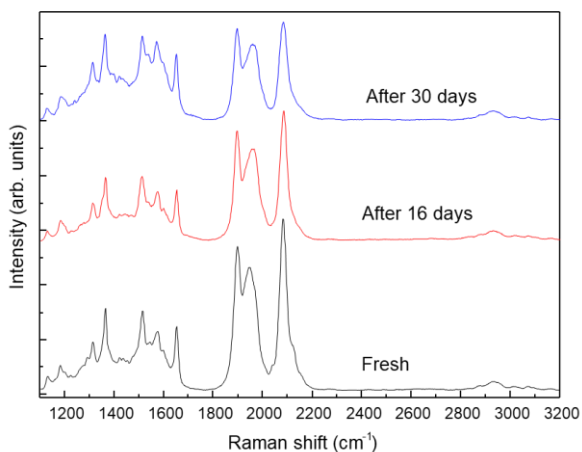

Figure 7 Time evolution of SERS spectra for nanofibers embedding HC_8H polyynes

4. Conclusions

In this thesis, the investigation of two different endcapped polyynes, embedded in electrospun nanofibers, was performed. The low concentration of analytes required the exploitation of Surface Enhanced Raman Scattering effect. The experimental work consisted in testing various samples configurations with the purpose of finding the most efficient method for polyynes detection. Even if the analysis of halogenated polyynes (C_4Cl chains) was achieved in solution and PVA films, the tests performed with polyynes integrated in nanofibers did not bring any satisfying result. On the contrary, one sample configuration proved to be extremely successful for the detection of hydrogenated polyynes: SERS response of polyynes was clearly observed embedding them in PVA nanofibers produced from a solution with concentrated AgNP. The investigation was conducted for polyynes mixtures from ablation in water and ACN, and for a solution containing size-selected chains (HC_8H). These results demonstrated that it is possible to integrate and detect low concentrated polyynes, obtained from a physical method (PLAL), in electrospun nanofibers. Moreover, they open to the possibility of adapting this configuration for the detection of other polyynic systems. The comparison between hydrogenated and halogenated polyynes behavior suggests the existence of a different interaction with silver nanoparticles. It is possible to suppose that endgroups role is determinant in favoring or not the SERS enhancement; a more focused investigation could be the aim of future works.

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