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Polyacetylene Prepared by Chemical Dehydration of Poly(Vinyl Alcohol)

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Abstract: Recently, polyacetylene (PA) has been receiving renewed scientific attention due to its electrical properties, potentially useful for energy applications (e.g., fabrication of electrodes for rechargeable batteries and supercapacitors), and unique functional characteristics (e.g., gas trap, oxygen scavenger, EMI shielding, etc.). This chemical compound can be obtained in the form of polyacetylene–PVOH copolymers simply through the chemical dehydration of poly(vinyl alcohol) (PVOH), which is a very common type of polymer, widely used in packaging and other technological areas. This very inexpensive chemical reaction for the large-scale synthesis of PA/polyvinylenes is investigated by reacting PVOH with sulfuric acid at room temperature. In this process, PVOH, shaped in the form of a film, is dipped in sulfuric acid (i.e., H_2SO_4 at 95%–97%) and, after complete chemical dehydration, it is mechanically removed from the liquid phase by using a nylon sieve. The reduction process leads to a substantial PVOH film conversion into PA, as demonstrated by infrared spectroscopy (ATR mode). Indeed, the ATR spectrum of the reaction product includes all the characteristic absorption bands of PA. The reaction product is also characterized through the use of UV–Vis spectroscopy in order to evidence the presence in the structure of conjugated carbon–carbon double bonds of various lengths. Differential scanning calorimetry (DSC) and thermogravimetric analysis are used to investigate the PA solid-state cis–trans isomerization and thermal stability in air and nitrogen, respectively. XRD is used to verify the polymer amorphous nature.

Keywords: polyacetylene; polyenes; polyvinylenes; polyvinylalcohol; chemical dehydration; sulfuric acid; infrared spectroscopy; optical spectroscopy; isomerization; thermal analysis (DSC; TGA); XRD

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1. Introduction

Among the electrically conductive organic materials, polyacetylene (i.e., -[CH=CH]$_n$-) is the first intrinsically conductive polymer to have been developed. Initially, only the cis and trans isomers with undoped conductivity values of 10^{-11} and 10^{-6} $\mathrm{ohm}^{-1}\cdot\mathrm{cm}^{-1}$, respectively, have been studied. In the most famous synthesis scheme, polyacetylene (PA) was obtained by Zielgler–Natta through the polymerization of acetylene [1]. A polymeric film formed on the surface of the glass reactor following exposure of the acetylene gas to a titanium salt catalyst. Subsequently, several complex chain and step polymerization methods for the highly regular PA synthesis have been developed (e.g., ring-opening metathesis polymerization from precursor, reverse Diels–Alder reaction processes, modified Ziegler homogeneous, radiation polymerization) [1].

Polyacetylene (PA) has very attractive electrical and nonelectrical properties, potentially useful for different technological applications. In particular, the good electrical conductivity of doped PA can be advantageously exploited in the field of energy for fabricating electrodes for rechargeable batteries, current collectors, supercapacitors, etc. [2,3]. The most important drawback in relation to PA technological exploitation is represented by the very poor processability of this polymer type, followed by its complete insolubility in organic solvents and failure to yield a molten phase upon heating. However, this problem could be overcome by generating PA through chemical transformation of an easily processable polymeric precursor. In this case, the polymeric precursor is first shaped based on the required geometry (e.g., planar electrode) and then this piece is chemically converted into polyacetylene. In this respect, there are a few little-known approaches for PA synthesis that use the conversion of a polymeric precursor into PA. These approaches are based on the dehydrohalogenation of polymers [4] and on polyvinyl alcohol (PVOH) thermal dehydration [5–7]. The dehydrochlorination of poly(vinyl chloride) (PVC) through treatment with a very strong base (e.g., $t\text{-BuO}^-K^+$) in a polar medium is the first example of PA synthesis based on the reduction of a plastic precursor; however, this elimination reaction never reaches completion and, therefore, is unsuitable for producing a highly electrically conductive material. Conversely, the PVOH thermal dehydration used for PA film synthesis [5,6] has shown great technological potential because it leads to a high yield conversion. Before the discovery of the PA Ziegler–Natta synthesis, it had been found that extended polyenic groups, $(\text{-CH=CH–CH=CH-})_n$, at that time named 'polyvinylenes', could be generated in polyvinyl alcohol (PVOH) molecules simply by exposing the polymer to a very common chemical dehydrating agent, known as fuming sulfuric acid (H_2SO_4) [8]. This chemical treatment leads to the formation of whole PA molecules by operating under H_2SO_4 refluxing conditions for a few days. A great potentiality of this very simple chemical approach is represented by the possibility to control the heterogeneous reaction conversion degree. For example, the process of solid PVOH reduction to PA can be ended at a desired conversion degree by slightly diluting the sulfuric acid or by acting at room temperature for different time periods. The whole PVOH conversion into PA can occur only under very drastic dehydration conditions (i.e., hot/boiling fuming sulfuric acid), while polyene–PVOH copolymers (i.e., $\text{-(CH=CH)}_n\text{–(CH}_2\text{–CH(OH))}_m\text{-}$, with $n > m$) are usually achieved through polymer dehydration treatments based on H_2SO_4 aqueous solutions. Thus, depending on the H_2SO_4 concentration and reaction temperature, different polyene/PVOH ratios are possible in the final linear macromolecular product. The physical properties (color, fluorescence, isomeric composition, etc.) of these polyene–PVOH copolymers significantly differ and, consequently, the obtained polymeric product is suitable for numerous technological applications (color filters, fluorescent plastics, molecular memories, etc.).

In particular, at rather high concentrations ('fuming conditions'), sulfuric acid contains a small percentage of sulfuric anhydride (SO_3), with this in situ generated chemical species constituting an extremely strong dehydrating agent. As it is well known, fuming sulfuric acid is capable of acting on alcohols and polyols at 140–180 °C to generate olefins and polyenes [9]; also, carbohydrates are readily converted into carbon materials through dehydration with fuming sulfuric acid at room temperature [10]. Similarly, sulfuric acid can act on the hydroxyl groups present in the linear PVOH molecules to generate conjugated polyenic groups of different extensions in the molecular chain, up to the limit case of a whole PA molecule formation. In this case, a hydrocarbon (C_nH_n) is obtained instead of a carbon material, as PVOH has a hydrogen content slightly higher than that of carbohydrates. Indeed, one H_2O molecule per carbon atom is contained in carbohydrates (the carbohydrate formula can be written as: $C_m(H_2O)_n$, with $m = n$ or very close) and, therefore, pure elemental carbon results from their dehydration. Concerning the exact type of chemical species acting as a dehydrating agent under such drastic reduction conditions (i.e., highly concentrated sulfuric acid), a compound named pyrosulfuric acid ($H_2SO_4.xSO_3$), also known as disulfuric acid ($ySO_3.H_2O$), should be present. However, when PVOH dehydration takes place under milder conditions, for example, under treatment with H_2SO_4 aqueous solutions (e.g., 50% by volume of H_2SO_4) at room temperature, sulfuric anhydride (SO_3) is not present, and only protons/hydrogenions (H^+, H_3O^+) are involved in the dehydration process. Consequently, acid solutions lead to a mild PVOH reduction to polyene–PVOH copolymers and, during this reaction, a chemical cross-linking process with condensed sulfate bridge formation could also take place [11].

Here, the fabrication of small PA pieces through chemical dehydration of conveniently shaped PVOH films with H_2SO_4 at room temperature is investigated. PVOH is a hydrophilic polymer, highly soluble in polar solvents like water and ethanol. A number of coating technologies (spray, solution casting, dip coatings, spin coatings, etc.) can be conveniently adopted to deposit thin PVOH layers on chemically resistant hydrophilic substrates (e.g., glass, ceramics, polymers). Aqueous PVOH solutions can be used also as an ink to achieve coating layers of complex geometry. The possibility to quantitatively convert these PVOH films into a PA layer through exposure to sulfuric acid at room temperature allows to effectively overcome the problem of the extremely poor PA workability. Many substrates are resistant to sulfuric acid and, therefore, can be conveniently used for such a purpose. This process can be usefully exploited for the preparation of electrode materials, lithium anode coatings, and separators for supercapacitors and rechargeable batteries. In order to prove the formation of amorphous cis-PA isomer and quantify its amount, the dehydration product is characterized by using spectroscopic techniques (ATR and UV–Vis), X-ray diffraction (XRD) and thermal analysis (DSC and TGA).

2. Experimental Part

2.1. Materials and Methods

The poly(vinyl alcohol) (PVOH) was provided by Aldrich Chemistry (St. Louis, MO, USA). This chemical product was a semicrystalline powder prepared via complete hydrolysis of the poly(vinyl acetate) (PVAc); indeed, the hydrolysis degree was greater than 99%. The PVOH molecular weight was M_W = 89,000–98,000. Sulfuric acid (H_2SO_4) was provided by J.T. Baker and had a sulfuric acid content of 95%–97% by weight. Both reactants were used without further purification treatments.

PVOH was dispersed into H_2SO_4 under stirring at room temperature. According to the white powder change into a reddish-brown/black solid mass, the dehydration reaction took place immediately. During the process, H_2SO_4 was largely absorbed by the PVOH grains and a PVOH/H_2SO_4 gel was formed. The starting PVOH/H_2SO_4 gel rapidly evolved into a new gel made of a PVOH–PA copolymer and sulfuric acid, and further H_2SO_4 was absorbed. When the dehydration process reached completion (full conversion of PVOH into PA), H_2SO_4 was stripped via the addition of distilled water.

In order to easily isolate the product (reduced polymer, adequately shaped) from the very aggressive (i.e., strong and hygroscopic acid) liquid medium at the end of the dehydration process, this heterogeneous reaction was preferentially performed by reacting PVOH in the form of films. Indeed, in this case, the reduced PVOH film could be mechanically separated from the liquid phase, for example by using a plastic (nylon) sieve. In particular, PVOH films with the desired thickness (ca. 0.5 mm) were prepared using the solution casting technique. The PVOH semicrystalline powder was dissolved in hot, distilled water (3 g of PVOH in 30 mL of H_2O at 70 °C) and the obtained stable aqueous solution was cast into a petri dish. After water evaporation, the achieved films were cut into small pieces and successively dried in an oven under vacuum (3 h at 60 °C) in order to achieve a completely dried solid reactant. During the heterogeneous reaction (polymeric films dipped in H_2SO_4 without stirring), the formation of extended polyenic groups in PVOH caused a slow darkening of the initially transparent and colorless films (a copolymer: $-(CH=CH)_n-(CH_2-CH(OH))_m-$ with $n >> m$ was obtained). In particular, the films were swollen as a result of the sulfuric acid absorption and became gradually reddish-brown and then reddish-black colored. Such darkening process can be attributed to the formation of chromophoric groups in the PVOH films with nonselective optical absorption in the visible spectral region. These chromophores consisted of both conjugated carbon–carbon double bonds and some isolated olefinic groups in the macromolecular backbone. When the darkened residual films were removed from the reaction medium, they had a gelatinous consistency because of the swelling phenomenon caused by the absorbed sulfuric acid.

In a typical preparation, the film was reacted for one week at room temperature, the reduced solid material (swollen by H_2SO_4) was mechanically separated from the polyene/H_2SO_4 liquid solution, and, in order to eliminate residual sulfuric acid, it was repeatedly washed, first with distilled water and then with ethanol in the presence of ultrasounds. While the reduced film was air drying, a significant volume decrease occurred. Figure 1A shows a piece of dehydrated PVOH film after the washing/drying treatment. Over time, a little amount of sulfuric acid became segregated to the surface of the solid phase, probably because of a progressive H_2SO_4 release from the solid material. In addition to the solid-state PVOH dehydration, a small fraction of this polymeric reactant (probably the PVOH low-molecular-weight fraction) dissolved in the viscous liquid (H_2SO_4), thus leading to a progressively increasing coloration of the liquid phase. Like the solid phase, the liquid medium coloration changed to reddish-brown and then to reddish-black because of the presence of reduced oligomers dissolved in it (see Figure 1B). This remaining part of the produced PA was recovered from the reactive medium by precipitating the polymer with distilled water (with stripping of H_2SO_4 from it). In particular, the reactive medium was added dropwise to distilled water under magnetic stirring (typically, 80 mL of liquid medium was dissolved in 300 mL of distilled water), and a PA flocculation process followed. The flocculated PA was separated by vacuum filtration on a paper filter (Whatman filter papers no.2, hydrophilic membrane). In order to completely remove residual sulfuric acid from this product, it was washed repeatedly with distilled water and ethanol and then recovered from the filter using a spatula and left to air dry.

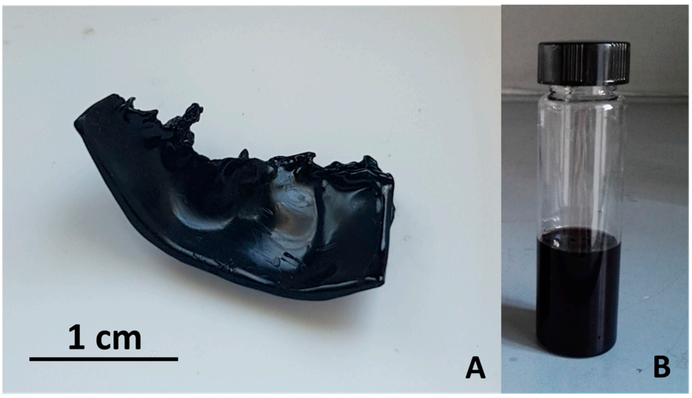

Figure 1. Piece of synthesized PA as isolated from the reaction medium (**A**) and sulfuric acid containing the dehydrated PVOH oligomers (**B**).

2.2. Instrumentation

Infrared analysis of the PA samples (ATR mode) was performed by using a Fourier-Transform Infrared Spectrometer (FT-IR) (PerkinElmer, Frontier NIR with micro-ATR, Milan, Italy). Optical characterization of the absorption process was performed using a double-beam UV–Vis spectrophotometer (VWR, UV-6300PC, Wuhan, China). In particular, distilled water, H_2SO_4, and H_2SO_4 aqueous solution (50:50 by volume) were used as both solvents and reference systems for pristine PVOH, PA, and polyvinylene, respectively. Quartz cuvettes were used for optical tests. The solid-state cis–trans isomerization of PA samples was investigated using differential scanning calorimetry (DSC, PerkinElmer, Discovery), and the PA thermal stability was investigated by thermogravimetric analysis (TGA) (Q500, TA Instruments). The electrical properties of the PA sample thin films (0.2 mm) were measured by using an LCR meter (UT612, Uni-Trend Technology, Dongguan, China). In particular, the copolymer was deposited on a paper substrate. Four different samples were prepared for electrical measurements with electrodes made using silver paint (XeredEx, XD-120, SGS, Shenzhen, China). Five electrical measurements were made for each sample. Electrical measurements were performed using a sinusoidal signal with a frequency of 1 kHz, at room temperature and in a chamber with dry air. Both surface conductivity and bulk conductivity were measured, obtaining results close to the values given in the literature [1]. XRD characterization was performed using an X'Pert-PRO powder diffractometer (PANalytical, Oxford, UK), with Cu $K_{\alpha 1}$ radiation.

3. Results and Discussion

At the beginning of the chemical dehydration process, the PVOH films turned a purple color, which was slightly fluorescent and characterized by a white emission when observed under the UV light of a mercury vapor lamp (TLC lamp, short wave: 254 nm) (see Figure 2A,B). Such a visible coloration/fluorescence phenomenon, which decreased and then disappeared with the progression of the PVOH conversion into PA, has been already described in the literature for thermally dehydrated PVOH films [12]. The visible coloration/fluorescence of partially reduced PVOH could be ascribed to the initial formation of short chains of conjugated carbon–carbon double bonds (i.e., dienes, trienes, etc.). The final polymeric sample was a rubbery black solid with a density higher than that of water (relative density: 1.2). The dry reaction product (deposited on a paper substrate) was found to be electrically conductive and behaved like a highly resistive material (ca. 287.0 ± 0.7 kΩ/sq. at 1 kHz), as measured by an LCR meter.

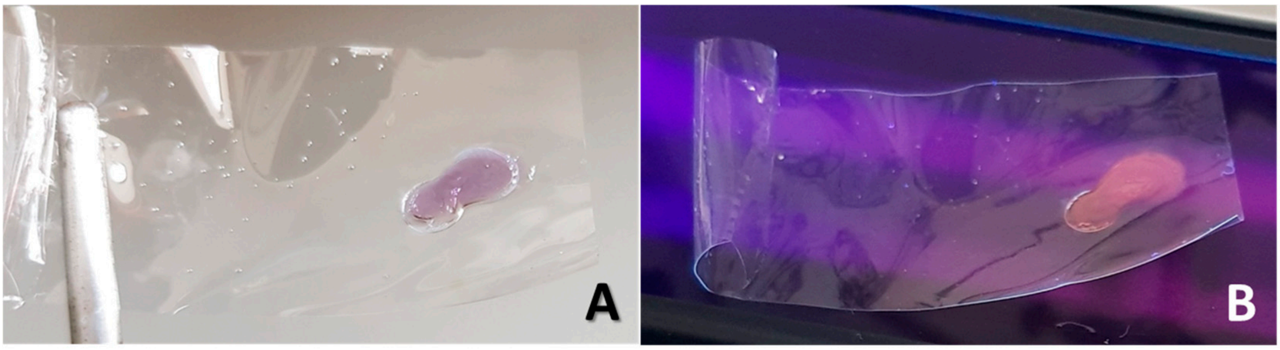

Figure 2. A drop of sulfuric acid dyes a PVOH film purple (**A**), with this colored spot also appearing to be fluorescent (white-emitting) under UV light (254 nm) exposure (**B**).

Since the synthesized PA was insoluble in all types of organic solvents (e.g., chloroform, acetone, ethanol), its characterization was conducted at the solid state. In particular, the degree of PVOH conversion into polyene molecules was established by ATR analysis of the solid reaction product. Spectroscopic analysis is very sensitive to the presence of adsorbed water molecules, which produce a strong and broad signal at 3400 cm^{-1} (OH stretching vibration) and a medium-intensity signal at 1650 cm^{-1} (HOH bending vibration) [13], with these two bands possibly obscuring important sample information within the mid-IR spectrum. Therefore, the reaction product was adequately dried before ATR-mode analysis by mildly heating the sample under vacuum, first at 40 °C for 8 h and then at 60 °C for 3 h. The ATR spectrum of the pure dehydrated product is shown in Figure 3A. The incomplete reduction of the polyalcohol to an unsaturated hydrocarbon is readily noticeable, owing to the presence of residual hydroxyl groups (OH) absorption in the spectrum. Indeed, these groups produced the characteristic intense and broad absorption band as a result of the O–H stretching vibration, which was centred at 3398 cm^{-1}. Such absorption was accompanied by the small intensity absorption band caused by the C–O stretching vibration at 1041 cm^{-1} and a less intensive OH bending vibration band located at 1250 cm^{-1}. The small IR resonance appearing at 2934 cm^{-1} was generated mainly by the terminal methyl groups, which were present also in the PA molecules; however, the stretching vibration of methylene/methine groups in the residual PVOH may have contributed. Such aliphatic groups also generated bending vibrations appearing at 1039 cm^{-1}. As for the case of -OH stretching, these signals had strongly reduced intensities compared to that in the pristine PVOH spectrum (see spectral comparison in Figure 3B). However, the IR spectrum of the reduction product also showed clear evidence of conjugated olefinic group formation. Indeed, the IR spectrum of the dehydration product contained the four main characteristic absorption bands generated by conjugated olefinic groups: conjugated carbon–carbon double bond (C=C) stretching vibration, conjugated C–C single bond stretching vibration, in-plane =C–H olefinic (vinyl) =C–H bending vibrations, and out-of-plane olefinic =C–H bending vibrations [14–19]. In particular, the C=C stretching vibration band appeared at a wavenumber of ca. 1632 cm^{-1} and was characterized by medium intensity absorption. This band extended over a wide spectral region (from ca. 1602 cm^{-1} to ca. 1705 cm^{-1}) because the conjugation phenomenon variously extended in the linear polymer chains and even isolated C=C could be present in these molecules. In particular, the wavenumber of the carbon–carbon double bond absorption band decreased with the extent of conjugation, since the bond order (i.e., force) decreased. On the other hand, owing to the same conjugation phenomenon, the C–C single bond stretching absorption appeared at a higher wavenumber (i.e., 1387 cm^{-1}), with an absorption band of rather high intensity. Very intensive absorption bands were also generated by the in-plane =C–H bending resonance, visible at 1192 cm^{-1}, and by the out-of-plane (oop) =C–H bending absorptions, located at 851 cm^{-1} for the cis isomer and 902 cm^{-1} for the trans isomer. In particular, the comparison between the intensities of these =C–H oop bending vibration bands allows to easily distinguish the product between cis and trans isomers [17]. In the present case, both isomers seemed to be present in the dehydrated product; however, according to the band intensities, conformation mostly corresponded to the cis type. The generated molecular structure should largely consist of cis PA, also because cis alkenes have a nonsymmetric structure and, therefore, are capable of absorbing more strongly than trans alkenes at 1632 cm^{-1}, as found with respect to our sample. It must be pointed out that polyenes should also show vinyl =C–H bond stretching absorption, appearing at ca. 3080 cm^{-1}; however, in our PA sample, this band was probably obscured by the broader residual hydroxyl absorption centered around ca. 3000 cm^{-1} (stretching vibration). Yet the carbon–carbon double bond (C=C) bending vibration is typically located outside the explored infrared spectral region (i.e., below 400 cm^{-1} [14]). Finally, comparison between the ATR spectra of pristine and dehydrated PVOH, shown in Figure 3B, clearly evidences that the most intensive absorption bands of the two compounds did not correspond. The sulfuric acid treatment caused variations in the intensity and position of bands and the appearance of completely new absorptions corresponding mostly to that of a cis-rich PA sample.

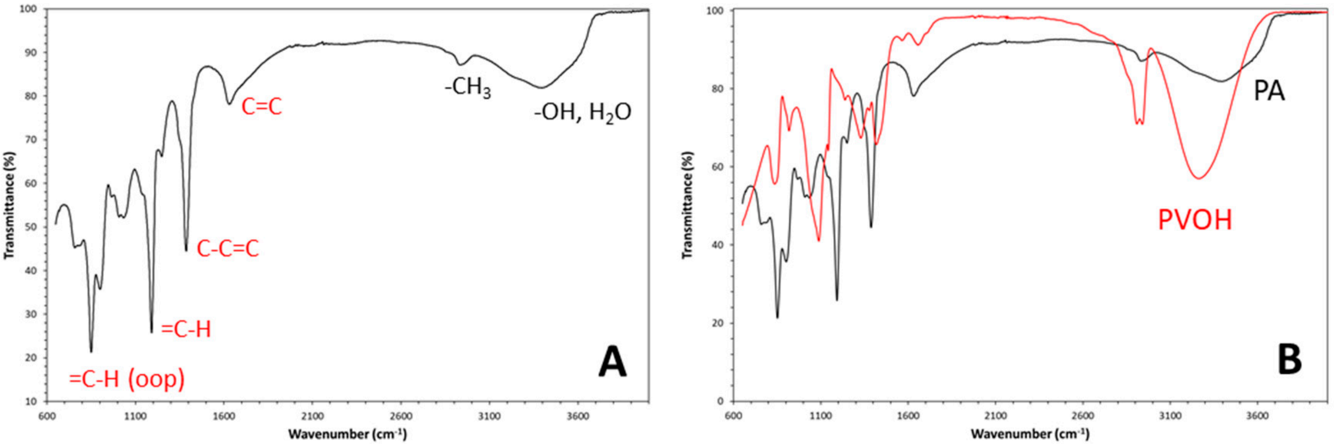

Figure 3. ATR spectrum of dehydrated PVOH film (**A**) and overlap between PVOH and dehydrated PVOH spectra (**B**).

Similarly, the process of PVOH dehydration caused a drastic change to the optical properties of the polymeric material. Indeed, the perfectly transparent and colorless PVOH film shows an optical absorption spectrum, measured on PVOH aqueous solution using a double-beam UV–Vis spectrophotometer, with no absorption peaks above 400 nm (see the red curve in Figure 4A). This type of spectrum indicates the absence of conjugated carbon–carbon double bonds as defects in the original polymeric sample. Conversely, the spectrum of the dehydrated fraction recovered from the liquid phase showed a broad and strong absorption band in the visible spectral region whose exact profile strictly depended on the dehydration extent. In particular, as it can be seen from Figure 4A, this electronic absorption spectrum of PA was characterized by a wide absorption band, which extended over the 250–600 nm spectral range and was generated by the convolution of five main elementary absorptions with maxima located at 272 nm, 324 nm, 433 nm, 489 nm, and 589 nm, generated by π→π* electronic transitions. These elementary bands correspond to the optical absorption of the generated linear polyenes, which are characterized by a variable number of conjugated carbon–carbon double bonds as predicted by the Fieser–Kuhn law [20]. In particular, the positioning of some bands up to a rather high wavelength value indicates the presence in the product of polyvinylene unities with highly extended conjugation (higher than 14 carbon–carbon double bonds). The observed UV–Vis absorption bands exhibited exactly the optical behavior usually ascribed to PA [21] (these spectra were obtained by using sulfuric acid as both a dispersing medium for the PA molecules/nanoparticles and a reference).

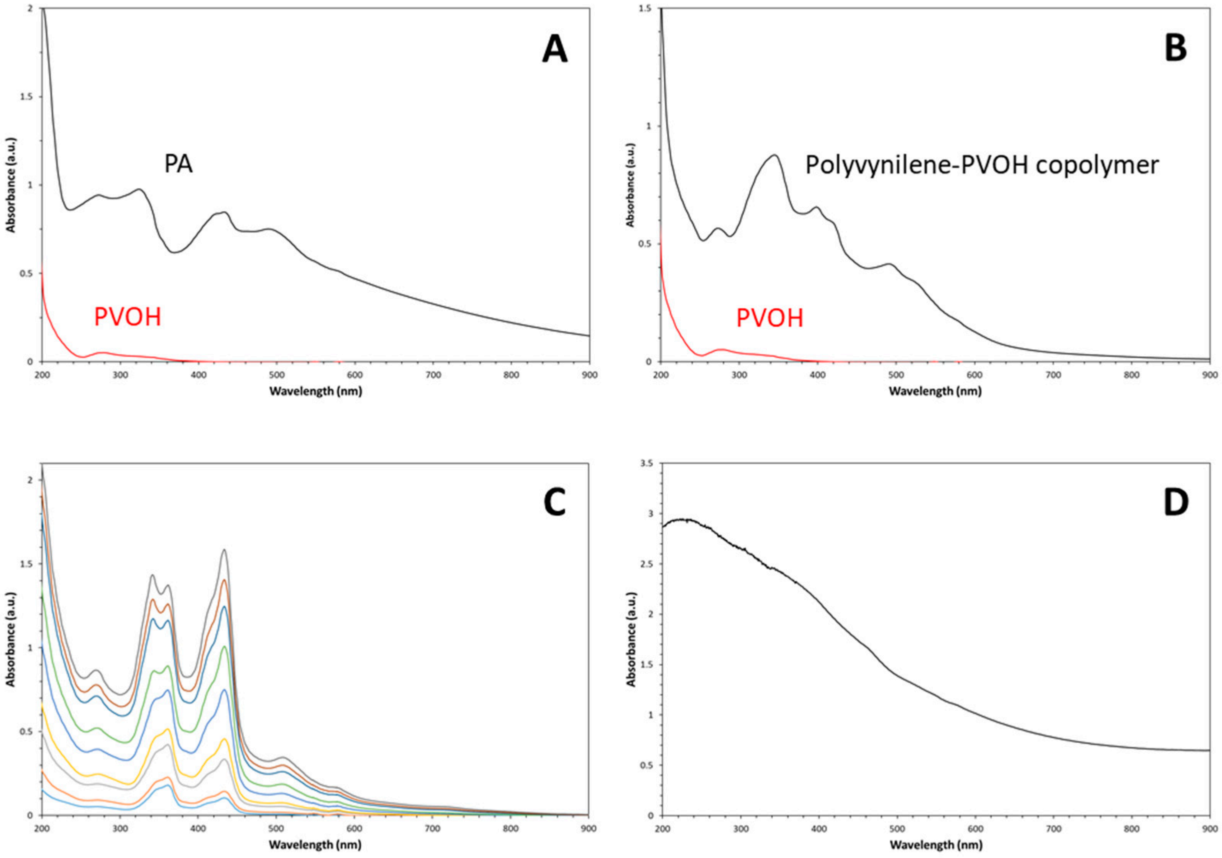

Figure 4. UV–Vis spectra of the starting PVOH film (H_2O was used as solvent/reference) and reaction product in liquid phase (H_2SO_4 was used as solvent/reference) (**A**); comparison between PVOH and polyene UV–Vis spectra (H_2SO_4 aqueous solution 50:50 by volume was used as solvent/reference) (**B**); temporal evolution of UV–Vis spectrum of the reactive liquid phase (spectra were recorded at time intervals of 15 min, using H_2SO_4 as reference) (**C**); UV–Vis spectrum of the solid phase (**D**).

Polyenes obtained by reacting PVOH with H_2SO_4 aqueous solutions (e.g., 50% by volume of H_2SO_4) showed a rather similar UV–Vis spectrum (see Figure 4B). Owing to the different dehydration conditions, the absorption maxima were distributed differently. The temporal evolution of the optical spectrum of the liquid phase during the chemical dehydration reaction using H_2SO_4 at room temperature is shown in Figure 4C; these spectra were acquired at time intervals of 15 min. According to the distribution of peak intensities in the spectra shown in Figure 4A–C, highly conjugated carbon–carbon double bonds were much more abundant in PVOH films treated with H_2SO_4 compared to those in samples subjected to dehydration with a concentrated H_2SO_4 aqueous solution (50% by volume of H_2SO_4). The optical spectrum of the purified PA solid film is shown in Figure 4D. As it can be observed, the absorbance spectrum showed a continuum absorption band, covering half of the visible spectral region, and was characterized by a barely visible fine structure.

Solutions of the PVOH–PA copolymer in H_2SO_4 optically behaved according to the Fieser–Kuhn equation, written with numerical coefficients adequate for this molecular structure. In particular, the mathematical expression capable to predict the spectral properties of the PVOH–PA copolymers assumes the following parabolic form [20]:

$$\lambda_{\text{max}} = -1.7\text{n}^2 + 48\text{n} + 124 \tag{1}$$

where λ_{max} is the wavelength of the electronic absorption band maximum and n is the number of conjugated carbon–carbon double bonds contained in the copolymer blocks. Indeed, the PVOH blocks present along the linear copolymer molecules did not contribute to the electronic spectrum, because they had only $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ electronic transitions that fell outside the experimentally measured ultraviolet spectral region (i.e., below 190 nm). Only the various polyene families in the copolymer chains, which are characterized by different lengths, may contribute to the optical spectrum. In particular, the above mathematical law predicts an increase in the wavelengths of absorption maxima of polyene bands up to 14 conjugated carbon–carbon double bonds and then a decrease in the absorption band maximum wavelength. In particular, with the increase in polyene block extension (n) from one to 14, the band moves from the ultraviolet spectral region (UV–A) to the middle of the visible spectral region, while it comes back to the blue region and then to the ultraviolet spectral region with further increases in the polyene block extension (i.e., n > 14). A graphical representation of the absorption band wavelength vs. the number of carbon–carbon double bonds present in each polyene unit is given in Figure 5.

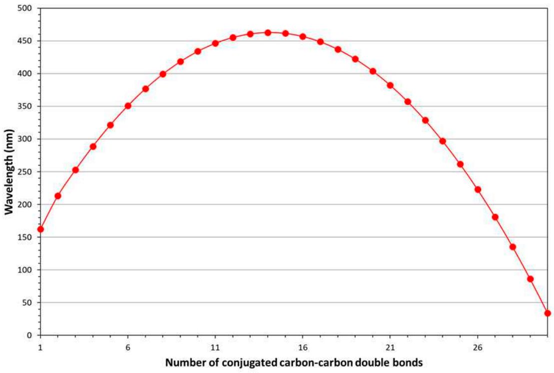

Figure 5. Behavior of the polyene block absorption wavelength (electronic band peak) with the number of carbon–carbon double bonds in the block.

The unique optical absorption features of the prepared copolymer could allow for the development of very useful optical devices like the optical limitators, attenuators, and high-pass filters (that is, optical media quite transparent in the NIR spectral region and fully opaque to the visible and ultraviolet electromagnetic radiations). The variable conjugation of the carbon–carbon double bonds generate multiple absorption bands (named 'elementary absorption bands') that are located close to each other; indeed, these elementary bands are centered around wavelength values differing only by a few tens of nanometers. The high concentrations of different families of conjugated C=C in the solid copolymer cause elevated values with respect to the optical extinction coefficients, which represent an essential characteristic for the generation of a saturation absorption band.

According to the differential scanning calorimetry (DSC) thermogram (1st run, 10 °C/min) shown in Figure 6, the obtained chemical product underwent an exothermic thermal transition in the 100–150 °C temperature range. Such an exothermic transition should correspond to a solid-state cis–trans isomerization [17], which consists of the conversion of the synthesized cis isomer into the more thermodynamically stable trans isomer. However, this thermally activated solid-state transition is characterized by a complex behavior; indeed, the exothermic signal is superimposed on an endothermic signal. The phenomenon starts as an exothermic process (I step of thermal activation in the range of 100–150 °C), but an endothermic signal (II step from 150 °C to ca. 220 °C) immediately follows. Such endothermic peak shows a complex profile, consisting of the overlap of three different endothermic signals that are probably produced by phenomena like the evaporation of contaminants (sulfuric acid, water, and other solvents trapped in the PA crystalline structure) and/or the thermal dehydration of residual PVOH blocks.

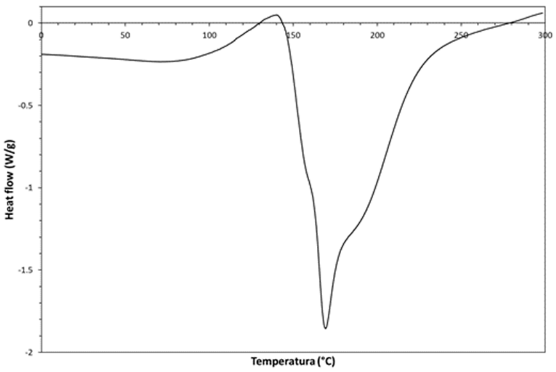

Figure 6. DSC thermogram (1st heating run) showing the solid-state cis–trans isomerization of the synthesized PA.

Obviously, such a thermal behavior is an irreversible phenomenon; indeed, as shown in Figure 7A,B, there were no signals in the subsequent DSC cooling/heating runs performed on the same DSC specimen (a thermal decomposition is visible in Figure 7B, at temperatures above 300 °C). Indeed, the generated trans-PA isomer could melt (and completely decompose) only above the investigated temperature range (i.e., at ca. 467 °C [22]). Owing to these unique thermal properties of the synthesized cis PA, the material could be technologically exploited to develop new types of thermally activated molecular memories [23].

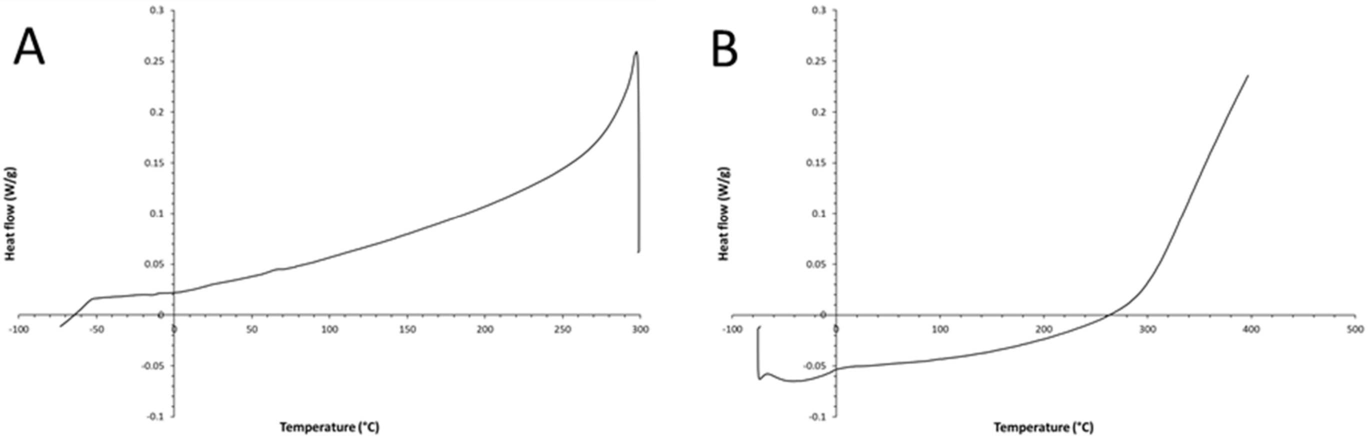

Figure 7. DSC thermograms (second and third runs): sample cooling thermogram from 300 °C to −80 °C (10 °C/min) (**A**) and sample heating thermogram from −80 °C to 400 °C (10 °C/min) (**B**).

The synthesized cis PA was investigated also by thermogravimetric analysis (TGA), both in fluxing nitrogen and air atmospheres, in order to evaluate its thermal stability, possible solvent or reactant release, etc. As it can be observed from Figure 8, TGA thermograms in air and nitrogen showed a rather similar behaviour, characterized by two weight losses occurring at different temperature values. The first weight loss was centered around ca. 150 °C and it was probably caused by different phenomena, for example, the thermal dehydration of residual PVOH blocks present in the copolymer chain, the elimination by evaporation of H_2SO_4 molecules trapped in the copolymer, etc. The second weight loss was centered around ca. 450 °C and it could be related to molecular hydrogen elimination from the PA molecules [24]. Therefore, the mechanism of thermal decomposition should be the same, independently of the type of adopted atmosphere. The ratio between these two weight variations depends on the conversion degree of the chemical dehydration process, product purification level, etc. The residual weights in the two thermograms had different values (0.05 mg in air at 964 °C) and, according to these values, the synthesized PA sample was characterized by an exceptional thermal stability in a nitrogen atmosphere. Indeed, 30%–40% of the polymer endured a temperature of ca. 1000 °C under nitrogen (and up to ca. 500 °C under fluxing air). Such a behaviour could be explained on the basis of a 'quasi-carbon' nature of this type of polymer.

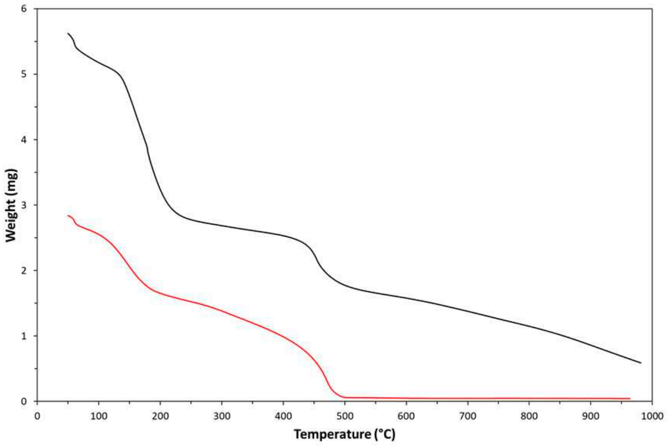

Figure 8. TGA thermograms of the synthesized cis polyacetylene sample under fluxing air (red curve) and nitrogen (black curve).

Figure 9 shows the XRD analysis of PVOH before and after the dehydration process. As it is visible in Figure 9A, the XRD pattern of pure PVOH was characterized by two characteristic broad peaks at ca. 19.5° and 38.6°, owing to the semicrystalline nature of this polymer. The main peak corresponded to the PVOH (101) crystal plane. The crystalline nature of PVOH was the result of the strong intermolecular interaction between the PVOH chains through hydrogen bonding. According to the XRD diffractogram of the PA sample shown in Figure 9B, the achieved polymer was an amorphous solid completely free from any crystalline signals.

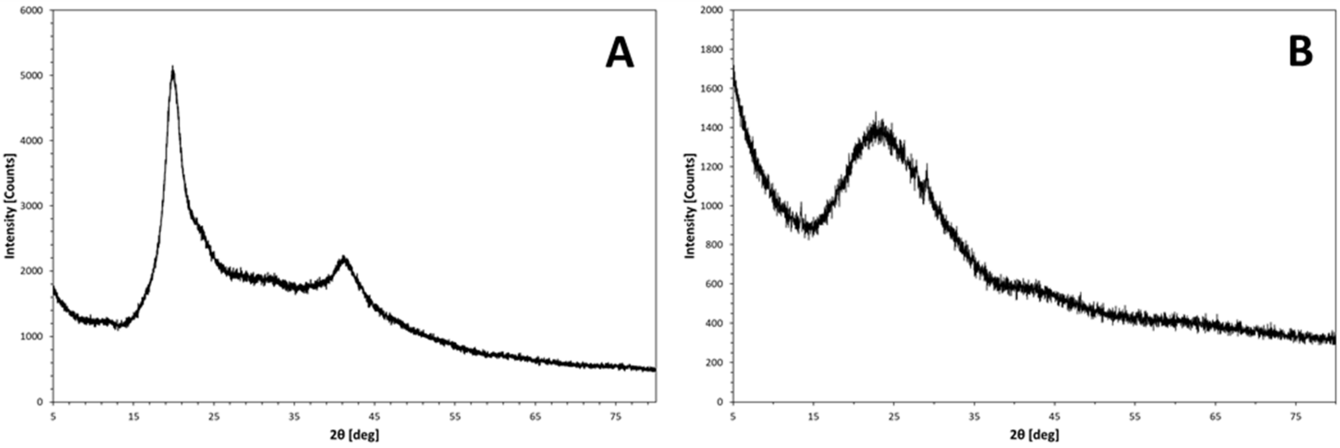

Figure 9. XRD of the starting PVOH (**A**) and PVOH dehydrated by using sulphuric acid (**B**).

4. Conclusions

A quantitative conversion of PVOH into PA occurred during the chemical treatment of the polymeric precursor by using sulfuric acid at room temperature. The IR spectral assignments showed that the chemically synthesized compound mostly corresponded to a cis-rich PA sample with a little amount of residual alcoholic blocks (PVOH) along the linear macromolecules. DSC confirmed the conformational hypothesis based on the ATR data; indeed, the exothermic signal characteristic of the solid-state cis–trans isomerization appeared in the DSC thermogram, and this transition extended over the 100–150 °C temperature range. The presence of residual sulfuric acid in the obtained dehydrated PVOH was also hypothesized based on the weight loss observed in the TGA thermogram and the endothermic signal in the DSC thermogram. The UV–Vis investigation of the synthesized product showed the presence of conjugated carbon–carbon double bonds of different extensions along the polymer chain. A good surface electrical conductivity, corresponding to ca. 287.0 ± 0.7 kΩ/sq., was measured with respect to a thin layer of dehydrated PVOH deposited on paper substrate.

About the implications of this study, PA is considered to be potentially useful as a polymer principally for its very good electrical conductivity after doping that can be exploited in the energy field for the fabrication of electrodes for rechargeable batteries, supercapacitors, etc. PA films have also been used as a coating for anodes in lithium batteries in order to prevent dendrite formation, which may cause rechargeable battery explosion [25]. In addition, PA could be very useful also in other technological fields for the production of coatings, films, or filaments to be used as electrical wires, sensors, electrical collectors, etc. Owing to PA infusibility and insolubility in all organic solvents, the PVOH precursor polymer should be used to fabricate electrodes with the desired shape and then this component should be converted into the electrically conductive PA using the H_2SO_4 treatment. As described in the literature [26], PA can be produced also as a nanopowder to make possible its processing in the form of a colloidal suspension. However, PA could have a number of nonelectrical applications [19,27–30], where it is used in the form of a powder or granular material. For example, owing to the presence of a very large number of carbon–carbon double bonds, PA can be exploited for EMI shielding, as a gas trap, an antioxidant, an oxygen scavenger, an adsorbent for organic substances, a hydrogen storage medium (in a transition metal decorated form), etc. The very simple chemical reaction scheme described herein allows to produce high quality cis PA films or powders to be used for both electrical and nonelectrical applications. In addition, this approach could be used also for the recycling of PVOH plastic waste; indeed, PVOH is an appealing target for recycling because it is a high production volume polymer.

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