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(Article begins on next page)



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Crosslinking and carbonization processes in PAN films and nanofibers.

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Cast PAN films and nanofibers have been investigated as a means to study the chemical reactions that occur during the stabilization and carbonization steps in the thermal PAN to carbon conversion process. Cast films have been subjected to thermal ramps, from room temperature to 600°C in air and nitrogen, while chemical modifications were observed in situ using infrared spectra in reflection-absorption mode. The fibers were monitored across two differing thermal treatments of up to 800°C. The thermal process performed on the fibers consists of a stabilization step in air (half an hour at 250°C), followed by a carbonization step in nitrogen at up to 800°C. Chemical modifications started at temperatures over 300°C. The majority of nitriles take part in the cyclization and trimerization reactions at temperatures below 400°C. Oxygen causes the formation of oxidized species and faster effective dehydrogenation during the treatment performed in air; at the end of this treatment, the sample is closer to a graphitized structure than samples heated under nitrogen flow. The oxidation process is much more effective and chemical reactions occur during the isothermal step. The products obtained using this heating program on the nanofibers are comparable with products produced in air on film, but show a higher carbon content. A new IR signal appears around 800 cm⁻¹ in all thermal treatments. This has been attributed to substituted triazine rings formed in the trimerization of the nitrile groups of the various chains. Data supports the hypothesis of the appearance of fiber crosslinks at the beginning of thermal conversion. Infrared and Raman spectra at 800°C confirm the nanofiber carbonization process.

Keywords: Polyacrylonitrile, crosslinking, triazine, FTIR spectroscopy, carbonization, carbon nanofibers

1. Introduction

Polyacrylonitrile (PAN) is commonly used as precursor for carbon fibers production [1, 2]. Nowadays, the technological knowledge does not allow production of carbon fibers of few nanometers in diameter using the classical methods, but recently the use of electrospinning has been risen in attention, since through it, polymeric fibers of a very small diameter were produced. The consequence is the possibility of obtaining carbon nanofibers, using PAN nanofibers as precursor [3]. After this finding, many efforts were placed in research to improve a better understanding of the PAN thermal conversion process, with particular attention to the chemical reactions occurring there [4-6].

The thermal process that converts PAN fibers into carbon fibers is characterized by three main steps: oxidative stabilization, high temperature carbonization and graphitization. The oxidative stabilization is responsible of the formation of a ladder structure that allows processing of the stabilized precursor at higher temperature. This step is generally performed at low temperature (200-300°C) in air. Thereafter, heating in nitrogen up to 1600°C, the carbonization occurs keeping out noncarbon atoms, such as hydrogen, nitrogen and oxygen. Eventually graphitization, occurring by still heating in inert atmosphere up to 2000°C, improves the orientation of the basal planes and the stiffness of the fibers [5].

Both the first and second step have a significant role in the PAN conversion, since they play an important role in the formation of carbon char and in the structure of the carbon fibers.

The PAN stabilization is a complex step, because it involves several reactions, like cyclization, crosslinking, oxidation, dehydrogenation and aromatization [6-8].

To understand the reactivity of PAN during the conversion process, it is necessary to consider in particular the features of the polar nitrile group; its high dipole moment induces a specific interaction between pairs of CN. In the solid state, the intramolecular distance among CN groups is of few tenths of nanometers, so adjacent nitrile groups give an intramolecular repulsion, leading to an irregular helical conformation of the chain [9, 10]. In this conformation CN groups are potentially available for intermolecular dipole interaction. The resulting nitrile interaction is a combination of intramolecular repulsion and intermolecular attraction. In addition, the nitrile group possess a lone pair and the presence of these electrons in the π orbital of the triple bond makes it a highly reactive group [11]. These features cause a nitrile self-association that has been well-documented.

The intermolecular associations through dipole-dipole interaction were hypothesized using theoretical calculation and confirmed by experimental results performed on small organic species containing the nitrile group and on polymer chains [12, 13]. The associated species were different oligomers, including dimers and trimers. Among them, the cyclic trimers, based on the possibility of

self-association through a hydrogen bond between the nitrogen lone pair and one α -hydrogen of a neighbor molecule, is considered the most stable structure [12, 14]. About the polymer features, PAN is characterized by a glass transition temperature around 110°C and a melting point centered at 320°C [15], but normally it undergoes chemical reaction before melting. In the solid state, it is necessary to take into account these steric considerations and the orientation of both pendant groups and main chain. The tacticity of PAN is characterized by the co-presence of all the triad tacticity: iso, atactic and syndiotactic configurations are all present in the chain, in different amount depending on the polymerization route..

In literature various reactions and different structures were proposed for the oxidative stabilization and for the carbonization processes [6, 8, 16]. The mechanisms and the products formed during these two steps are still under debate and a definitive solution was not formulated.

In the presence of co-monomers the degradation is considered based on ionic mechanism, instead the PAN homopolymer is subjected to an autocatalytic radical mechanism [1, 16, 17]. High temperatures can generate free radicals due to homolytic scission of the weaker bonds contained in the chain imperfection. The most stable radical in PAN structure is produced through the abstraction of hydrogen from the carbon bearing the nitrile group. [16, 18]. This tertiary carbon radical is in equilibrium with a structure containing the odd electron on the nitrogen of the nitrile group which is responsible of the initiation reaction of cyclization through a typical propagation reaction among adjacent nitrile group of the same chain [1, 16]. In fact, the most accredited structure regards the formation of the ladder structure, in which through the propagation of the cycling, a series of condensed six member ring containing a C-N double bond is formed [16, 19], formally a cyclic polyimine structure. This propagation could also be intermolecular, leading to a crosslinked ladder structure [20]. A tautomerization of the double bond may give different partially aromatic structure, in which one double bond is distributed in different ring position, forming polyenamine [21, 22]. It was postulated also a dehydrogenation of the main chain, in some case coupled with cyclization, leading to partially aromatic structure, containing unsaturation conjugated with the CN double bond [5, 6, 23].

During the stabilization step, oxygen is not directly involved in cyclization, but it supports the dehydrogenation of the main carbon chain [16, 24, 25]. Oxygen promotes inter and intramolecular reaction, supporting intramolecular crosslink and aromatization. Various structures containing oxygen were proposed, in these structures oxygen was involved in ether bridges, in carbonyl group or in interaction with the nitrogen, through donation of the lone pair from nitrogen to oxygen atom [25]. Also intermolecular reactions were proposed: the formation of azomethine crosslink and an

intermolecular nitrile crosslink were suggested [2, 20, 26]. The crosslinked form does not allow the solubilization of the polymer.

During the carbonization step, there is the formation of condensed aromatic ring, through the condensation of a series of ladder structures. This step is accompanied by the elimination of almost all nitrogen as HCN and NH₃, of oxygen atoms as CO and CO₂, and a minor elimination of carbon as oligomers [7].

In this paper mainly the stabilization step and part of the carbonization step were considered in details, in order to understand the reactions that occur during the thermal treatment and the product formed. PAN cast films were heated up to 600°C in a heating cell using air or nitrogen atmospheres. The infrared spectra collected in situ during both heating processes were compared, in order to identify the products obtained in the two different atmospheres and to verify the role of the oxygen.

In the second part of the paper, PAN nanofibers were considered. The conversion process applied to the PAN nanofibers was a heating process performed at low temperature in air and then switched to nitrogen; similar to the stabilization and carbonization processes applied in the conventional PAN conversion. The effect of the heating was considered and compared with the results obtained on the cast film. The chemical changes and the physical modification of the fibers were considered and discussed as well.

2. Experimental section

2.1 Materials and sample preparation.

Polyacrylonitrile (PAN) powder ($M_w \sim 150,000$, $T_g \sim 100^\circ\text{C}$) and N,N-dimethyl formamide (DMF) solvent were purchased from Sigma Aldrich and were used as received.

The studies were performed on both cast films and nanofibers obtained from DMF solution of PAN (around 10% W/W). very thin PAN cast films were prepared on aluminum support, by evaporating the solvent.

PAN nanofibers were prepared using electrospinning technique on DMF solution of PAN on aluminium support. In the electrospinning process, the following parameters were used: voltage 30 kV, distance 15 cm (from needle to collecting plate), polymer solution flux 10 $\mu\text{l}/\text{min}$ and room temperature. The nanofibers network was cut out in little squares for the thermal treatments and after this, each square was subjected to infrared investigation.

2.2 Methods.

2.2.1 Heating treatment.

Heating treatment were performed for the cast films on the aluminium support on a THMS600 heating/cooling stage (Linkam Scientific Instruments Ltd.), in the heating/cooling stage either in air (60 ml/min) or in nitrogen

(60 ml/min) at 20°C/min from 25 C up to 600°C. FT-IR spectra of the film were collected *in situ* during the thermal treatment at several temperatures.

The nanofibers were heated on the aluminium support in a thermal gravimetric analyzer (Hi-Res TGA, Q500 balance, TA Inc.) (very thin thickness) at 10°C/min in air (60 ml/min) up to 250°C followed by 30 minutes isotherm (stabilization step), then in nitrogen flow (carbonization step) at 10°C/min up to 800°C or in high-resolution (Hi-Res) ramp, factor + 4, from 250°C to 800°C. To collect FT-IR spectra of nanofibers the heating was stopped at selected temperatures. The infrared measurements were performed on the treated samples cooled down to 50°C in nitrogen atmosphere

2.2.2 FTIR

All the infrared measurements were performed with a FT-IR microscope Spectrum Spotlight 300 (Perkin Elmer Instruments). in reflection-absorption mode on samples held on the aluminum support, with 4 cm⁻¹ resolution, 16 scans from 700 to 4000 cm⁻¹ and area of analysis of 100×100 μm² [27]. The chemical modifications detected by IR were correlated with the weight loss, detected with the thermal gravimetric analyzer

Spectra were collected in different and random regions of the surface to evaluate the homogeneity of the treatment and in all case the measurements were comparable to each other. It is necessary to point out that the spectra of the cast film were collected *in situ* during the thermal treatment performed with the hot stage coupled with the infrared spectroscopy; instead the spectra of fibers were collected after the treatment on samples at room temperature.

The most interesting samples were studied with ATR-FTIR Spectrum Two (Perkin Elmer Instruments) and Raman in the range 2000-400 cm⁻¹. A dispersive Renishaw Micro-Raman instrument equipped with a exciting laser line operating at 785 nm was used. The samples were subjected to the heating treatment in air up to 250°C, then after 30 minutes of isotherm, the samples were heated to 500°C or to 800°C in nitrogen.

2.2.3 Morphological analyses

A scanning electron microscopy (SEM) on a Zeiss EVO 50 with filament of LaB₆ was used. To evaluate the carbonization process, SEM measurements were performed on gold coated and also on non-coated samples. For each experiment, the average fibers diameter was determined from a series of random measurements, using the graphical software Image Tool.

3. Results and Discussion

3.1 Carbonization performed on PAN cast film

3.1.1 Thermo gravimetric analysis.

The thermo gravimetric analyses (TGA) performed in inert and oxidative atmospheres are compared in Figure 1. The thermal degradation in air of samples starts below 300°C and over 300°C in nitrogen atmosphere. In presence of oxygen, the degradation starts earlier than in nitrogen., PAN shows a first step of weight loss of

40% wt. between 300°C and 400°C under N₂ and of 24 % between 300°C and 350°C in air,. This result is comparable with that reported for commercial PAN in previous works, in which HCN and NH₃ were detected as main gaseous products, accompanied by a considerable amount of oligomers [7, 28].

The lower bond dissociation energy of PAN was reported at 297 kJ/mol for the C-C dissociation in the main chain [2], corresponding to 330°C as 30 min half weight loss temperature [29]. This behavior is comparable with the weight loss of oligomeric products observed in the TGA curves [7]. At the end of this step, either in air or in nitrogen a further step of weight loss occurs, confirming the dissociation of the C-C bond, since cyclization (19,20) does not cause weight loss. In air a residue of 1% wt. is left at 800°C. In nitrogen instead, the residue left at 800°C is 28% wt., but the curve does not reach a plateau, suggesting that this residue is not yet stable.

The effect of the heating on PAN chains is believed to involve principally cyclization and dehydrogenation (19,20) The lower temperature detected for the first weight loss under oxidative atmosphere could be explained considering that the oxygen supports the hydrogen elimination as water [16, 24].

3.1.2 Infrared evolution of the PAN during conversion in inert atmosphere

The infrared signals and their assignments for undegraded and degraded PAN are reported in Table 1 (22, 34). In Figure 2 the infrared spectra collected in situ at temperatures from 25°C to 580°C are depicted.

The cast film samples, still contains DMF which evaporates nearly at 250 °C, since the DMF signals at 1668, 1387 and 1094 cm⁻¹, detected at 25°C, disappear in the spectra run at that temperature.

The first changes in the spectra appears near 250°C, spectra collected in this temperatures show a reduction in the absorption at 2241 cm⁻¹, matching with an increase in the absorption at 2230 cm⁻¹. These frequencies are assigned respectively to nitrile and double bond conjugated nitrile [30]. Considering the spectrum collected at 300°C, the CN stretching shifts from 2241 to 2230 cm⁻¹. The detection of new weak bands at 1610 and 1575 cm⁻¹ indicates the formation of double bonds (C=C and C=N). The appearance at 300°C of the C=N stretching in the infrared spectra is due to inter- or intra-molecular reaction of the nitrile group with adjacent nitrile, forming the ladder structure [31]. At 315°C, the signals of the unsaturated species increase, as the signals at 1380 and 1327 cm⁻¹. The significant decrease of CH₂ bending signal at 1453 cm⁻¹ confirms that dehydrogenation occurs in a large part of the chain, leading to a partial aromatization of the ring of the ladder structure. Over 3000 cm⁻¹, a broad band is detected, characterized by two recognizable peaks at 3375 and 3230 cm⁻¹, respectively referred to amines and imines [21]. The presence of amines and imines is related to the tautomerization of the cyclic and unsaturated structure [22] or to the conversion of nitrile group into imine as termination reaction of cyclization. The signal at 2196 cm⁻¹ comes up by the side of the signal at 2230 cm⁻¹; this band is typical of the presence of β-amino nitrile [22] or enamionitrile [32]. Below 1000 cm⁻¹ it is interesting to note the appearance of an intense band at 792 cm⁻¹, never discussed in literature. This signal could be related to the presence of a substituted triazine, as supported by the presence of its other typical vibrations in the ranges at 1580-1525 and at 1430-1350 cm⁻¹[33, 34], that will be discuss later.

During the heating up to 400°C, the CH₂ stretching of aliphatic species decreases in a significant way and a new signal around 3000 cm⁻¹ is detected, indicating the presence of C-H in unsaturated species. The low intensity of the bands related to the presence of aliphatic species, could be explained with the extended condensation of aromatic ring, as confirmed by the presence of the signal at 745 cm⁻¹, assigned to C-H vibration in aromatic rings. In addition, the relative intensity of the signal at 1610 and 1575 cm⁻¹ reverses, and the signals at 1575 and 1327 cm⁻¹ decrease, confirming that the thermal process induces the elimination of part of the nitrogen atoms from the structure [17].

Over 400°C, all the CH₂ stretching vibrations disappear; the bands related to ammine at 3407 and 1530 cm⁻¹ are still present in the spectra, indicating the presence of aromatic amines, rather than the aliphatic ones and imines. A new signal at 2210 cm⁻¹ instead of the doublet at 2236 and 2196 cm⁻¹, is detected. This signal may be attributed to the isolate nitriles [35] or imine groups bonded with a aromatic structure, which are difficult to eliminate or convert into a carbonized product.

All the other signals are not subjected to changes till 600°C. In particular, the bands at 3407 and 792 cm⁻¹ remain till 600°C. A broad band between 1650 and 1050 cm⁻¹ is detected also, containing intense peaks at 1580, 1370, 1270 and 1150 cm⁻¹. Therefore in nitrogen at 600°C the carbonization process is still not complete.

3.1.3 Infrared evolution of the PAN during conversion in oxidative atmosphere.

In the case of air also, reactions in PAN occur from 250°C on, with formation of unsaturation in the 1610-1575 range (Figure 3, Table 1).

Nevertheless, the presence of oxygen partially changes the degradation path and the degradation products at higher temperatures. Considering the spectra collected at 300-350°C, the band of the CN stretching shifts from 2241 to 2230 cm⁻¹, because the decrease of the unreacted nitriles (2241 cm⁻¹) and the increase of the conjugated nitriles (2230 cm⁻¹), as it occurred in nitrogen . Similarly the decrease of CH₂ bending (1453 cm⁻¹) confirms that dehydrogenation also occurs in air. However in the range of the unsaturated bond, the heating in air induces a different reactivity. Two new bands appear at 1660 and 1590 cm⁻¹ related to the presence of C=O species. In air a new peak appear at 805 cm⁻¹ assigned in literature to out-plane-bending of =C-H in aromatic rings [31], but most probably attributable in this case to a triazine ring bearing different substituents in respect to the triazine ring absorbing at 792 cm⁻¹ that was detected in nitrogen. This triazine signal was already detectable at 300°C; whereas the peak of triazine at 792 cm⁻¹ appeared at 315 ° in nitrogen.

At 320°C, the signals of the double bonds (C=C, C=N and C=O, 1610, 1575 cm⁻¹) increase in intensity and the signals of CH₂ (1453, 2937 cm⁻¹) and CN (2230 cm⁻¹) continue to decrease. A new weak band appears at 2196 cm⁻¹, as in nitrogen.

At 350°C, a broad band over 3000 cm⁻¹ is detected, characterized by two peaks at 3375 and 3233 cm⁻¹ and a shoulder at 3465 cm⁻¹, as it was detected in nitrogen and assigned to amine and imine respectively. In addition the signals at 2196 and 805 cm⁻¹ increase.

Over 350°C, the stretching and bending signals related to the CH₂ disappear, indicating that a complete dehydrogenation of the main chain in air occurs 50°C earlier than in nitrogen.

The spectrum collected at 410°C exhibits signals at 3375 cm⁻¹, (amines), at 2210 cm⁻¹ (aromatic nitriles), at 805 cm⁻¹, (substituted triazines). There is also a broad band between 1800 and 1000 cm⁻¹ with two peaks at 1595, 1370 cm⁻¹ and three shoulders at 1656, 1477, 1224 cm⁻¹. Above this temperature, the shoulder at 1575 disappears, but all the other signals remain the same till 580°C, temperature at which the signal of the triazine and of nitrile are both very weak. The broad band is an indication that the carbonization took place, but the presence of the other species assesses that it is not complete. Comparing the spectra collected at 580°C in the oxidative and inert treatment, it can be seen that the carbonization step is delayed in nitrogen.

3.2 Carbonization performed on PAN nanofibers using an oxidative stabilization and a nitrogen carbonization step.

3.2.1 Thermo gravimetric analysis.

Weight loss curves are displayed in Figure 4 for the two different heating treatments. There is no loss of weight in the ramp in air up to 250°C, However this step greatly affects the following carbonization process.

During the oxidative isothermal treatment there is a loss of weight of 1-2%.

The use of a 10°C/min heating rate in the subsequent nitrogen treatment leaves 50% wt of residue at 800°C, instead if the high resolution mode is used the residue at 800°C is 55%wt. Therefore, the yield of the carbonization raises of 5% for the slower heating ramp (Figure 4). These results are obtained probably thanks to a slower propagation step –exotherm- which limits the overheating of the sample and the consequent chain scissions, which make the quality of the carbon fibers poor. [1] Another explanation could be the lower rate of the reaction, since it happens in the solid state and may require more time to be completed.

3.2.2 Infrared spectroscopy on nanofibers.

The FTIR spectra collected on nanofibers treated at different temperatures are shown in Figure 5 and Table 1. The reactivity of PAN begins in the isothermal step at 250°C in air, as confirmed by the yellowing of the fibers and by the changes occurred in the infrared spectra. The spectra were collected after 15 and 30 minutes at 250°C. Three new signals were detected at 3350 and 3230 cm⁻¹, (amines and imines), and at 3057 cm⁻¹, (aromatic CH). In the C=O stretching zone there were two shoulders at 1715 and 1660 cm⁻¹, indicating the formation of ketones, close to saturated and unsaturated species respectively (1590 cm⁻¹, C=C and C=N) [21, 36]. The signal at 2196 cm⁻¹ is also detected in this case.

During the isotherm in air, all these new signals increase over time. The other signals related to CH₂, that at 1070 cm⁻¹ and the nitrile signal (2241) decrease. A new signal is detected at 805 cm⁻¹, that shows a shoulder at 792 cm⁻¹ from 300°C when the atmosphere is changed to nitrogen. These two signals were already detected respectively in the air and in the nitrogen treatment performed on the cast film. Both signals were related to substituted triazine, but with different substituents.

Increasing the temperature in nitrogen, all the signals referable to aliphatic chains completely disappear. At 400°C the nitrile signal was detected at 2210 cm⁻¹, suggesting that the nitriles are bonded with an aromatic structure as it occurred in cast films, whereas the other signals remain almost the same.

Between 500°C and 700°C, a broad and unresolved band is detected in the range from 1800 to 1000 cm⁻¹, as for the air treatment performed on cast films. The NH absorptions (3350 and 3230 cm⁻¹) decreases, as those at 2210 and 805 cm⁻¹. In this case also, these signals are still present at high temperature.

At 800°C, a spectrum ascribable to almost complete carbonized structure is detected [37]. No other signals were detected, despite the high noise of the spectra due to the black color of the fibers.

The most interesting samples were subjected to Raman evaluation and compared with ATR infrared spectra collected in the same range (2000-400 cm⁻¹). The degradation causes the fluorescence of the sample during Raman measurements, which did not allow collecting spectra for all the samples considered in this paper and treated at temperature below 500°C. Therefore the ATR-FTIR and Raman spectra collected on the sample treated up to 500°C and up to 800°C, are show in figure 6A and B respectively.

In the Raman spectra of the sample heated up to 500°C, it is possible to notice the presence of an intense doublet with maximum at 1583 and 1345 cm⁻¹, assigned to the typical vibration of graphitization process [38]. Two other weak signals are present at 1100 and 615 cm⁻¹. The ATR spectrum of the signal heated up to 500°C, in addition to the signals of the carbonized species and the signal at 805cm⁻¹, shows another signal at 615 cm⁻¹. The comparison of these results gives an additional confirmation of the assignment of the signals at 805 cm⁻¹ to the vibration of a triazine ring: in fact the band at 805cm⁻¹ is no active in Raman for species with this symmetry.

3.2.3 Fibers Morphology

Figure 7 shows the SEM images of PAN nanofibers treated at different temperatures. The morphology of the fibers is maintained till 800°C; in fact the PAN fibers do not collapse during the thermal treatments. In order to preserve fiber morphology during stabilization and carbonization steps, it is essential that once the polymer reaches the softening temperature, close to the melting temperature, it does not flow. Since the involved temperatures overcome the melting temperature, it is possible to suggest that a crosslink reaction has occurred. The size of the fiber diameter during the heat treatment is reported in Figure 4, compared with the weight loss of the sample. The behavior of the dimensions can be split in two principal steps. The first decreasing in the fiber diameter is between 150°C and 250°C. After the electrospinning process, the fibers are not yet compacted; only over 150°C the polymer have the right energy and mobility to close the pore left from the evaporation of solvent. So during the heating, the polymer chains can move and stabilize the structure throughout intermolecular interaction, decreasing the diameters of the fibers from 500 nm to 450 nm, around the 15% of the initial diameter. Between 250°C and 400°C, where no weight loss was detected in the TGA, the fibers maintain a constant diameter despite the reactions that go on through the carbonization step. From 400°C to 800°C, where the infrared spectra and SEM images indicates the beginning of the carbonization, there is the second step of diameters reduction to 300 nm (around 40% of the original size), Moreover, it has

been possible to collect image of these samples without metallization, which support the occurrence of a progressive graphitization with the temperature, coupled with the diameter decrease.

3.3 Crosslinking process.

Considering the features of PAN and the temperatures involved in stabilization and carbonization steps, several reactions could take place .

Recent publications report crosslinking on PAN fibers observed after γ -irradiation [41]. The radiation γ induces the breaking of the C-H and C-C bonds with the formation of different radical species [18, 42], summarized in Figure 8a, involving elimination of H₂ and HCN [18]. It was suggested that the γ -radiation induces crosslinking by the formation of a new bond between the nitrogen in two different chains. It was reported that the presence of this crosslinked species was highlighted by the band at 1668 cm⁻¹ [43], but this frequency must be related to the presence of DMF in the film (fig 2 and 3 and Table 1).

After irradiation, the yellowing of the samples was observed and the formation of radicals was documented as their decrease in presence of oxygen [42], The samples that after irradiation were subjected to thermal treatment above the T_g, showed a significant degradation. Their IR spectra showed a numbers of new bands and among them the band around 800 cm⁻¹. This band was never discussed in details in literature, but at least assigned to the presence of generic aromatic structures [44]. This band, as in all cases reported in this work, must be referred to the presence of triazine ring.. In fact the radical formation on the nitrile group [42] may create a specie that reacts to give the classical ladder structure, such as that obtained with the thermal treatment (Figure 8b) [16]

Several factors induced to confirm this hypothesis.

Firstly, the bands around 800 cm⁻¹ is located in the typical ring breathing range [44]. Secondly, the signal was detected at 792 cm⁻¹ in nitrogen and at 805 cm⁻¹ in air, whereas both these absorption were present in the case of the treatment in air and then in nitrogen. The infrared behavior of this band is reported in Figure 9, a magnification of the range between 850 and 750 cm⁻¹ of the infrared spectra reported in Figure 2, 3 and 5. This absorption appears in infrared spectra of cast films beyond 300°C in nitrogen and at 300°C in air whilst during the isotherm at 250°C in air in the case of the nanofibers. These temperatures can be considered too low to hypothesize the complete aromatization of the ladder structures. For this reason it is necessary to take into account other explanations. A possible structure which absorbs in this range, is the trisubstituted triazine ring. The difference in the absorption frequencies for the samples must be related to the different substituents in the ring [33, 45].

In a PAN chain, adjacent nitrile groups reject each other, instead a nitrile group attracts nitriles of other chains by dipole-dipole interaction and hydrogen bond to form intermolecular links. The helical conformation of the chain also may help this intermolecular reactivity.

Moreover, it is very important the relationship between the physical transformation and chemical reactivity.

Considering that radical process is the most probable polymerization route, the predominant configuration is the atactic one. This configuration allows the formation of only short segments of ladder polymer on the main chain because of the polymerization of the nitrile group: the mutual repulsion of adjacent CN group in the same chain makes the probability of having the right orientation of the pendant group very low. On the opposite the strong dipole-dipole interaction among CN groups of neighboring chains brings them into an ideal position for interaction.

Over 250°C the physical transformation already happened and the polymer chains have the mobility necessary to reorganize them. As an example, the nitrile group of acetonitrile, a low molecular nitrile, reorganized itself in dimers or trimers owing to dipole-dipole interaction and hydrogen bonds [12]; in the experimental condition here adopted it is possible to suppose that the nitrile group can establish the same interaction also in PAN: beyond the glass transition the nitrile groups of PAN, can reach the right position and distance to react, since radical attack takes place at temperature higher than PAN T_g [46]. The consequence of the nitrile reaction is the cyclotrimerization and the formation of the very stable triazine ring, as reported in Figure 8b. This is a typical reaction for simple molecule containing nitrile [47], so it is possible to hypothesize that the pendant groups in PAN also gives this reaction, at 250°C-300 °C without a catalyst, which is instead necessary for this reaction to occur at room temperature [47]. In addition, the right orientation and the chain mobility help this reactivity among different chains.

As discussed in the thermo gravimetric part, the heating at 250°C-300°C allow the scission of a C-C bond in the main chain, because of the low energy request for this dissociation. After their formation, the radicals can move to the nitrile groups closer to the radical center. In fact nitrile group is characterized by a low lying orbital that may stabilize the radical species. Otherwise, this group can accommodate the additional electron in its π antibonding orbital. The presence of the odd electron in this molecular orbital destabilizes the triple bond and activates the nitrile group. As consequence, the nitrile radical may react with other nitrile groups giving the ladder structure; alternatively it may react with other two nitrile groups of different chains forming the trisubstituted triazine ring. This reaction does not take place after irradiation when the sample is in the solid state and the chains cannot move.

The cyclization products are different in nitrogen and in air, because oxygen in air can abstract a α -hydrogen with the consequent formation of a hydroperoxide [48], which starts the thermo-oxidative process. Suggesting that the oxidation may involve the α position to the nitrile group, there are two possibilities: the formation of a α -keto triazine, suggesting a chain scission, or the formation of an insaturation. In both cases the presence of a double bond conjugated with the triazine ring shifts the triazine band to higher frequencies.

Another confirmation of the assignment of the band around 800 cm⁻¹ to the triazine ring is that it is stable to 600°C, temperature at which all the other species are destroyed or eliminated from the carbon structure. Only this kind of ring exhibits a so high thermal stability [33].

The formation of triazine with an intermolecular reaction involving three nitriles of three different chains is responsible of the crosslinking. The crosslinking is in agreement with the fiber behavior observed using SEM. They in fact exhibit the same morphology during stabilization and carbonization because crosslinking does

not allow the melt to flow during the thermal treatments and the shape and the organization of the fibers are not modified during the conversion process.

5. Conclusion

This work shows the formation of carbon species using PAN as raw material. In particular carbon nanofibers were produced from PAN nanofibers obtained by electrospinning subjected to thermal treatments that combine air stabilization and nitrogen carbonization. It was demonstrated that the stabilization process is more successful if it is performed in air and with a subsequent slow heating ramp in nitrogen.

Considering the morphological behavior of the nanofibers, it is possible to suggest that the reactivity of PAN generates structures that allow to maintain this morphology. This is possible since between the glass transition temperature and the melting temperature, a crosslinking reaction occurs among nitrile groups belonging to different chains. The product of this reaction is a substitute triazine ring, with different substituents, depending on the atmosphere of thermal treatment. The oxidation of the species closer to the triazine ring shift its IR-out-of- plane vibration. The triazine ring was detected in the infrared spectra on very thin cast films, using absorption/reflection mode that allow detection of very weak bands on carbonaceous substrates also. In fact The triazine formation was never reported in literature, in the infrared spectra of sample treated at 800°C showing the graphitization of the PAN.

References

- [1] Gupta AK, Paliwal DK, Bajaj P. Acrylic Precursors for Carbon-Fibers. *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics*. 1991;C31:1-89.
- [2] Henrici-Olivé G, Olivé S. The chemistry of carbon fiber formation from polyacrylonitrile. *Industrial Developments*. 1983;51:1-60.
- [3] Nataraj SK, Yang KS, Aminabhavi TM. Polyacrylonitrile-based nanofibers - A state-of-the-art review. *Progress in Polymer Science*. 2012;37:487-513.
- [4] Griбанov AV, Sazanov YN. Polyacrylonitrile: Carbonization problems. *Russian Journal of Applied Chemistry*. 2008;81:919-32.
- [5] Rahaman MSA, Ismail AF, Mustafa A. A review of heat treatment on polyacrylonitrile fiber. *Polymer Degradation and Stability*. 2007;92:1421-32.
- [6] Bashir Z. A Critical-Review of the Stabilization of Polyacrylonitrile. *Carbon*. 1991;29:1081-90.
- [7] Xue TJ, McKinney MA, Wilkie CA. The thermal degradation of polyacrylonitrile. *Polymer Degradation and Stability*. 1997;58:193-202.
- [8] Dalton S, Heatley F, Budd PM. Thermal stabilization of polyacrylonitrile fibres. *Polymer*. 1999;40:5531-43.
- [9] Krigbaum WR, Tokita N. Melting point depression study of polyacrylonitrile. *Journal of Polymer Science*. 1960;43:467-88.
- [10] Andreeva OA, Burkova LA. Spectroscopic manifestations of nitrile group intramolecular repulsion in PAN. *Journal of Macromolecular Science-Physics*. 1999;B38:321-8.
- [11] Henrici-Olivé G, Olivé S. Molecular interactions and macroscopic properties of polyacrylonitrile and model substances. *Chemistry. Advances in Polymer Science*. 1979;32:123-52.
- [12] Alia JM, Edwards HGM, Fawcett WR, Smagala TG. An experimental Raman and theoretical DFT study on the self-association of acrylonitrile. *Journal of Physical Chemistry A*. 2007;111:793-804.
- [13] Andreeva OA, Burkova LA. Spectroscopic manifestations of nitrile group intermolecular attraction in PAN. *Journal of Macromolecular Science-Physics*. 2000;B39:225-34.
- [14] Cabaleiro-Lago EM, Hermida-Ramon JM, Pena-Gallego A, Martinez-Nunez E, Fernandez-Ramos A. Intermolecular interactions and cooperative effects in acetonitrile clusters. An ab initio molecular orbital study. *Journal of Molecular Structure-Theochem*. 2000;498:21-8.
- [15] Korte S. Physical constants of Poly(acrylonitrile). In: Brandrup J, Immergut EH, Grulke EA, editors. *Polymer Handbook*. Fourth edition ed. New York: Wiley Interscience; 1999. p. V/59-66.

- [16] Huron JL, Meybeck J. Etude cinétique des réactions de dégradation du polyacrylonitrile par entre 200°C et 300°C par des techniques associées et combinées. *European Polymer Journal*. 1977;13:553-62.
- [17] Hay JN. Thermal reactions of polyacrylonitrile. *Journal of Polymer Science Part A-1: Polymer Chemistry*. 1968;6:2127-35.
- [18] Hill DJT, Lang AP, O'Donnell JH, Pomery PJ. The effects of γ -radiation on polyacrylonitrile. *Polymer Degradation and Stability*. 1992;38:193-203.
- [19] Grassie N, Hay JN, McNeill IC. Coloration in acrylonitrile and methacrylonitrile polymers. *Journal of Polymer Science*. 1958;31:205-6.
- [20] Grassie N, Hay JN. Thermal coloration and insolubilization in polyacrylonitrile. *Journal of Polymer Science*. 1962;56:189-202.
- [21] Coleman MM, Petcavich RJ. Fourier transform infrared studies on the thermal degradation of polyacrylonitrile. *Journal of Polymer Science: Polymer Physics Edition*. 1978;16:821-32.
- [22] Fochler HS, Mooney JR, Ball LE, Boyer RD, Grasselli JG. Infrared and Nmr Spectroscopic Studies of the Thermal-Degradation of Polyacrylonitrile. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*. 1985;41:271-8.
- [23] Houtz RC. "Orlon" Acrylic Fiber: Chemistry and Properties. *Textile Research Journal*. 1950;20:786-801.
- [24] Benson SW, Nangia PS. Some unresolved problems in oxidation and combustion. *Accounts of Chemical Research*. 1979;12:223-8.
- [25] Frank E, Hermanutz F, Buchmeiser MR. Carbon Fibers: Precursors, Manufacturing, and Properties. *Macromolecular Materials and Engineering*. 2012;297:493-501.
- [26] Schurz J. Discoloration effects in acrylonitrile polymers. *Journal of Polymer Science*. 1958;28:438-9.
- [27] Costa L, Avataneo M, Bracco P, Brunella V. Char formation in polyvinyl polymers I. Polyvinyl acetate. *Polymer Degradation and Stability*. 2002;77:503-10.
- [28] Grassie N, McGuchan R. Pyrolysis of polyacrylonitrile and related polymers II: The effect of sample preparation on the thermal behaviour of polyacrylonitrile. *European Polymer Journal*. 1971;7:1091-104.
- [29] Mita I. Effect of structure on degradation and stability of polymers. In: Jellinek HHG, editor. *Aspects of Degradation and Stabilization of Polymers*. Amsterdam: Elsevier; 1978. p. 247-94.
- [30] Qin XY, Lu YG, Xiao H, Song YP. Improving stabilization degree of stabilized fibers by pretreating polyacrylonitrile precursor fibers in nitrogen. *Materials Letters*. 2012;76:162-4.
- [31] Jing M, Wang CG, Wang Q, Bai YJ, Zhu B. Chemical structure evolution and mechanism during pre-carbonization of PAN-based stabilized fiber in the temperature range of 350-600 degrees C. *Polymer Degradation and Stability*. 2007;92:1737-42.

- [32] Sen K, Bajaj P, Sreekumar TV. Thermal behavior of drawn acrylic fibers. *Journal of Polymer Science Part B-Polymer Physics*. 2003;41:2949-58.
- [33] Costa L, Camino G. Thermal behaviour of melamine. *Journal of Thermal Analysis and Calorimetry*. 1988;34:423-9.
- [34] Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. Aromatic and Heteroaromatic Rings. In: Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG, editors. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*. San Diego, CA: Academic Press, Inc; 1991. p. 277-306.
- [35] Beltz LA, Gustafson RR. Cyclization kinetics of poly(acrylonitrile). *Carbon*. 1996;34:561-6.
- [36] Ouyang Q, Cheng L, Wang HJ, Li KX. Mechanism and kinetics of the stabilization reactions of itaconic acid-modified polyacrylonitrile. *Polymer Degradation and Stability*. 2008;93:1415-21.
- [37] Brooks JD, Taylor GH. The formation of some graphitising carbons. In: PL WJ, editor. *Chemistry and physics of carbon*. New York: Marcel Dekker; 1968. p. 243-86.
- [38] Ko TH. Raman spectrum of modified PAN-based carbon fibers during graphitization. *Journal of Applied Polymer Science*. 1996;59:577-80.
- [39] Larkin PJ, Makowski MP, Colthup NB. The form of the normal modes of s-triazine: infrared and Raman spectral analysis and ab initio force field calculations. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*. 1999;55:1011-20.
- [40] Goubeau J, Jahn EL, Kreuzberger A, Grundmann C. Triazines. X. The Infrared and Raman Spectra of 1,3,5-Triazine. *The Journal of Physical Chemistry*. 1954;58:1078-81.
- [41] Liu WH, Wang MH, Xing Z, Qi YN, Wu GZ. Radiation-induced crosslinking of polyacrylonitrile fibers and the subsequent regulative effect on the preoxidation process. *Radiation Physics and Chemistry*. 2012;81:622-7.
- [42] Liu WH, Wang MH, Xing Z, Wu GZ. The free radical species in polyacrylonitrile fibers induced by g-radiation and their decay behaviors. *Radiation Physics and Chemistry*. 2012;81:835-9.
- [43] Miao PK, Wu DM, Zeng K, Xu GL, Zhao CE, Yang G. Influence of electron beam pre-irradiation on the thermal behaviors of polyacrylonitrile. *Polymer Degradation and Stability*. 2010;95:1665-71.
- [44] Celina M, Ottesen DK, Gillen KT, Clough RL. FTIR emission spectroscopy applied to polymer degradation. *Polymer Degradation and Stability*. 1997;58:15-31.
- [45] Takimoto M. Infrared absorption spectra and structure of cyanamide derivatives. *Nippon Kagaku Zasshi*. 1964;85:168-76.
- [46] Henrici-Olivé G, Olivé S. Inter-versus Intramolecular Oligomerization of Nitrile Groups in Polyacrylonitrile. *Polymer Bulletin*. 1981;5:457-61.

[47] Martin D, Bauer M, Pankratov VA. Cyclotrimerisation of Cyano-compounds into 1,3,5-Triazines. RUSS CHEM REV. 1978;47:975-90.

[48] Memetea LT, Billingham NC, Then ETH. Hydroperoxides in Polyacrylonitrile and Their Role in Carbon-Fiber Formation. Polymer Degradation and Stability. 1995;47:189-201.

Table 1. Assignments of infrared signals of PAN and its degradation products (22,34).

Wavenumbers (cm ⁻¹)	PAN Assignments	Degradation product assignments
3407		aromatic NH ₂ stretching
3375 3350		NH ₂ stretching
3230		C=N-H stretching
3057		CH ring stretching
2940	CH ₂ asymmetric stretching	
2870	CH ₂ symmetric stretching	
2241	C≡N symmetric stretching	
2230		conjugated C≡N stretching
2210		aromatic C≡N stretching
2196		β-amino C≡N stretching
1715		conjugated C=O stretching
1668		C=O stretching (solvent)
1610-1575		C=C and C=N stretching
1530		NH ₂ bending or C-N-H
1453	CH ₂ bending	
1377		C-H of CC
1360	CH bending and CH ₂ wagging	
1327		C-H of CN
1251	CH wagging	
1070	C-C stretching	
1040	C-C≡N combination mode	
805 792		out of plane triazine ring
780	CH ₂ rocking	
745		out of plane aromatic ring

Figure 1 TGA curves and their derivatives of PAN cast films in air and nitrogen atmospheres from 50°C up to 800°C at 20°C/min

Figure 2 FTIR spectra collected in situ during heating of PAN cast films in nitrogen at different temperatures

Figure 3 FTIR spectra collected in situ during heating of PAN cast films in air at different temperatures

Figure 4 TGA curves with heating ramp at 10°C/min (—) and in high resolution (res. 4) (----), in a combined air/nitrogen program, switching at 250°C; behavior of the fiber diameter during the high resolution ramp (—□—□—) (*the square must be black*)

Figure 5 FTIR spectra collected on fibers treated at different temperatures with the combined program in air and nitrogen.

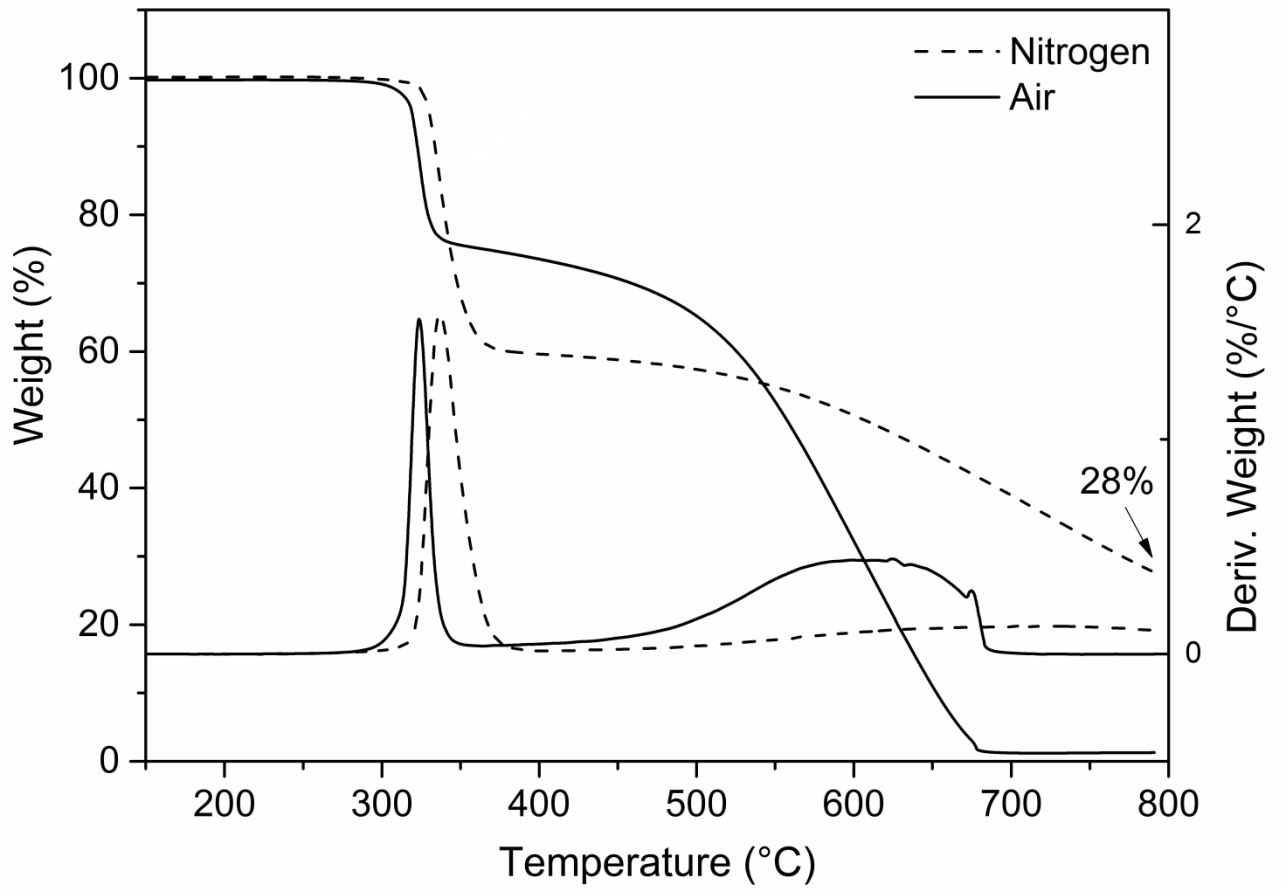
Figure 6 ATR (A) and Raman (B) of the nanofibers treated at 500 and 800°C

Figure 7 SEM images of the treated nanofibers at different temperatures, a) 300°C, b) 500°C, c) 600°C and d) 800°C, in the square the not metalized sample.

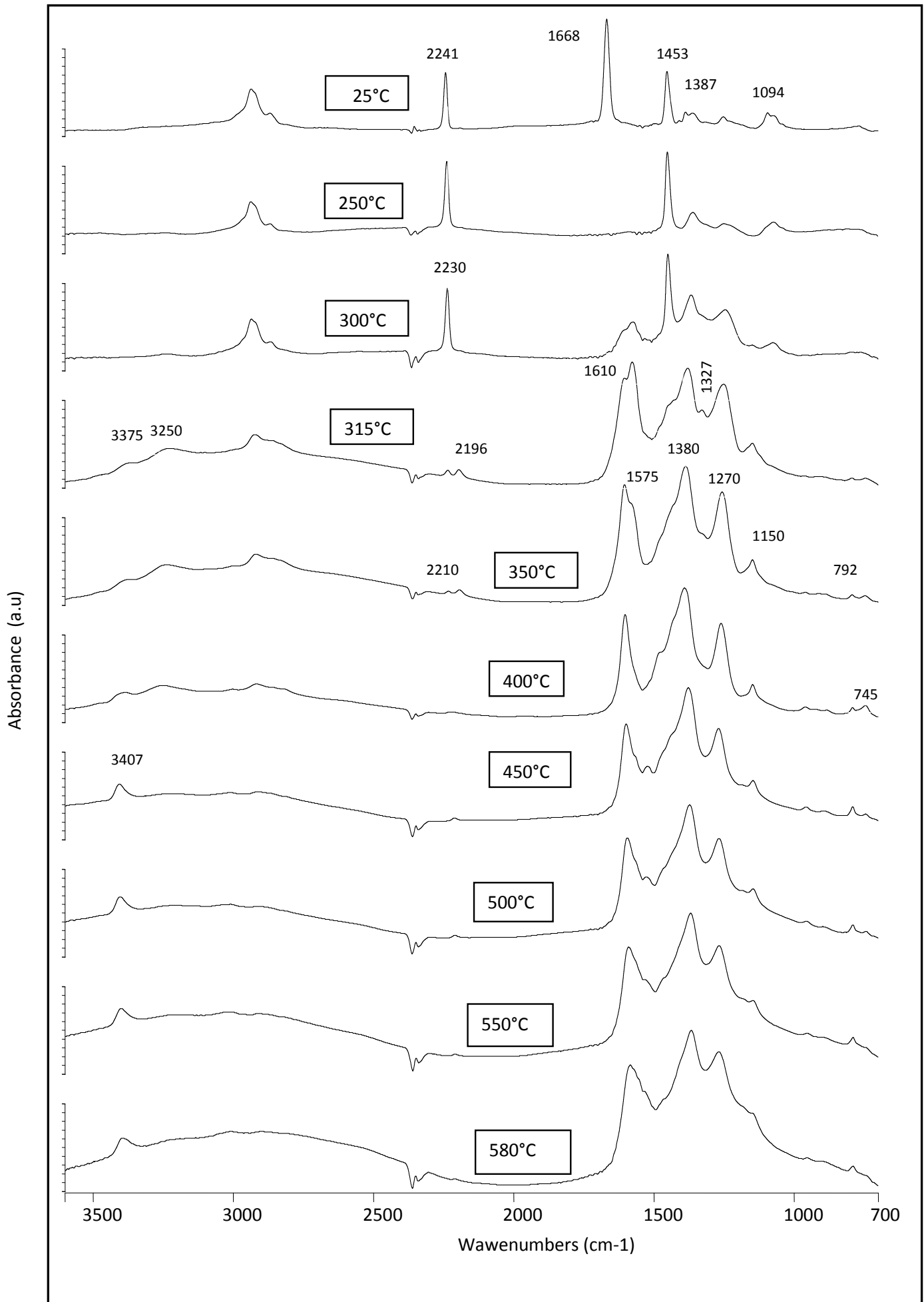
Figure 8 Radical formation in γ irradiation (a) and hypothesis of trisubstituted triazine ring formation during PAN stabilization through a trimerization reaction of the nitrile groups (b).

Figure 9 Magnification of the FTIR spectra between 850 and 750 cm^{-1} , A) cast film in nitrogen, B) cast film in air, C) fibers in air/nitrogen treatment.

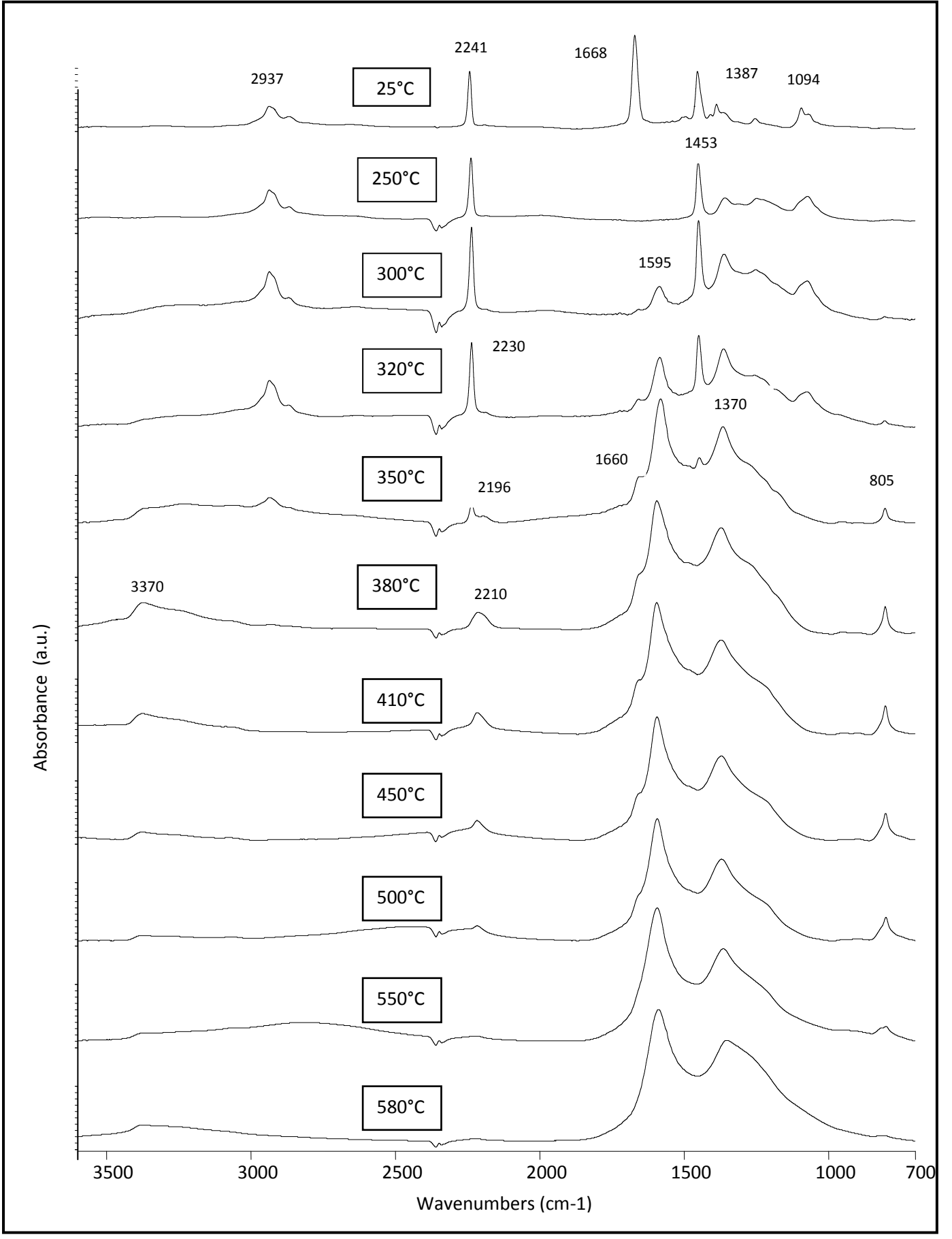
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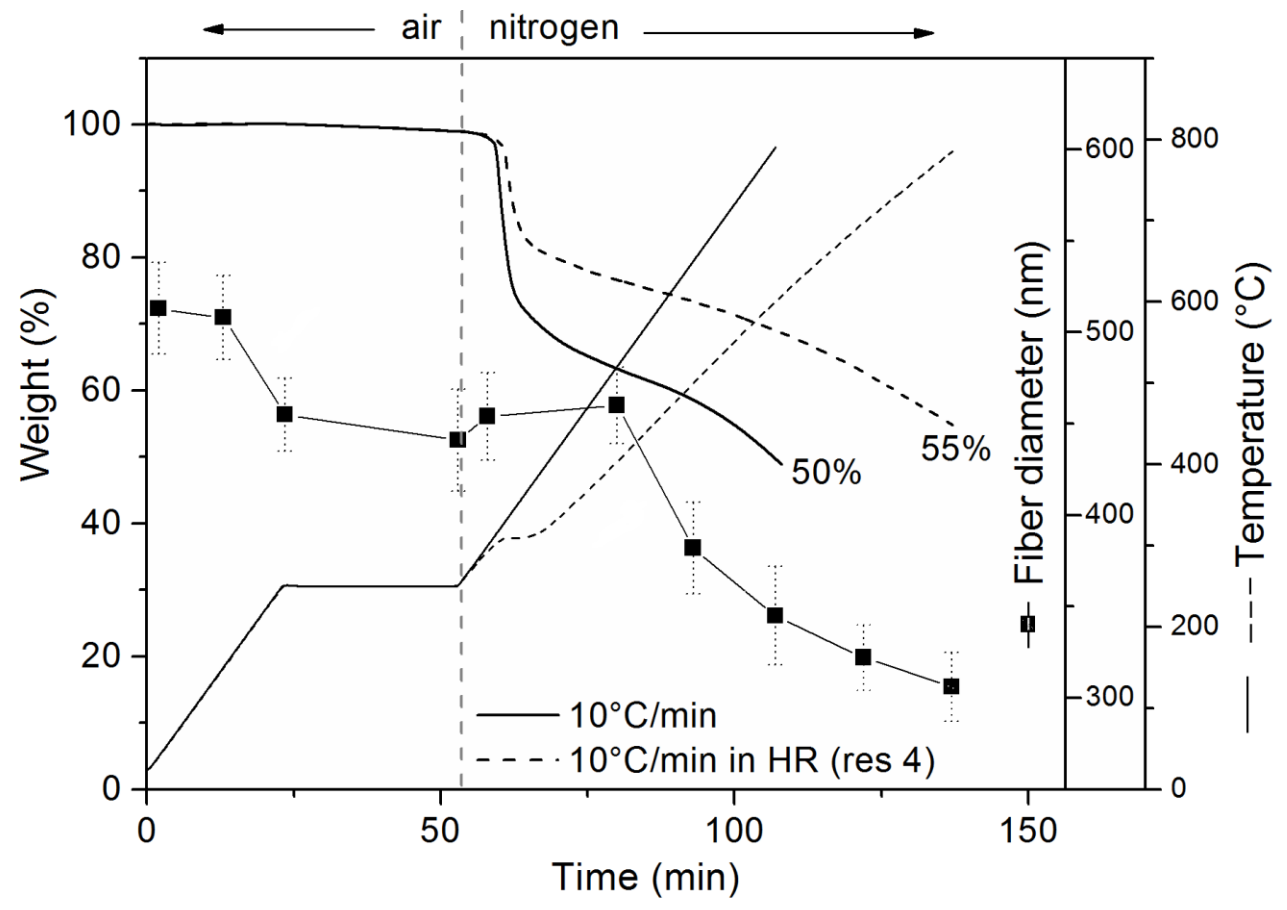
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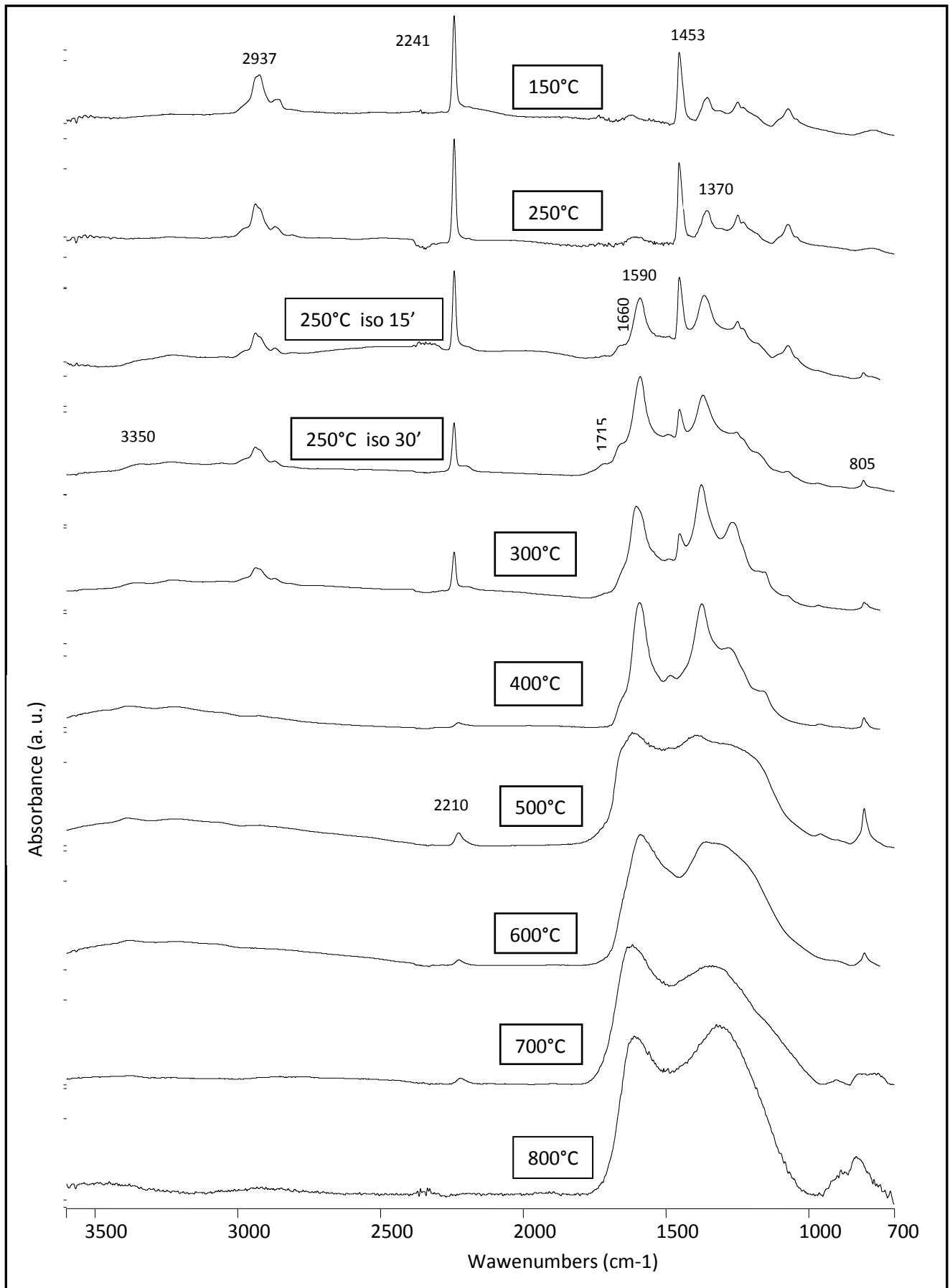
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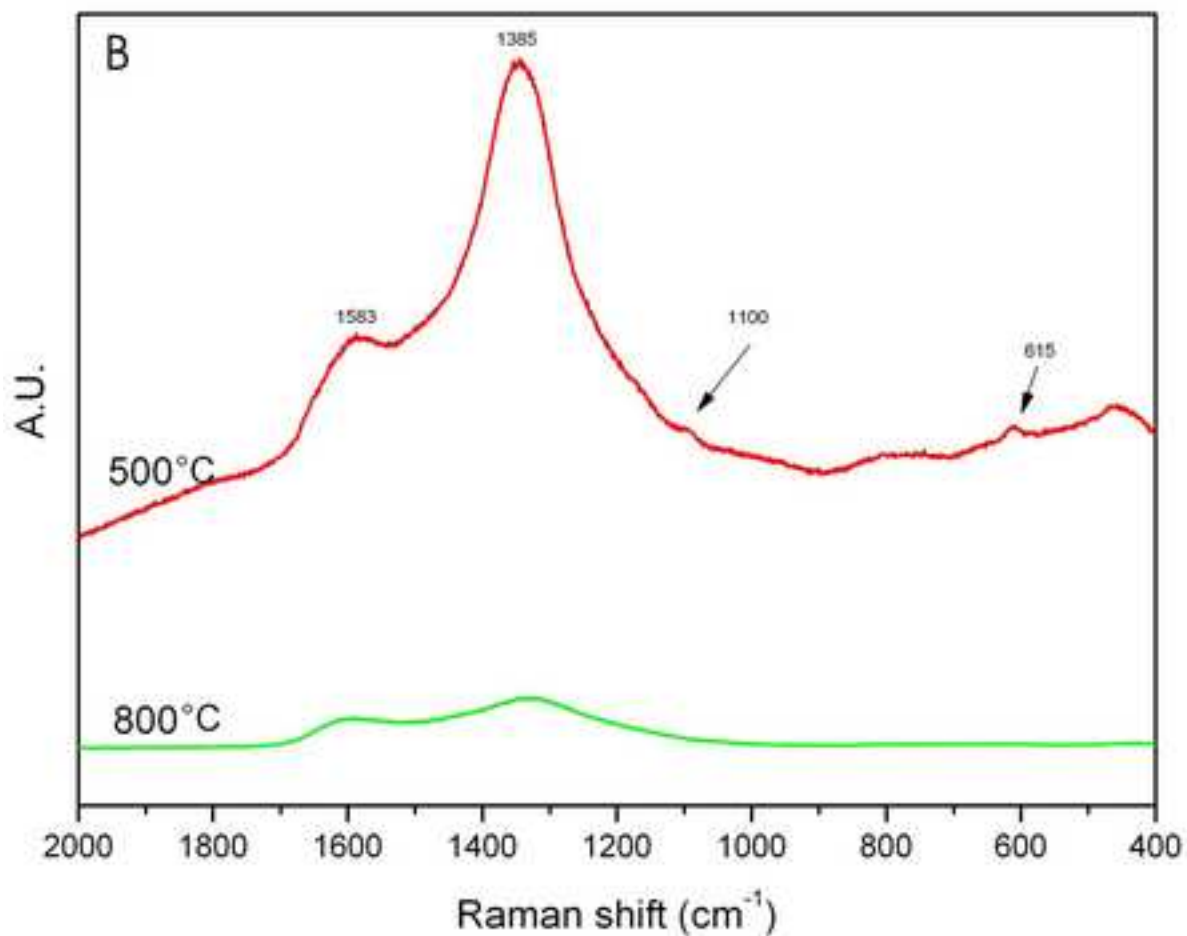
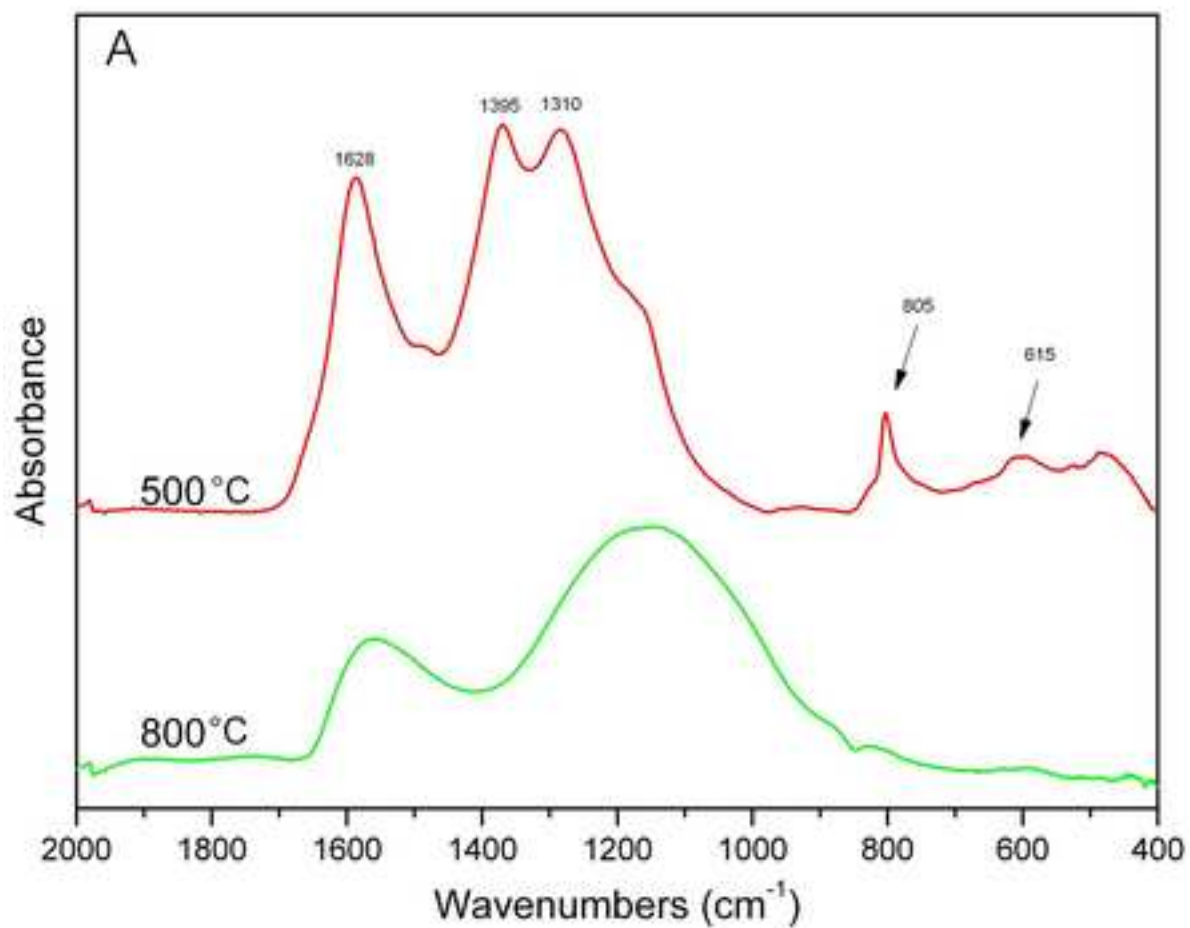


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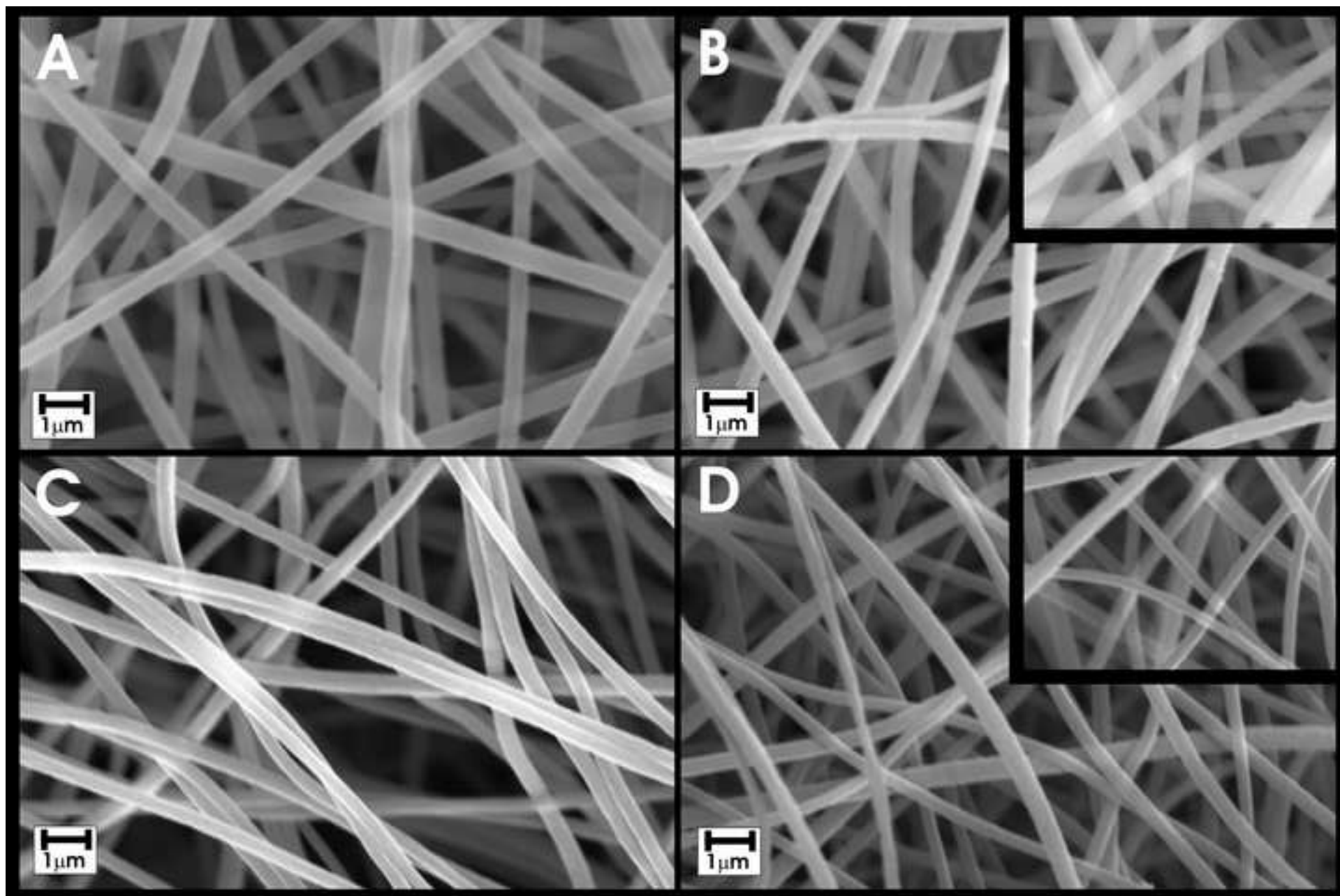
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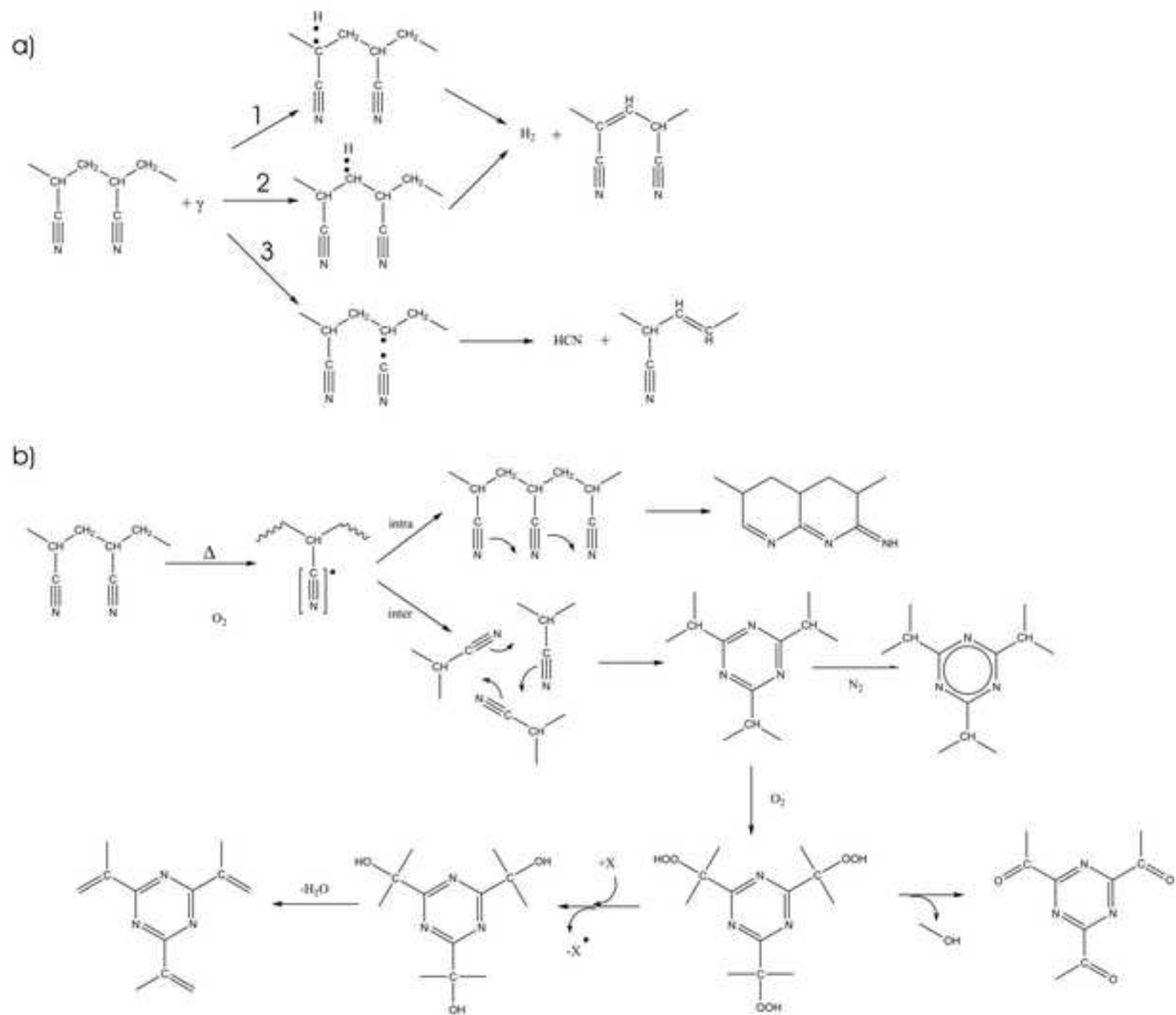
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