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THE MECHANISM OF THERMAL STABILIZATION OF POLYACRYLONITRILE

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ABSTRACT

The two-step stabilization of a thoroughly characterized PAN homopolymer was studied by various methods including thermogravimetric analysis (TGA), evolved gas analysis (EGA), differential scanning calorimetry (DSC), Fourier transformed infrared spectroscopy (FTIR), oxygen microanalysis and theoretical energy calculations. Stabilization was carried out with pre-treatment in inert atmosphere, and the reactions taking place as well as the structure of the polymer formed were compared to those occurring in one-step (direct) oxidation. Five separate exothermic regions were detected in DSC measurements and they were assigned to seven reaction steps, for which appropriate mechanisms were proposed together with the relationship among individual reactions. The effect of stereoregularity on ring formation is discussed and a new scheme is suggested, which includes the cyclization of alternating nitrile groups in the *gauche* conformation. The number of successive rings formed during cyclization is determined with three independent methods and compared to previous concepts reported in the literature. The positive effect of pre-treatment in inert atmosphere on the structural stability of PAN during the subsequent pre-carbonization treatment is also demonstrated and explained by considering the mechanism of the reactions taking place during the process.

KEYWORDS: stabilization, cyclization, oxidation, reaction mechanism, thermal analysis, evolved gas analysis

1. INTRODUCTION

As the most common precursor for carbon fiber production, polyacrylonitrile (PAN) has been the subject of many research efforts in past decades. The thermo-oxidative stabilization process that allows PAN to sustain the subsequent high-temperature

carbonization step is very important especially today, when carbon nanotubes made of PAN are of growing interest as well [1,2]. Despite the large number of research papers that have been published already on the topic, the fundamental understanding of the processes that take place during stabilization is still missing, as stated unanimously by each of the comprehensive reviews written in 1991, 2009 and 2017 [3-5].

The commonly accepted scheme of this stabilization process have been assumed to consist of three distinct chemical reactions for a long time, and the concept is widely used for the explanation of experimental results even in very recent reports [1,6-9]. The three reactions are called cyclization, dehydrogenation and oxidation (sometimes cross-linking), and they are usually assigned to the exothermic peaks of thermograms obtained in differential scanning calorimetric (DSC) measurements. PAN is studied predominantly in oxidative atmosphere, since the common industrial process used in practice is based on oxidative stabilization [2,4,5,9,10]. The approach yields complicated overlapping exothermic signals, the resolution of which depends primarily on the rate of heating and the weight of the sample used for DSC analysis. On the other hand, some groups report results obtained in a non-oxidative, partial stabilization process of PAN, which excludes oxidative processes. Only a few groups studied the behavior of PAN in a two-step stabilization procedure, which consists of an inert pre-treatment and a subsequent oxidative step [7,9,11,12]. The two-step approach provides a deeper insight into the chemical changes taking place during stabilization as compared to the direct oxidation of PAN. A different sequence of reactions occurs in this approach as evidenced by the dissimilar exothermic heat release recorded in DSC [11,12]. Moreover, the structure of stabilized PAN obtained by this approach is also different, which might have a considerable impact on the structure, stability and properties of the carbon fibers obtained.

The goal of our study was to answer yet unclear questions regarding the stabilization

of PAN. These include the stereochemistry of cyclization [3,13-16], the requirement of a cyclized structure for oxygen inclusion [9,17], the effect of inert pre-treatment on oxygen up-take [9], the average zip-length of cyclization [7,15,16], the relationship between chemical changes and exothermic peaks observed in DSC measurements [1,6-9,11,12] and the mechanism of the reactions occurring. The complexity of the stabilization process makes the answering of these questions extremely difficult. In order to overcome these difficulties and to compare the two different approaches, we subjected our material to a two-step and a one-step stabilization (direct oxidation) procedure. We applied a variety of independent methods, like thermogravimetric analysis (TGA), evolved gas analysis (EGA), differential scanning calorimetry (DSC), Fourier transformed infrared spectroscopy (FTIR), oxygen microanalysis and theoretical energy calculations for the exact identification of individual reactions and processes taking place during the treatments.

2. EXPERIMENTAL

2.1. Materials

In order to make comparison possible, we have used a commercial material that is available also for other researchers. The sample is a PAN homopolymer provided by Aldrich (Sigma-Aldrich Co., US) with a weight average molecular mass of $M_w = 150.0$ kDa (information provided by the supplier), glass transition temperature, $T_g = 109.8$ °C, melting temperature, $T_m = 185.0$ °C (determined from DSC), and intrinsic viscosity $IV = 1.52$ dL/g measured by PSL Rheotek (UK).

2.2. Characterization

TGA measurements were done on approximately 20 mg powder samples with a simultaneous thermal analyzer STA 6000 (PerkinElmer, US). PAN samples were subjected

to either a two-step or a one-step stabilization process followed by subsequent pre-carbonization, in which the sample was heated up to 600 °C (Fig. 1). The two-step treatment consisted of an isothermal stage carried out at 260 °C for 50 minutes in nitrogen (5.0 purity, 100 mL/min) and a subsequent oxidative step done at 240 °C for 40 minutes (synthetic air atmosphere, 21 % oxygen, 100 mL/min). The pre-treated sample was heated up to 600 °C with the rate of 5 °C/min and then kept at 600 °C for 20 minutes. The only difference of the one-step method is that the first isothermal segment was carried out in air instead of nitrogen. The structural stability of the material is characterized by the weight loss measured during the pre-carbonization treatment in nitrogen, since 600 °C is considered as the upper temperature limit for inert dehydrogenation (400-600 °C) [18], which is a step with high impact on the yield of carbonization.

The infrared spectra of the original PAN and the stabilized samples were recorded with the help of a Spectrum-Two FTIR (PerkinElmer) apparatus equipped with a diamond crystal universal attenuated total reflectance (UATR) cell and a deuterated triglycine sulfate (DTGS) detector. The samples were pressed down with 100 N force and after recording a background spectrum (accumulated by 36 scans), sample spectra were recorded in 36 scans in combined scan directions from 4000 to 700 cm^{-1} with 4 cm^{-1} resolution.

Stabilized samples were sent to Galbraith Laboratories (Tennessee, US) for oxygen microanalysis. The measurements were done on approximately 2 mg samples with a FlashEA 1112 Elemental Analyzer (Thermo Scientific, US).

Evolved gas analysis (EGA) was carried out by coupling the exhaust line of the STA 6000 apparatus to the FTIR spectrophotometer with a heated transfer line TL8000 (PerkinElmer). The UATR cell was replaced by a heated zero-gravity-effect gas cell with KBr optics. The constant transfer of the gas phase was controlled by a mass flow controller unit (RedShift, Italy). Prior to the analysis, a background spectrum was recorded with 16

scans in nitrogen in the range 4000-600 cm^{-1} . One sample spectrum was collected from the gas phase every 7-8 seconds with background phase correction and magnitude apodization, without $\text{H}_2\text{O}/\text{CO}_2$ suppression.

DSC thermograms were recorded with a model Q2000 (TA Instruments, US) apparatus. Glass transition temperatures were determined in the first heating scan carried out at 10 $^{\circ}\text{C}/\text{min}$. Melting endotherms were measured in pressurized crucibles on approximately 5 mg powder samples mixed with 5 mg deionized water at 10 $^{\circ}\text{C}/\text{min}$ heating rate [19]. Exothermic heat release values were determined at 5 $^{\circ}\text{C}/\text{min}$ heating rates in open aluminum crucibles; sigmoidal baselines were used for integration. Individual exothermic processes were separated in measurements carried out at 0.7 $^{\circ}\text{C}/\text{min}$ heating rate under nitrogen or synthetic air.

3. RESULTS AND DISCUSSION

3.1. Pre-treatment in inert atmosphere

The heating of PAN in inert atmosphere results in two exothermic peaks in the DSC trace indicating the occurrence of two distinct groups of reactions, shown by peaks I and II in Fig. 2a. Based on this thermogram, 260 $^{\circ}\text{C}$ was selected for further analysis since isothermal heat treatment at this temperature results in moderate reaction rates. The FTIR spectrum [20] of the polymer shows a significant decrease in the absorption of the nitrile group (2243 cm^{-1}), and a strong, overlapping peak appears at around 1587 cm^{-1} corresponding to the vibration of the $-\text{C}=\text{N}-\text{C}-$ type (secondary) imino groups (Fig. 3 a,b). These changes in the chemical structure of the polymer show that during inert treatment ring formation is one of the main reactions, often referred to as cyclization. The rapid weight loss that accompanies this process is shown on the first part of Fig. 4a.

Usually intramolecular reactions lead to cyclization, but intermolecular ring

formation may also occur with the participation of the nitrile groups of adjacent chains, as illustrated in **Fig. 5b**. The first step of the scheme (intermolecular nitrile reaction that result in a single-point cross-link) was suggested by Olivé and Olivé in 1981 [21]; we propose that this reaction can be followed by the elimination of HCN and the presented intermolecular ring formation.

The weight loss of the sample was recorded by TGA under the same conditions. The loss of weight determined was 13.3 wt% and the evolution of NH_3 (930 and 965 cm^{-1}) and HCN (713 cm^{-1}) was detected by EGA (**Fig. 6**). The most intensive gas evolution was observed after 18 minutes, which coincides with the start of the rapid weight loss detected by TGA. The absorption peak appearing at 807 cm^{-1} in the FTIR spectra of the treated material corresponds to the formation of olefinic ($-\text{C}=\text{C}-\text{H}$) bonds on the polymer backbone, while a slight decrease in the intensity of the signal at 1452 cm^{-1} indicates that some methylene groups are also involved in the process (**Fig. 3b**). These observations suggest the elimination of non-cyclized nitrile and terminal $=\text{N}-\text{H}$ type (primary) imino groups. The corresponding reactions are presented in **Fig. 7**. The driving force of the elimination reaction is the formation of a conjugated electron system, i.e. cyclization reactions are usually followed by elimination, and not the opposite, as some literature sources claim [9,17]. Consecutive cyclization and elimination reactions result in a polycyclic, partially aromatic structure, which is characterized by the average number of successive rings, which essentially determines the behavior of the material during the subsequent oxidation and pre-carbonization steps.

The length of the conjugated nitrile sequences (often called as zip-length) in PAN is relatively short, in copolymers the number of successive rings is not more than two or three [22] indicating a repeatedly interrupted radical polymerization reaction. In the case of copolymers, it is convenient to explain this interruption by the presence of comonomers,

which inhibit the intramolecular propagation of cyclization. However, this argument seems to be false, since short cyclized sequences of two to five nitrile groups form also in PAN homopolymers [23,24]. A more suitable explanation for the discussed phenomenon might be offered by the stereochemistry of ring formation, which has been a source of debate, and not answered satisfactorily yet [3,13,14]. Frequently, the stereochemistry of cyclization is conventionally not discussed, and the reaction is often presented in a non-stereospecific manner instead. The authors, who consider stereochemistry, like Wang and Liu [15,16], accept a strictly isotactic concept.

The authors supporting the occurrence of non-stereospecific cyclization claim that the tacticity of nitrile groups does not affect the reaction. Chen et al. [14] did not observe any change in tacticity during the partial stabilization of an atactic PAN sample, concluded that isotactic triads are not preferred during ring formation and even alternating nitriles can take part in this reaction [14]. They drew their conclusion from the analysis of samples before and after cyclization. However, the analysis was carried out in solution by NMR spectroscopy thus the results are biased by the insolubility of chains containing partially cyclized sequences. Coleman et al. [13] proposed that cyclization occurs exclusively between adjacent isotactic nitrile groups, in all-*trans* conformation. However, typical triad tacticity ratio *mm:mr:rr* is estimated to be 29:50:21 in atactic PAN [24]. Based on these probabilities, a zip-length of only two to three nitrile units (1-2 rings) is predicted for PAN homopolymers. The prediction contradicts the hypothesis of Grassie and Kim [23,24], who expected the formation of 2-5 successive rings, and supports the conclusions of Wang and Liu [15,16] at the same time, who explained their results with a structure containing predominantly isolated rings following a heat treatment at 250 and 300 °C.

Our opinion is that the steric configuration of the nitrile groups is important in the cyclization reaction, although isotacticity is not strictly required for ring formation.

Alternating nitrile groups arranged in the *gauche* conformation are also located within suitable distance for cyclization (**Fig. 8**). If this conclusion is true, it means that a carbon atom of different configuration does not necessarily interrupt the conjugation of neighboring nitriles, and ring formation can propagate through syndiotactic sequences as well. The ratio of *gauche* conformers is estimated to be 10-20 % in atactic PAN [25], which extends the probable length of cyclized sequences up to an average of four to five nitrile units (3-4 rings).

The weight loss in the elimination reactions mentioned above provides an estimate for the length of one reaction segment, which consists of approximately six monomer units (see the reaction scheme presented in **Fig. 7**). Keeping in mind that some of the nitrile groups remain unchanged during the pre-treatment in inert atmosphere (**Fig. 3b**), one can assume that four to five nitriles form the cyclic structure, which result in 3-4 successive rings, supporting the theories that assume this zip-length.

The presented scheme for the elimination and cyclisation processes can be supported also by the theoretical calculation of reaction heats. Energy values for the dissociation and formation of bonds during the stabilization of PAN were provided by Gupta et al. [26]. The formation energies of HCN and NH₃, +145 and -36 kJ/mol, respectively, were obtained from the National Institute of Standards and Technology database (NIST). Based on the scheme presented above (**Fig. 7**) and using these values, the reaction heat of the cyclization and elimination reactions can be calculated theoretically. Reaction enthalpy values of -155, -424 and -617 J/g are expected when two, three and four successive rings form, respectively. The analysis of the first peak of the DSC trace recorded in inert atmosphere (peak I in **Fig. 2a**) provided an enthalpy value of -420 ± 10 J/g confirming that a structure with an average zip length of three rings develops in PAN pre-treated under the conditions used in this study.

We associate the reactions discussed above with the exothermic peak observed on

the non-isothermal DSC thermogram, denoted as peak I. The second peak (peak II) corresponds to a different chemical process. If the sample is heated at a moderate rate, e.g. at 0.7 °C/min, the resolution of the two peaks increases significantly and allows the distinguishing of the processes taking place during heating. The analysis of the traces shows that the kinetic features of the first group of reactions, i.e. intra- and intermolecular cyclization and elimination, differ considerably from those of the subsequent process. This latter is considered a cross-linking reaction that requires higher temperature and possesses a longer induction period. This reaction is assumed to occur only in PAN homopolymers, as it could not be observed in a PAN copolymer containing methyl acrylate [11]. Cross-linking is made possible by the relatively high regularity and lateral order of the homopolymer [27]. This reaction leads to further evolution of HCN and its proposed mechanism and a cycloalkane cross-link formed as a result are shown in Fig. 5a [28]. A possible alternative reaction pathway is Diels-Alder addition [11,29].

3.2. Oxidative stabilization of pre-treated PAN

During the heating of pre-treated PAN in air, three exothermic regions (peaks III, IV and V in Fig. 2b) can be distinguished by DSC indicating three major processes. The inclusion of oxygen is evident; it is proved by the oxygen content of 13.9 wt% measured by oxygen microanalysis. Following the pre-treatment in inert atmosphere, PAN assimilates oxygen even at low temperatures, e.g. room temperature, as observed by Schimpf [12]. The observation is supported by our own experience as well. This process is related to the exothermic peak recorded at around 70 °C (peak III). The conjugated system formed during the cyclization and elimination reactions in inert atmosphere is most likely attacked by oxygen at carbon atoms located between two double bonds (allylic oxidation) leading to a hydroperoxide [30]. The subsequent elimination of water results in the formation of a

carbonyl group, which can tautomerize into a hydroxide. Both cyclic and open chain sections can oxidize in the way shown in the reaction scheme presented in **Fig. 9a**. The scheme seriously questions the dependence of oxygen inclusion on a pre-cyclized structure as claimed in Refs. 9 and 17.

The isothermal oxidation of the pre-treated sample resulted in a mass change of +2.9 wt%. However, as confirmed by oxygen microanalysis, the oxygen content of the material increased from 0.0 wt% to 13.9 wt% at the same time. Consequently, a mass-loss of 11.0 wt% is concealed by the oxygen uptake of 13.9 wt% indicating the occurrence of an elimination reaction, which can be assigned to the exothermic peak centered at 140 °C (peak IV in **Fig. 2b**). The evolution of CO₂ and H₂O is confirmed by EGA (**Fig. 10**). The source of the evolved gases can be identified by the FTIR analysis of the solid phase, since the small bands of the nitrile and methylene groups at 2242 and 1448 cm⁻¹, respectively, which remained in the material after the previous stage, disappear completely (**Fig. 3c**). The reaction scheme of oxidative dehydrogenation, responsible for the evolution of H₂O, is presented in **Fig. 9b**. The source of CO₂ is the oxidative elimination of remaining nitrile groups by a similar mechanism as the one shown in **Fig. 7** that results in the formation of a double bond on the backbone. The driving force of these processes is the formation of aromatic rings and the further stabilization of the structure.

The third peak on the DSC trace recorded under synthetic air (exothermic region V) can be assigned to the cross-linking reactions of oxygen-containing functional groups [10]. These processes increase the structural stability of the polymer through intermolecular condensation (**Fig. 11**).

3.3. Direct oxidation of PAN

Considering the complex overlap of various chemical processes, the one-step

stabilization of PAN is extremely challenging to study. The DSC trace obtained in the process amply demonstrates this statement (Fig. 12). Only a single exothermic peak can be observed on the thermogram without any hint of the underlying processes. However, a relatively clear picture can be obtained and additional information gained about these processes, if we compare results to the observations made during the two-step stabilization of PAN. The oxygen content of the PAN sample was 14.0 wt% after direct oxidation, i.e. practically the same as the value measured after two-step stabilization (13.9 w%). Based on oxygen content, certain similarity might be expected between the structures produced by the two methods. On the other hand, a total exothermic heat release of -4945 J/g was measured during the one-step treatment, while only a total enthalpy of -1175 J/g was released during the two-step stabilization indicating rather different reaction pathways.

The resulting structures must be also dissimilar, as the weight loss of the samples was 24.4 and 17.4 wt%, respectively, during their subsequent heating up to 600 °C after the corresponding one-step or two-step treatment (Fig. 4). Weight loss is regarded as a measure of the structural stability of PAN, which is determined by the length, ratio, 2D and 3D order of its cyclic and aromatic sequences, and their ability to arrange into a regular structure during carbonization at higher temperatures. From an industrial point of view, longer open-chain sections without intermolecular cross-links are potential locations for chain-scission and subsequent elimination resulting in increased weight loss and smaller carbon yield. Stability and the stabilized structure can be characterized by the ratio of the ¹H NMR signals of the aromatic, cyclic aliphatic and open-chain aliphatic protons, along with the weight loss detected by TGA up to a certain temperature (600-1200 °C) in inert atmosphere.

Unlike in the case of two-step stabilization, low-temperature exothermic heat release may not be observed on the DSC thermogram recorded with a linear heating rate during the direct oxidation of PAN [2,11] (see also Fig. 12). The lack of heat release proves that oxygen

inclusion and oxygen-mediated dehydrogenation occur at relatively low temperatures (50-60 and 100-140 °C at moderate reaction rate) only when they are catalyzed by the presence of a conjugated system. The onset of these reactions is shifted to higher temperatures in all other cases. We do not agree with the conclusions of Wu et al. [9] who proposed that oxidation occurs on cyclic structures rather than on double bonds. They also stated that a pre-treatment of PAN in inert atmosphere results in an "overabsorption of oxygen" and deteriorates the structure, which completely contradicts our experience showing equal amount of oxygen inclusion and better structural stability because of inert pre-treatment.

Following radical initiation, all the reaction steps are competing during direct oxidation in air. Intramolecular cyclization (1) starts around 260 °C and progresses at a controllable reaction rate, and then it is followed by the consecutive elimination (2) of HCN and NH₃. The double bonds formed on the backbone increase the inclusion of oxygen (3) and oxygen-mediated dehydrogenation (4) as well. Intermolecular cyclization (5) may also occur resulting in cross-links among polymer chains. Cross-linking can either take place by the slower intermolecular formation of six-membered carbon rings (6) or the condensation reaction (7) of the formed carbonyl and hydroxyl groups. The competition is leading to shorter cyclic sequences, as double bonds created by dehydrogenation (Fig. 9c) catalyze the conjugative elimination of nitrile groups, which are potential participants in ring formation otherwise.

These chemical processes can be assigned to the exothermic regions determined by DSC. The trace in Fig. 2a (peaks I-II) was recorded under nitrogen, therefore these peaks can be assigned to reactions that already occurred during the pre-treatment in nitrogen (processes 1, 2, 5 and 6). Some of these processes (1, 2, 5) cannot be separated from each other, they are accompanied by gas evolution (HCN, NH₃), and they are the initiation steps of stabilization. Consequently, they can be assigned to peak I. The slower intermolecular

cross-linking (6) can be assigned to the second peak (II). The first of the three peaks in Fig. 2b (III) can be assigned to the rapid mass gain resulting from oxygen inclusion (3). The slow perfectionation of the structure through condensation (7) can be assigned to the peak appearing at the highest temperature (V), while the oxygen mediated dehydrogenation (4) accompanied by weight loss results in peak IV. Based on the previous considerations, the reactions (1,2,5) are assigned to region I, (6) to II, (3) to III, (4) to IV and (7) to V in the case of a two-step stabilization procedure (Fig. 2). All the steps (1-7) appear in the same region in the case of direct oxidation, as shown in Fig. 12.

The reactions mentioned above may be controlled in some extent since their rate is influenced by reaction conditions (atmosphere, temperature). The determination of their kinetic constants (activation energy, rate constant) is challenging and the thorough understanding of the discussed competition is required for obtaining reasonable values.

4. CONCLUSIONS

The two-step stabilization of a thoroughly characterized PAN homopolymer was studied by various methods. The stabilization was carried out with pre-treatment in inert atmosphere, and the reactions taking place as well as the structure of the polymer formed were compared to those occurring in one-step (direct) oxidation. Five separate exothermic regions were detected by DSC measurements and they were assigned to seven reaction steps, for which appropriate mechanisms were proposed together with the relationship among individual reactions. The effect of stereoregularity on the ring formation is discussed and a new scheme is suggested, which includes the cyclization of alternating nitrile groups assuming the *gauche* conformation. The number of successive rings formed during cyclization is determined with three independent methods and compared to previous concepts reported in literature. The positive effect of pre-treatment in inert atmosphere on

the structural stability of PAN during the subsequent pre-carbonization treatment is also demonstrated and explained by considering the mechanism of the reactions taking place during the process.

5. ACKNOWLEDGEMENTS

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Szepcsik, Fig. 1

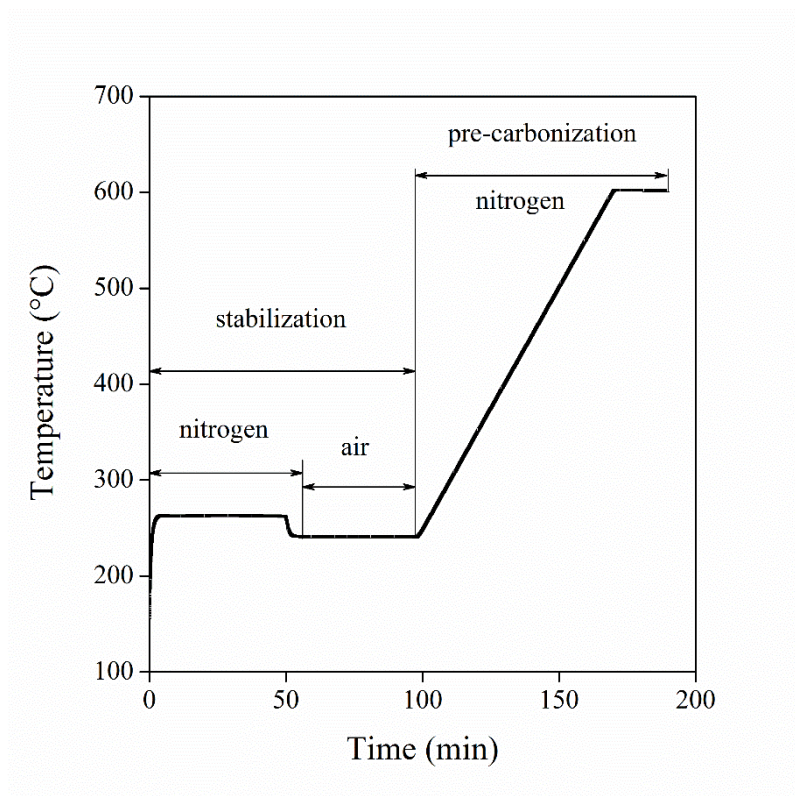


Fig. 1 Heating program for the two-step stabilization of PAN followed by pre-carbonization. Isothermal segments are 260, 240 and 600 °C for 50, 40 and 20 minutes, respectively. Direct oxidation only differs in the atmosphere of the first stabilizing stage.

Szepcsik, Fig. 2

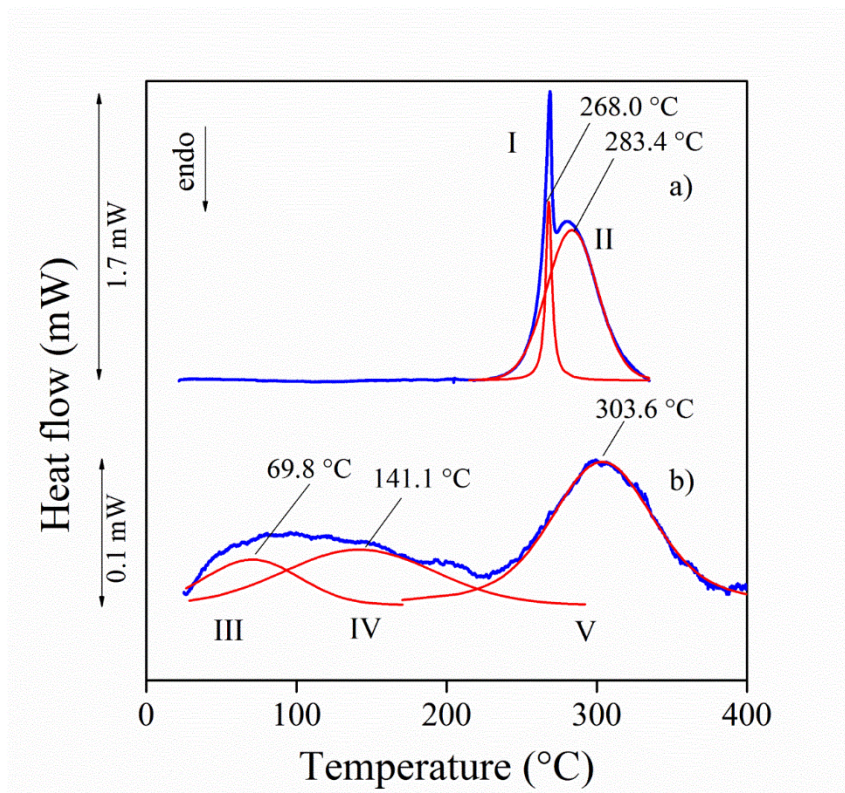


Fig. 2 Separation of the exothermic regions (I-V) observed during the heating of PAN in a DSC pan. Conditions: heating rate: 0.7 °C/min, a) in nitrogen, (b) subsequently in air.

Szepcsik, Fig. 3

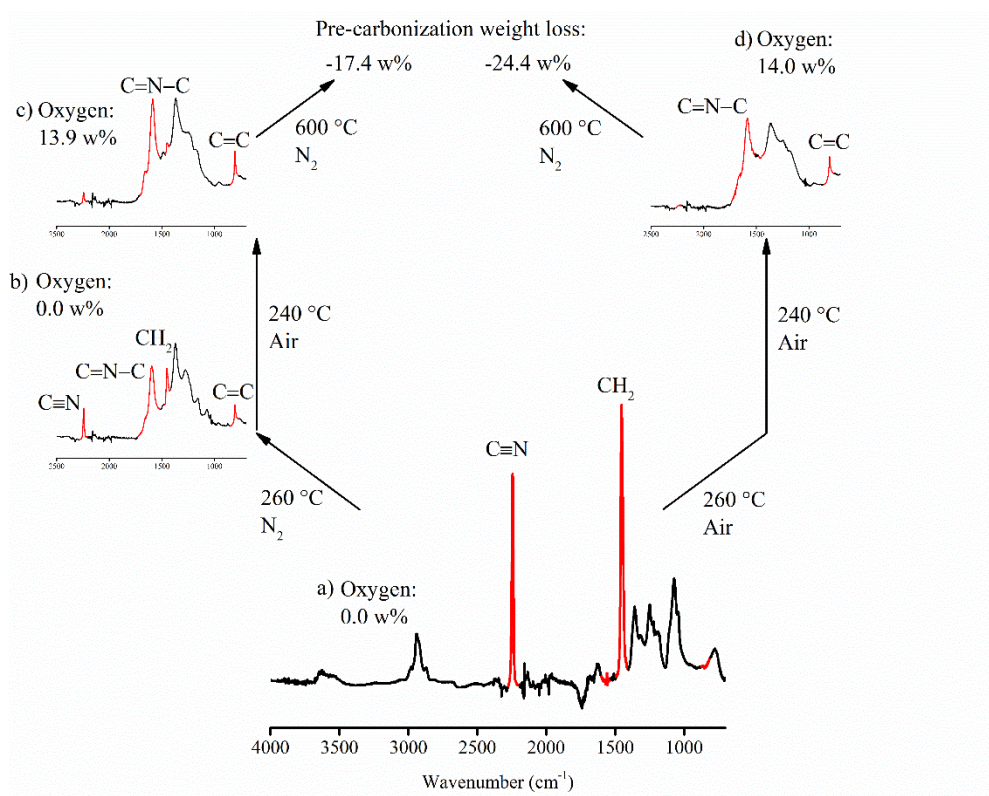


Fig. 3 FTIR spectra recorded on PAN samples subjected to the two-step a)-c) and one-step a), d) stabilization procedure. Samples were prepared in the TGA apparatus for FTIR and oxygen microanalysis. Oxygen content of the materials after the stabilization steps b), c) and d) is also indicated in the figure.

Szepcsik, Fig. 4

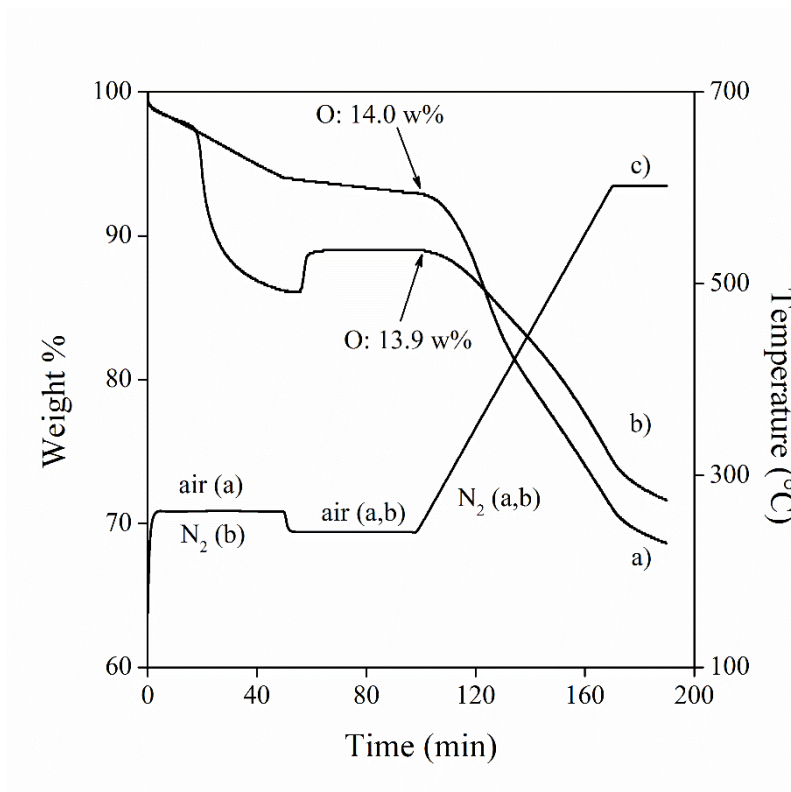


Fig. 4 TGA traces obtained for PAN during one-step (a) and two-step (b) stabilization, recorded with the same temperature program (c). Oxygen content determined at the end of the stabilization are values related to the initial sample weight. Atmospheres of each segment are indicated in the figure.

Szepcsik, Fig. 5

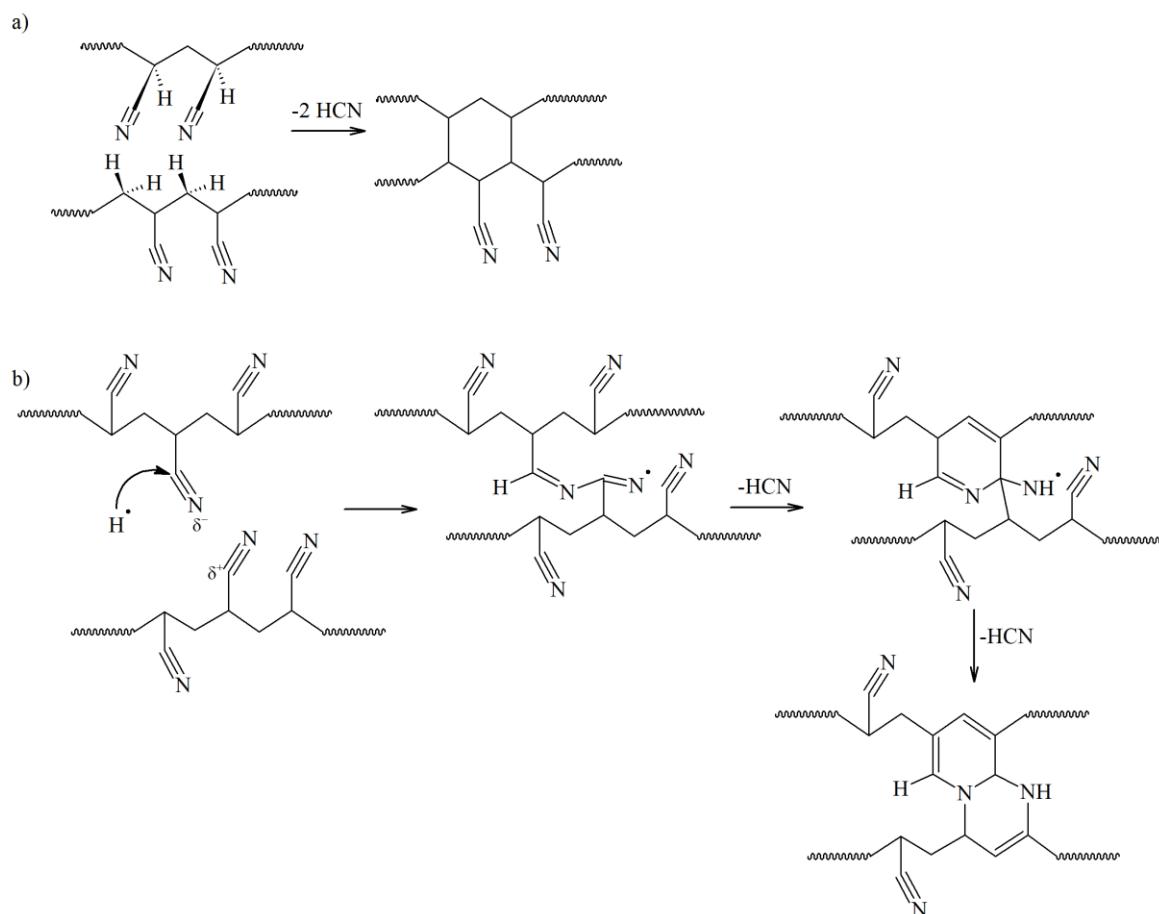


Fig. 5 The mechanism of intermolecular cyclization; a) the formation of cycloalkane cross-links, as proposed by Mathur et al. [28], b) radical transfer among chains (initiation [21] and further stabilization proposed).

Szepcsik, Fig. 6

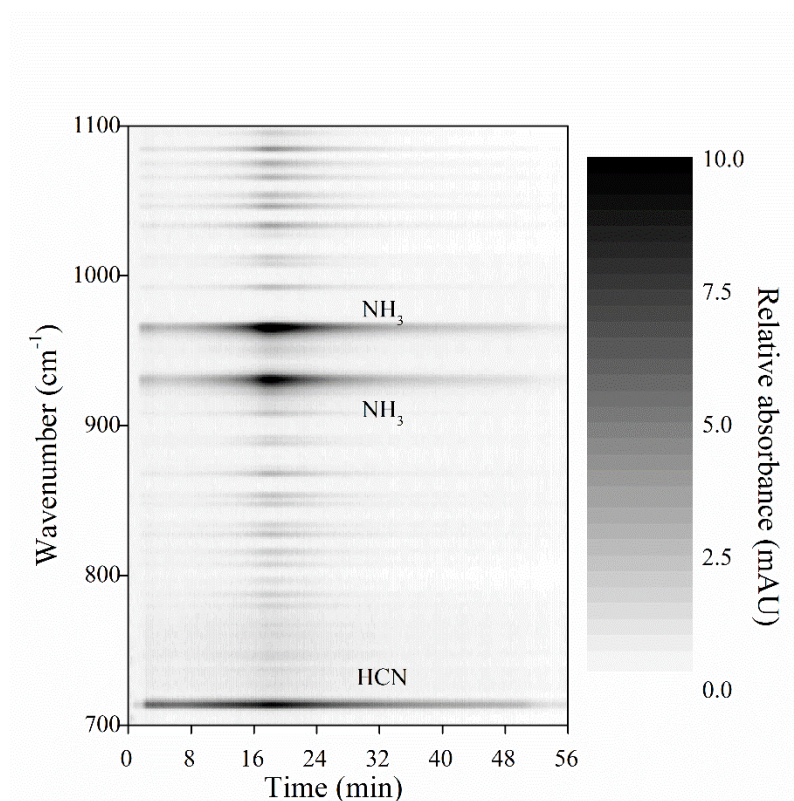


Fig. 6 Greyscale map of gas evolution during the pre-treatment of PAN in inert atmosphere (isothermal treatment at 260 °C, 100 mL/min N₂). The intensive line around 713 cm⁻¹ indicates the evolution of HCN, while the absorption at 930 and 965 cm⁻¹ is related to NH₃.

Szepcsik, Fig. 7

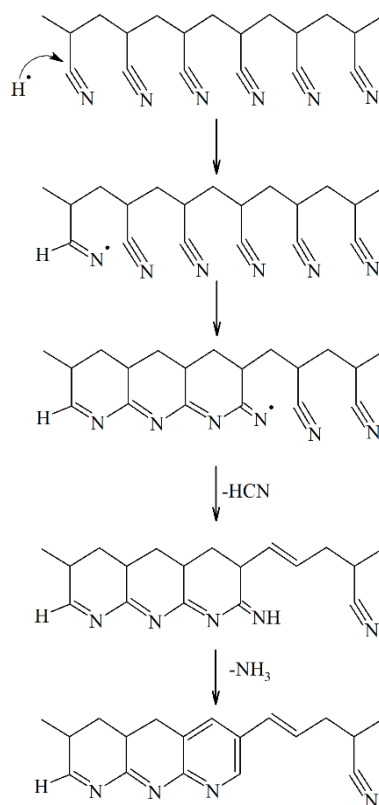


Fig. 7 The proposed mechanism of H radical induced intramolecular cyclization and elimination occurring during the thermal stabilization of PAN.

Szepcsik, Fig. 8

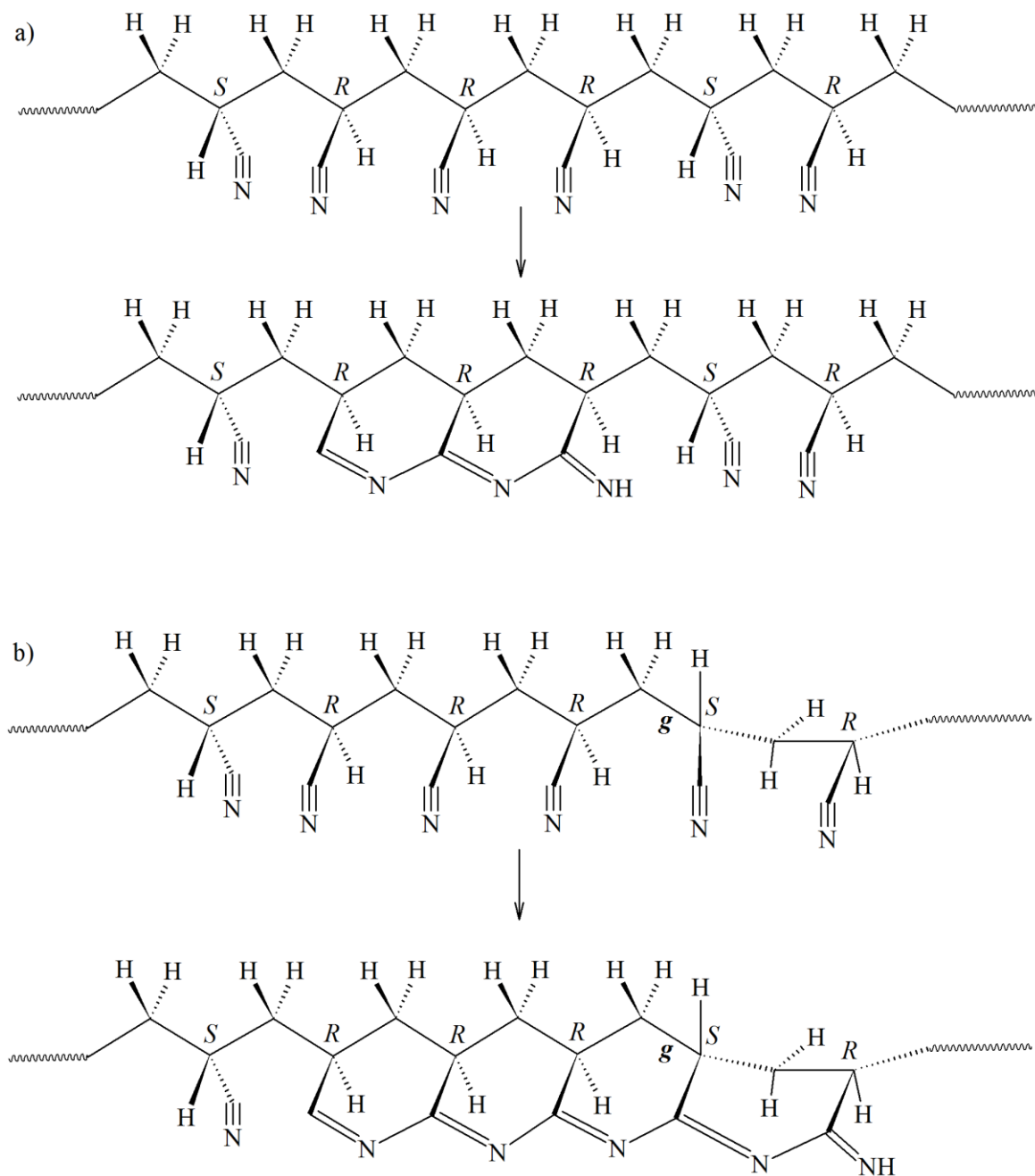


Fig. 8 The proposed effect of the configuration of the nitrile groups on cyclization. a) an *S,R,R,R,S,R* sequence in all-trans conformation, b) gauche conformation of one of the bonds, marked with *g*. Cyclization results in 2 (a) and 4 rings (b), respectively.

Szepcsik, Fig. 9

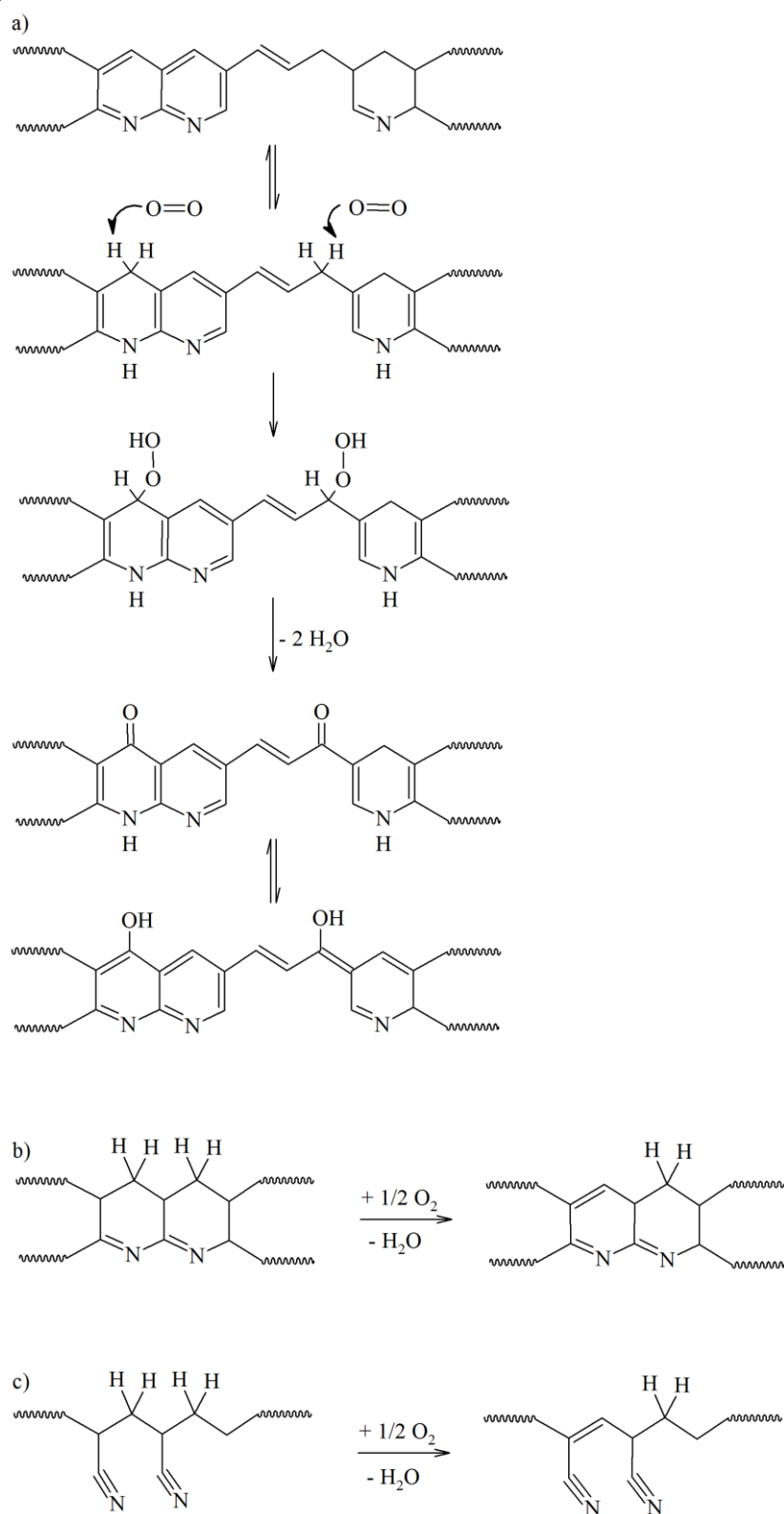


Fig. 9 Reaction scheme proposed for oxygen inclusion (a) and for the oxidative dehydrogenation of a cyclic (b) and an open-chain segment (c), supported by [30].

Szepcsik, Fig. 10

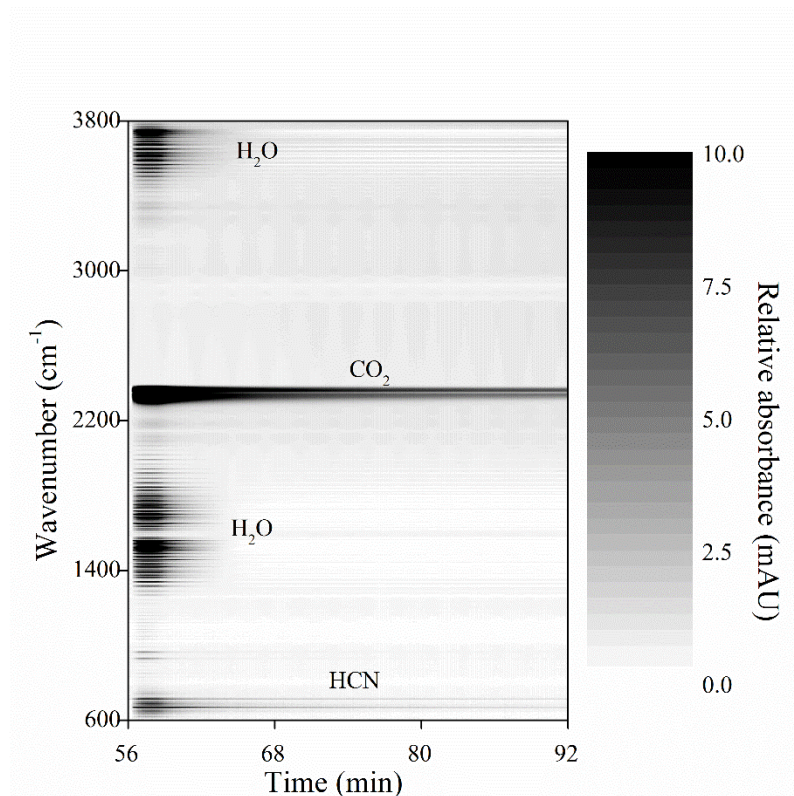


Fig. 10 The greyscale map of gas evolution during the oxidation of pre-treated PAN (isothermal treatment at 240 °C, 100 mL/min synthetic air). The strong absorption in the range of 2300-2400 cm⁻¹ corresponds to the evolution of CO₂, while bands in the range 1300-1800 and 3500-4000 cm⁻¹ indicate the evolution of H₂O. HCN (713 cm⁻¹) is also present, while the signals related to ammonia (930 and 965 cm⁻¹) decrease rapidly.

Szepcsik, Fig. 11

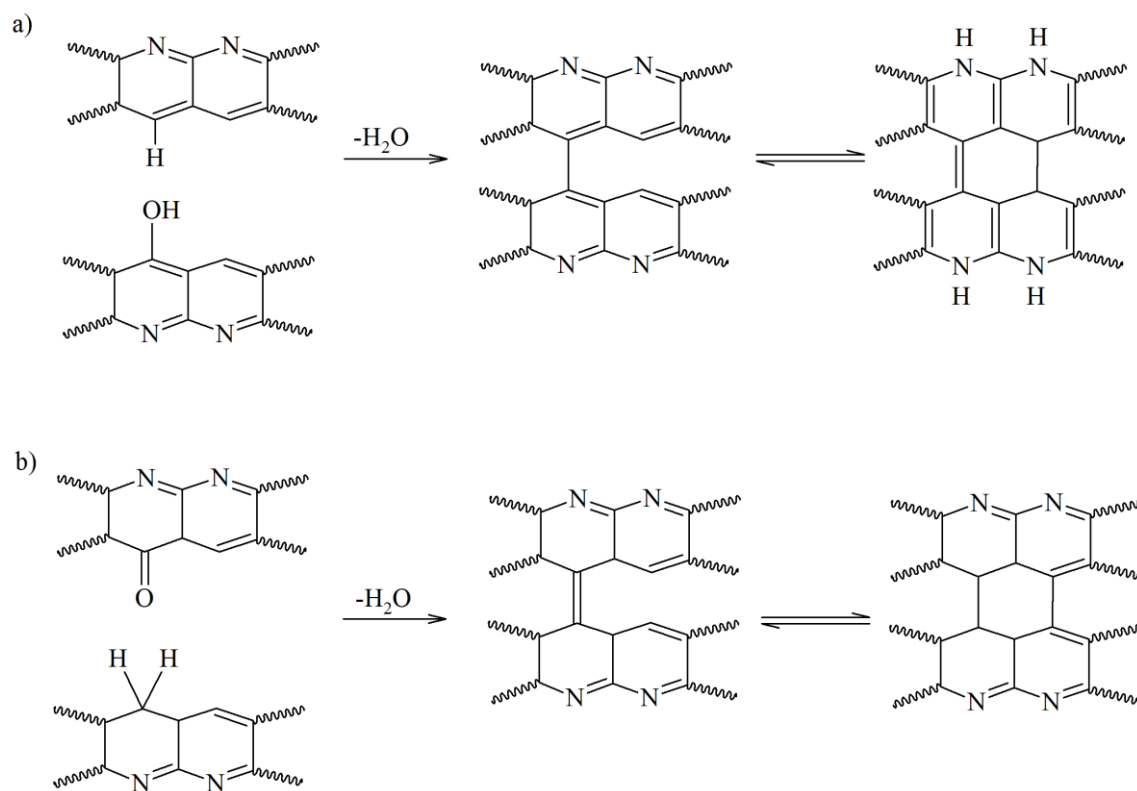


Fig. 11 The reaction scheme of the condensation of oxygen-containing groups in stabilized PAN [10] and the proposed tautomerization of the resulting structures.

Szepcsik, Fig. 12

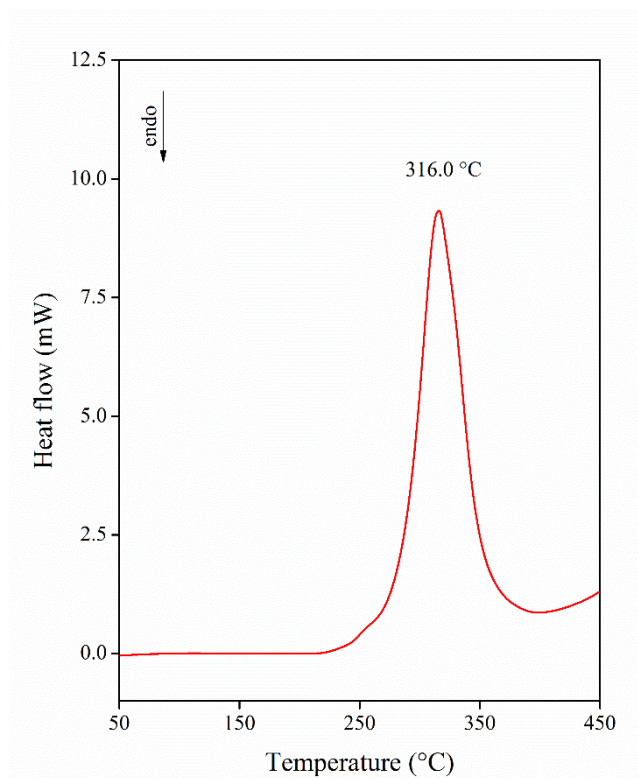


Fig. 12 DSC trace obtained for PAN during one-step stabilization at a heating rate of 5 °C/min under synthetic air atmosphere. The competition of chemical reactions result in an unresolved, extremely intensive exothermic peak.