Fourier Transform Infrared and Wide-Angle X-Ray Diffraction Studies of the Thermal Cyclization Reactions of High-Molar-Mass Poly(acrylonitrile-*co*-itaconic acid)

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ABSTRACT: The stabilization reactions of a high-molar-mass poly(acrylonitrile-*co*-itaconic acid) precursor in air at 200, 220, and 240°C were studied with Fourier transform infrared. Principally, the cyclization of nitrile groups leading to the ladder structures of tetrahydropyridine occurred. Evidence for oxidative reactions causing the conversion of the C—C structure to C═C and generating groups such as —OH and C═O was also obtained. As the temperature of stabilization was increased, the rate of the reaction increased without causing great changes in the Fourier transform infrared spectral patterns. The maximum nitrile conversion achievable was limited by the temperature of stabilization. Although the reaction stagnated at 40 and 80% at 200 and 220°C, it was practically complete in about an hour at 240°C. Higher temperatures also favored the formation of extended conjugated structures. Wide-angle X-ray diffraction studies of the polymer stabilized at 300 and 400°C in argon confirmed that the aromatization index value and the crystallinity of the polymer increased proportionally to the temperature of pyrolysis. An analysis of the wide-angle X-ray diffraction pattern and the elemental composition of the stabilized polymer implied the formation of the tetrahydropyridine structure at 400°C. The higher pyrolysis temperature favored the formation of the lattice constituted by this group. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3055–3062, 2006

Key words: fibers; FT-IR; kinetics (polym.); stabilization

INTRODUCTION

Among the various precursors, polyacrylonitrile (PAN)-based fibers remain some of the best materials for making carbon fibers.[1–5] A PAN precursor for carbon fibers usually incorporates a comonomer; itaconic acid (IA) is the most preferred. In previous works, we reported the copolymerization of acrylonitrile with IA.[6,7] Maleimidobenzoic acid was also explored as a potential comonomer in a PAN precursor.[8] IA was found to be more effective in catalyzing the nitrile cyclization reaction and increasing the char yield.[6,9]

The conversion of PAN precursor fibers to carbon fibers involves an intermediate step of stabilization reaction.[10–17] This is normally performed in the temperature range of 180–400°C. During this process, the polymer undergoes a number of physical and chemical changes; the most salient of them is the cyclization of nitrile groups to form an aromatized structure known as a ladder polymer. The ladder polymer forms the skeleton upon which the structure of the high-performance product will be ultimately based. The acid plays a catalytic role in the cyclization process, an important step during pre-oxidation, which stabilizes the polymer backbone before carbonization.[18] The extent of cyclization in the stabilized material has a strong bearing on the mechanical properties of the resulting carbon fiber product. Watt[19] and others[20] have reported that optimal performance requires the conversion to be approximately 50% complete. It is important that the initial conversion should proceed as fully as possible, preferably to 100%. The low-temperature stabilization is the most crucial step, whose efficiency decides to a great extent the quality of the carbon fiber formed during pyrolysis. Fourier transform infrared (FTIR) has been used to study the structural analysis of copolymers and to monitor the thermal reactions.[21] The thermal reactions can vary with the type of precursor and can depend on the PAN composition and molecular weight. We were interested in a high-molar-mass PAN precursor. An understanding of its stabilization behavior is imperative for the optimization of the carbonization process. In an earlier study, we reported the kinetics of the cyclization reaction based on the differential scanning calorimetry exothermicity.[9] However, this method (based on the relative heat output) might not be abso-

lute, unless the reaction temperature is sufficient to achieve full conversion. In this work, we have studied the absolute nitrile conversion by an FTIR technique. The associated chemical changes have also been investigated. A wide-angle X-ray diffraction (WAXD) technique has been used to complement the structural changes associated with the stabilization process.

EXPERIMENTAL

Characteristics of the polymer

The PAN precursor was synthesized by methods reported earlier.[6,7] The conditions were regulated to get a polymer with a viscosity-average molecular weight of about 1.0×10^6 g/mol that contained 1.5 mol % IA.

Stabilization

The samples (ca. 1 g) were heat-treated in static air in an air oven with a temperature accuracy of 1°C. Heat treatments at 300 and 400°C were carried out in a furnace under an argon atmosphere.

FTIR spectroscopy

FTIR spectra were recorded on a PerkinElmer (CT, USA) Spectrum GX spectrophotometer for a wavenumber range of 4000–400 cm^{-1}. The estimation of the nitrile conversion was done from the decrease in the intensity of the absorbance of this group at 2242 cm^{-1}. Weighed samples were mixed thoroughly with a known amount of KBr and pelletized. The quantitative IR estimation is based on the Beer–Lambert law:

$$A = \log\left(\frac{I_0}{I}\right)$$

where A, the absorbance, is given as $A = \varepsilon c t$; ε is the molar extinction coefficient; c is the concentration of the solid solution; t is the thickness of the KBr pellet; I_0 is the intensity of the incident light; and I is the intensity of the transmitted light

From the relative absorbance of the virgin and heat-treated materials, the nitrile conversion (%) was calculated.

WAXD studies

The WAXD pattern of the finely powdered samples was recorded on a Siemens (CT, USA) D5005 X-ray diffractometer operated at a voltage of 40 kV and a current of 30 mA with nickel-filtered Cu Kα radiation (wavelength = 1.5405 Å).

The Bragg equation was used to calculate the interlayer spacing (d):
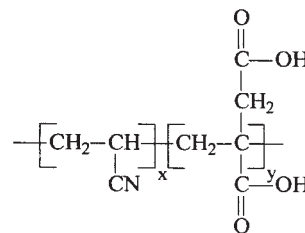
Scheme 1 Structure of poly(AN-*co*-IA).

$$n\lambda = 2d \sin\theta$$

where λ is 1.5405 Å, n is the order of reflection, and θ is the angle of reflection.

To acquire the average crystallite size (L_C) of the laterally ordered phase, the Scherrer equation was used:

$$L_C = \frac{K\lambda}{\beta \cos\theta}$$

where K is the apparatus constant (taken to be 0.89) and β is the half-value width (rad) of the curve of the X-ray intensity versus the Bragg angle.

The crystallinity index (χ_c) was calculated with the following relation:

$$\chi_c = \frac{W_c}{W_c + W_a} \times 100$$

where W_c is the area of the crystalline portion in the X-ray diffractogram and W_a is the area of the amorphous portion in the X-ray diffractogram.

Calculation of the aromatization index (AI)

AI is given by

$$AI = I_A/(I_A + I_P)$$

where I_A is the intensity of the diffraction peak associated with the aromatized structure at a 2θ value of 26.5° and I_P is the intensity of the diffraction peak at a 2θ value of 17°.

RESULTS AND DISCUSSION

The structure of the polymer is shown in Scheme 1. Figure 1 shows the IR bands in the poly(acrylonitrile-*co*-itaconic acid) [poly(AN-*co*-IA)] polymer. The absorption at 542 cm^{-1} has been assigned to C—C≡N, but Minagawa et al.[22] assigned this also to the effect of stereoregularity when the isotacticity is increased. The band at 1076 cm^{-1} is ascribed to the —CH bending mode. The absorption at 1224 cm^{-1} is due to the
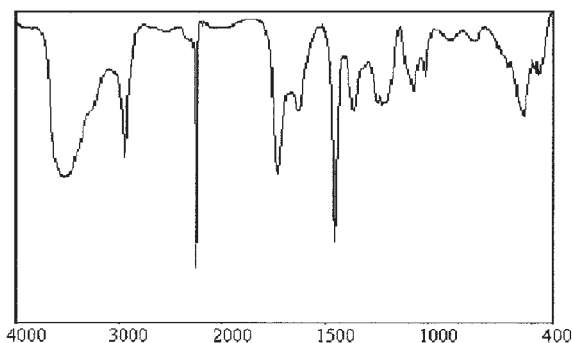
Figure 1 IR spectrum of the poly(AN-*co*-IA) polymer containing $\approx$1.5 mol % IA.

twisting mode of the methylene (—CH_2) coupled with the methine group. A small band at 1250 cm^{-1} is assigned to the bending mode of the methine group coupled with the rocking mode of the methylene groups. The bands appearing at 1220–1270, 1345–1375, and 1440–1465 cm^{-1} are assigned to the C—H vibrations of different modes. The strong band appearing at 2242 cm^{-1} is assigned to —C≡N stretching. The peak at 1731 cm^{-1} is due to the carbonyl stretching vibration of the carboxylic acid. The absorption at 2940 cm^{-1} has been attributed to the stretching motion of the —CH_2 group. The broad band extending from 3420 to 3520 cm^{-1} is caused by the —OH stretching vibration of the —COOH group.

Thermal reaction of poly(AN-*co*-IA) in an air atmosphere

In this study, the heat treatment was effected at three temperatures (200, 220, and 240°C) to study the variation of the rate of nitrile cyclization with temperature. The observed major variations are the decreases in the intensity of the nitrile band at 2242 cm^{-1}, the methylene band at 2940 and 1454 cm^{-1}, and the carbonyl stretching band at 1731 cm^{-1}. New bands appear at 1600 cm^{-1} because of the generation of C=C and C=N groups, whereas the new absorption at 1575 cm^{-1} arises from —NH bending vibrations.

Figure 2 shows the changes occurring in the IR spectra from 4000 to 400 cm^{-1} for poly(AN-*co*-IA) heated at 200°C in air. Figure 2(A) presents the original spectrum of PAN before heating, whereas Figure 2(B–D) illustrates the changes occurring in PAN during isothermal heating at 200°C for 1, 2, and 3 h, respectively. The reactions occurring during the thermal stabilization of PAN are[23]

1. Cyclization of pendant nitrile groups (those predominantly in the isotactic configuration), transforming the polymer into a ladder-type structure.

2. Dehydrogenation reactions occurring along the polymer backbone and in the condensed rings.
3. Oxygen uptake reactions during a thermal treatment leading to ladder-type polymers with different functional groups.

The general trend, as the stabilization proceeds, is that the nitrile peak at 2242 cm^{-1} and the peak due to —CH_2 bending in the open chain at 1453 cm^{-1} decrease in intensity, whereas the peak due to the aromatized structure at 1600 cm^{-1} and the peak due to the —CH_2 bending in the cyclized ring at 1378 cm^{-1} increase in intensity with an enhancement of the extent of the cyclization. Figure 3, featuring the spectral pattern between 2400 and 1300 cm^{-1}, shows the most significant changes during the pyrolysis in the temperature regime studied for the time intervals of 1, 3, and 6 h, respectively. A closer examination of Figure 3 shows the presence of intense doublets at 1731 and 1603 cm^{-1}. As the cyclization proceeds, the absorption band at 1731 cm^{-1}, attributed to the carbonyl stretching vibration of the —COOH group of IA, diminishes to a negligible intensity, and the peak at 1603 cm^{-1} becomes stronger. The cyclization initiated through an ionic mechanism by the IA comonomer results in the linear polymerization of nitrile groups, giving heterocyclic ladder systems similar to that shown in Scheme 2. The peak at 1600 cm^{-1} is assigned to a —C=N— conjugated double-bond system of a short length.
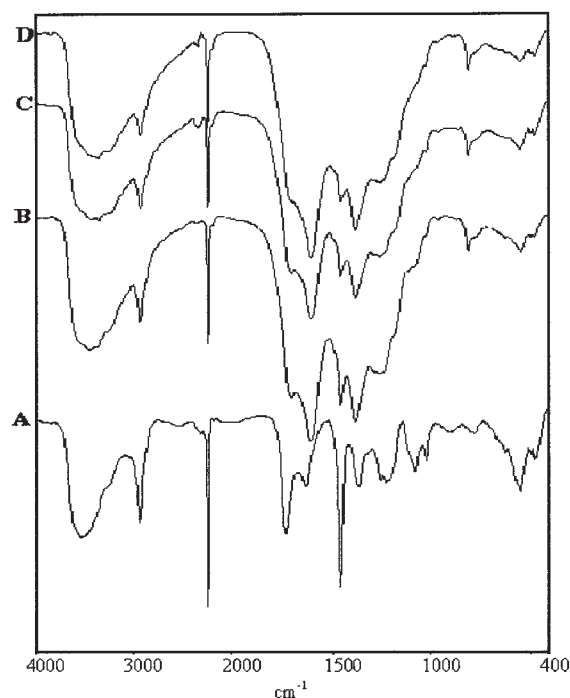

Figure 2 FTIR spectra of poly(AN-*co*-IA) heated at 200°C: (A) original poly(AN-*co*-IA) and (B–D) poly(AN-*co*-IA) treated for 1, 2, and 3 h, respectively, in air.
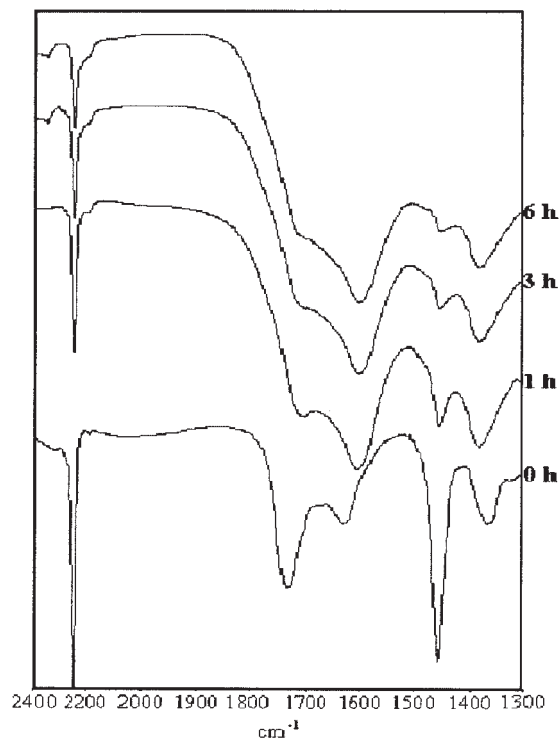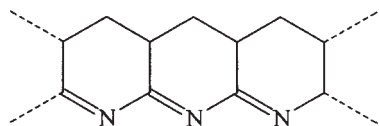
Figure 3 Spectral region from 2400 to 1300 cm^{-1} for poly(AN-*co*-IA) aged in air at 200°C.

Grassie and McGuchan[24] assigned the 1603-cm^{-1} band to the conjugation of —C≡N— or —C≡C— structures.

As the temperature of pyrolysis is increased, except for the change in the signal intensity (or broadening) and the rate of the reaction, the spectral patterns are similar (Figs. 3 and 4). The PAN sample treated at 240°C exhibited the most significant changes in the spectrum within the shortest time (see Fig. 4). In this case, the —C≡N absorption at 2242 cm^{-1} decreases drastically compared to those of samples heated at 220 and 200°C, whereas the intensity of the peak at 1603 cm^{-1} increases enormously. There is an increase in the intensity of the peak at 1377 cm^{-1}. This indicates the formation of cyclic conjugation leading to a tetrahydropyridine-type ladder structure, as shown in Scheme 2. The final product in the stabilization process after heating for 1 h has hardly any nitrile band left. This indicates that the structural changes involving the whole molecular chain of PAN take place in the stabilization process. These observations agree well with those of previous workers, suggesting the
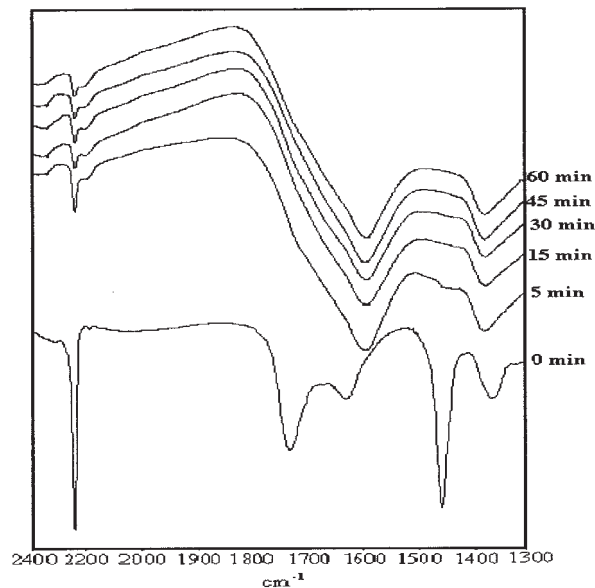

Figure 4 Spectral region from 2400 to 1300 cm^{-1} for poly(AN-*co*-IA) aged in air at 240°C.

formation of a ladderlike structure with conjugated unsaturated bonds, formed by the polymerization of nitrile groups and release of hydrogen, and with carbonyl group incorporation by thermal oxidation.[25] The decrease in the absorption at 2940 cm^{-1} and the disappearance of the methylene and methine groups indirectly indicate the formation of C=C in the cyclized structure. This is also supported by the disappearance of the 1450-cm^{-1} absorption band, which is characteristic of the bending vibration of the —CH$_2$ unit in the open chain. An enormous decrease in the intensity of the C≡N absorption at 2242 cm^{-1} and an increase in the signal at 1600 cm^{-1} (C=C and C=N) demonstrate the onset of the extended conjugation of the cyclized structure. The shoulder at 1715 cm^{-1} is indicative of carbonyl groups formed through an oxidative process. The most consistent observation throughout the investigation is that the nitrile absorption band at 2242 cm^{-1} decreases in intensity as a function of the heat-treatment time. As stabilization proceeds, relatively weak bands appear at 3363 cm^{-1}, and so does a shoulder at 2198 cm^{-1}, whereas strong bands appear at 1378 and 1610 cm^{-1}. The new absorption at 2198 cm^{-1} can be attributed to imino nitrile groups (Scheme 3) formed when the nitrile cyclization is blocked at the initiation step.[23] The extent of the

Scheme 2 Tetrahydropyridine ladder structure.
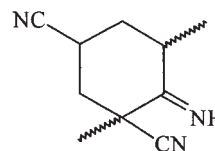
Scheme 3 Imino nitrile structure.

TABLE I
Extent of the Stabilization Reaction at Different Temperatures

200°C			220°C			240°C		
Time (min)	Nitrile absorbance	Conversion (%)	Time (min)	Nitrile absorbance	Conversion (%)	Time (min)	Nitrile absorbance	Conversion (%)
15	0.150	3.8	5	0.102	35.8	5	0.036	76.7
30	0.127	18.6	15	0.099	35.9	15	0.013	91.1
45	0.119	23.7	30	0.082	47.2	30	0.013	91.7
60	0.114	26.9	45	0.077	50.3	45	0.012	92.2
75	0.109	30.1	60	0.066	57.6	60	0.008	94.6
90	0.107	31.4	75	0.053	65.6	75	—	—
105	0.102	34.6	90	0.043	71.9	90	—	—
120	0.097	37.8	105	0.034	77.6	105	—	—
135	0.097	37.9	120	0.032	78.9	120	—	—
150	0.096	38.5	150	0.029	80.8	150	—	—
165	0.095	39.1	165	—	—	165	—	—
180	0.095	39.3	180	—	—	180	—	—
195	0.094	39.7	195	—	—	195	—	—
210	0.091	41.7	210	—	—	210	—	—

cyclization reaction calculated from the nitrile peak absorbance is given in Table I.

As shown in Table I, the higher the temperature is, the faster the stabilization reaction is. The cyclization proceeds to about 95% completion in 60 min at 240°C, whereas only about 42% conversion is achieved at 200°C. To better illustrate this point, a plot of the —C≡N conversion versus time is given for each temperature in Figure 5. At these three reaction temperatures, the extent of stabilization stagnates after a particular nitrile conversion is attained. The stagnation conversion point increases with the temperature, as shown in Figure 5.

Likely thermal processes in stabilized PAN

Many mechanisms have been proposed to adequately explain the reaction processes during stabilization. It has been claimed that the initiation of cyclization in the presence of an acidic comonomer takes place by an ionic mechanism. In this context, the following mechanisms have been proposed:
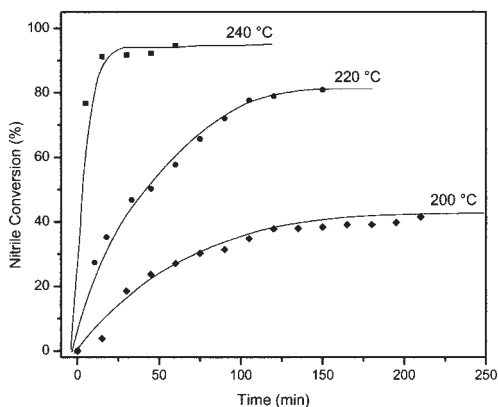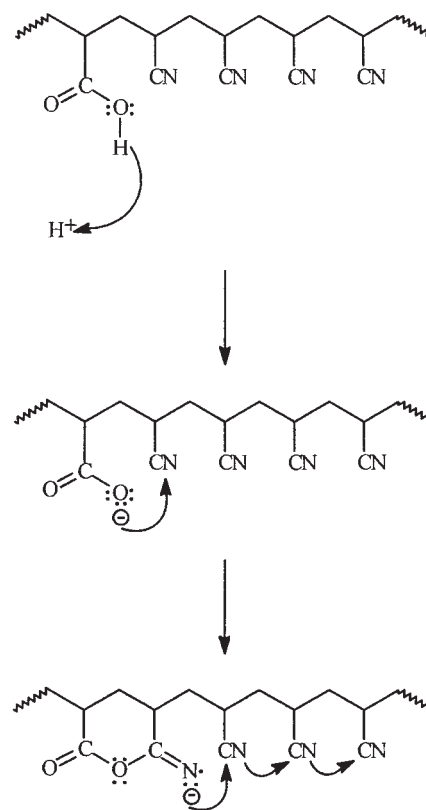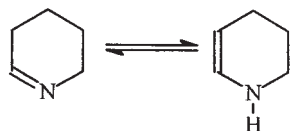
1. Nucleophilic attack on a nitrile group by —COO⁻ followed by the cyclization of isotactic sequences along the polymer chain (Scheme 4). The carbonyl group further helps in the

Figure 5 Nitrile conversion (%) as a function of time at different temperatures.

Scheme 4 Cyclization initiation through nucleophilic attack on a nitrile group by a —COO⁻ group.

Scheme 5 Rearrangement of the imine to enamine.

crosslinking of the chains through dehydroge-
nation reactions in the subsequent carboniza-
tion step.

2. Rearrangement of the structures to give enamine–
imine equilibrium followed by oxidation (by air),
as shown in Schemes 5 and 6.

In the tetrahydropyridine series, the enamine-like
structure is more stable. The enamine intermediate
reacts with trace amounts of oxygen to give a pyri-
dine-type ring. Being very sensitive to oxidation, het-
erocyclic enamines turn brown on standing in air; this
is consistent with our observations.

The spectral pattern is consistent with these postu-
lations. It is known that imines form hydroperoxides
with atmospheric oxygen and decompose to give cor-
responding alcohol. The absorption at 3363 cm^{-1} in
the stabilized product is most likely associated with
the hydrogen-bonded —O—H stretching. The band at
1715 cm^{-1} is assigned to the carbonyl stretching fre-
quency, which decreases to a negligible amount as
stabilization proceeds. The band at 1610 cm^{-1} is as-
signed to the C=N stretching frequency of the enam-
ine, and that at 1378 cm^{-1} is assigned to the methylene
group in the cyclized ring, both increasing as the
cyclization proceeds to form a linear ladder polymer.
These reactions are expected to take place almost si-
multaneously. Oxidation reactions have been reported
to precede cyclization but are slower during the ther-
mal treatment of PAN in air, and they have been
reported to continue even after the cyclization reaction
is completed.[12]

## WAXD of the stabilized polymer

For WAXD studies, the polymer was stabilized in
argon at 300 and 400°C. A typical X-ray diffraction
pattern of virgin poly(AN-*co*-IA) copolymer [Fig. 6(a)]
gives two peaks at 2θ values of 17 and 29°.[26–30] The
diffraction maximum around $2\theta = 17°$ has been inter-
preted as the (100) plane of the hexagonal unit of the
C≡N groups.[27] The molecular chains of PAN are of a
helical conformation because of the intramolecular di-
pole–dipole interactions among the nitrile group
pairs. This is not likely to change in a copolymer
incorporating trace amounts of the comonomer. In the
crystalline regions, the nitrile group pairs are formed
because of the intermolecular and intramolecular di-
pole–dipole interactions, whereas the intermolecular

nitrile group pairings are fewer in the amorphous
regions because of the random arrangement of molec-
ular chains.[27]

Upon the heating of the poly(AN-*co*-IA) sample (as
the stabilization proceeds), the intensity of the main
peak at $2\theta = 17°$ declines at 300°C, as shown in Fig-
ure 6(b). Similar observations have been reported
earlier.[26–28] When the pyrolysis temperature is in-
creased to 400°C, a much broader peak centered ap-
proximately at $2\theta = 26.5°$ swamps the secondary peak
at 29°, as shown in Figure 6(c). This new peak at 26.5°
corresponds to the sheetlike structure of the ladder
polymer. In this case too, some residual diffraction can
be observed at $2\theta = 17°$, as observed in previous
works.[26–31] This could be due to the scattering of the
ladder structures from a different plane because no
C≡N group is likely to remain at this stage.

As reported by Uchida et al.,[32] the WAXD technique
can be employed to quantify the conversion to a lad-
der polymer. The values of AI obtained for the two
samples heat-treated at 300 and 400°C are given in
Table II.

Data in Table II show that the χ_c and AI values
increase with the pyrolysis temperature. From the el-
emental compositions of the stabilized PAN given in
Table II, it becomes evident that an increase in the
pyrolysis temperature increases the carbon content at
the cost of the hydrogen and nitrogen contents. The
decrease in the nitrogen content is nominal, confirm-
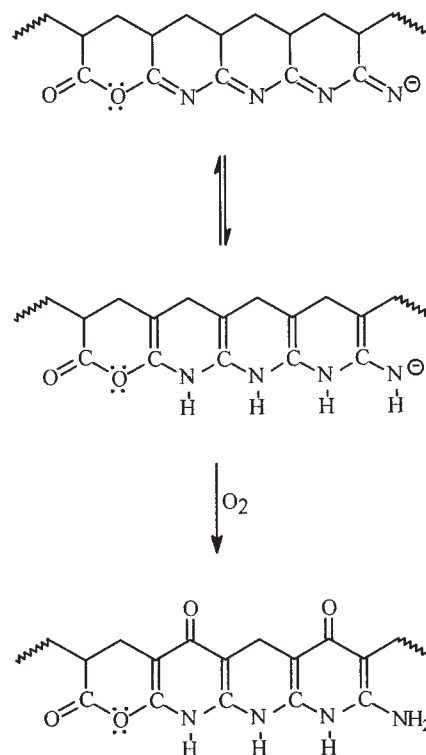
Scheme 6 Rearrangement and oxidative reactions of the
tetrahydropyridine structure.

ing that the tetrahydropyridine ladder structure formed at 300°C remains intact at 400°C. In the absence of air, the apparent oxygen content initially decreases and then increases because of a proportional evolution in the composition of the other elements. Although cyclization is completed at 300°C, the tetrahydropyridine lattice is favored at higher temperatures. It appears that a higher pyrolysis temperature is conducive to a better reorganization of the lattice originating from the tetrahydropyridine structure.

CONCLUSIONS

The stabilization reactions of a PAN precursor in air at three different temperatures (200, 220, and 240°C) have been studied by FTIR techniques. Oxidative reactions cause the conversion of the C—C structure to C=C and generate oxygen-containing groups such as —OH, C=O. Cyclization reactions lead to the development of ladder structures by oligomerization of nitrile groups. As the temperature of stabilization increases, the signal intensity (or broadening) and the rate of the reaction change, but the spectral patterns remain similar. The higher the temperature is of the
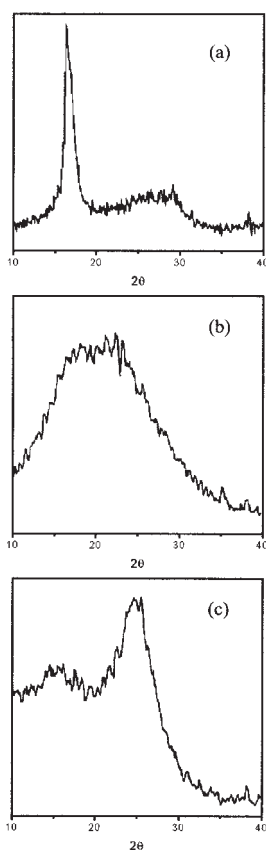
TABLE II
Parameters from the WAXD Studies and Elemental Composition of the Poly(AN-Co-IA) Copolymer after Pyrolysis

			Elemental analysis (%)			
Sample history	χ_c (%)	AI	C	H	N	O (by difference)
Virgin	48	0	63.6	4.4	23.5	8.5
Heated at 300°C in argon for 2 h	57	0.51	67.8	3.8	21.7	6.7
Heated at 400°C in argon for 2 h	68	0.68	68.7	3.6	19.6	8.1

stabilization reaction, the faster the —C≡N conversion is, and it stagnates after a particular time interval, depending on the temperature. The C≡N conversion is complete in about an hour when the stabilization temperature is 240°C. Temperatures lower than this are incapable of bringing about the conversion to a meaningful extent. Spectral studies confirm that the thermal reactions for this copolymer are on par with those reported for similar precursors.

WAXD studies have confirmed that the AI value and the crystallinity of the copolymer increase with the temperature of pyrolysis. The elemental composition of the heat-treated polymer implies the formation of the tetrahydropyridine structure in the temperature range of 300–400°C. A higher pyrolysis temperature favors lattice organization of these groups.

Figure 6 WAXD patterns of poly(AN-*co*-IA) samples: (a) a virgin sample (unpyrolyzed), (b) a sample pyrolyzed at 300°C for 2 h in an argon atmosphere, and (c) a sample pyrolyzed at 400°C for 2 h in an argon atmosphere.

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