Articles

Thermal Transformations of Kevlar Aramid Fibers during Pyrolysis: Infrared and Thermal Analysis Studies

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The main objective of this work was to get some further insight into the chemistry involved in the carbonization of aramid fibers. For this, the pyrolysis behavior of Kevlar [poly(*p*-phenylene terephthalamide)] fibers under argon was studied using thermoanalytical and FT-IR spectroscopic methods to get direct information on the progressive changes undergone by the solid material and its carbon fiber residues. Variations in concentration of major elements (C, H, N, S, and O) were also monitored as a function of pyrolysis temperature. Below 500 °C only minor changes associated with loss of hydrogen bonds occur. Above 500 °C the weight loss becomes significant. However, no noticeable framework changes take place until about 545 °C. Kevlar appears to be chemically stable up to this temperature. The main pyrolytic transformation occurs over a narrow temperature interval (550–575 °C) leading to the collapse of the initial framework, which proceeds mainly through the progressive decomposition of amide groups by C=O and C—N bond cleavage. Intermediate aryl nitrile products are formed during this process. Above 600 °C depolymerization gives way to progressive aromatization/condensation reactions leading to polynuclear aromatic compounds, the degree of condensation of the network increasing with treatment temperature.

Introduction

Activated carbon fibers are usually prepared from low-crystallinity feedstocks such as poly(acrylonitrile), viscose rayon, and coal tar pitch. Freeman et al.[1] have recently proposed substituting these precursors with crystalline linear polymers such as aramid fibers in order to obtain activated carbons with new adsorption properties. Tomizuka et al.[2] reported the formation of isotropic, nongraphitizable carbon fibers, while Fitzer et al.[3] indicated that porous residues with low strength are formed in the pyrolysis step.

Indirect information has usually come from the characterization of volatile degradation products, and thus numerous studies on the pyrolysis of Kevlar and other aramid polymers have dealt with the analysis of compounds evolved during pyrolysis. The volatiles have been identified by mass spectrometry, infrared spectroscopy or gas chromatography. Krasnow et al.[4] observed that the main products of Kevlar pyrolysis at 400 °C are H_2O and CO_2. At temperatures close to 500 °C

important amounts of HCN, benzene, toluene and benzonitrile were found. Khanna et al.[5] indicated that the volatile degradation products contain one or two aromatic rings whose substituent groups are essentially amino, nitrile, carboxyl, and phenyl. The occurrence of one or two rings mainly depends on the pyrolysis temperature: at 450 °C two-ring compounds are prevalent, whereas those with one ring predominate at 550 °C.

Brown and Power[6] studied the variation in the composition of volatiles with temperature for the 300–700 °C range. The nature of evolved products provided evidence for the occurrence of both homolytic and heterolytic ruptures of the amide unit, the first type being predominant at high temperatures and the second one at low temperatures. The existence of homolytic and heterolytic ruptures during pyrolysis of aramid fibers had already been proposed by Kalashnik et al.[7] Later, Gal et al.,[8] in studying the thermal transformation of polyaramid fibers by mass spectrometry, also concluded that pyrolysis occurs through homolytic and heterolytic pathways. The degradation begins by HN—

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Table 1. Analyses of Kevlar and Kevlar Chars (Dry Basis)

T (°C)	C (wt %)	H (wt %)	N (wt %)	S (wt %)	O_{diff} (wt %)	H/C (atomic)	H/N (atomic)	H/O (atomic)	O/N (atomic)
20	69.4	3.7	12.7	0.5	13.7	0.64	4.08	4.30	0.94
535	68.8	3.9	11.5	2.0	13.9	0.67	4.75	4.49	1.05
563	69.7	3.6	11.2	1.9	13.7	0.62	4.50	4.20	1.07
575	72.7	3.0	10.4	2.0	11.9	0.49	4.04	4.03	1.00
594	73.2	2.7	10.1	2.3	11.7	0.44	3.74	3.69	1.01
644	73.5	2.3	9.2	1.4	13.7	0.37	3.50	2.69	1.29
725	74.6	1.7	8.2	1.4	14.1	0.27	2.90	1.93	1.51
960	75.4	0.8	5.5	1.3	17.0	0.13	2.04	0.75	2.72

CO bond cleavage and continues through rupture of the C—CO bond.

Finally, a particularly comprehensive study carried out by Schulten et al.[9] using FIMS and GC must be mentioned. These authors identified in the volatiles evolving from Kevlar pyrolysis various aromatic products with one, two or three rings. These compounds were frequently formed from Ph—CO and HN—Ph bonds cleavage and mainly contained amino and nitrile substituents.

All of these studies based on analyzing the volatile decomposition products provide interesting indirect information on the chemistry involved in Kevlar pyrolysis. However, no direct information on the progressive changes undergone by the solid material is available. Only in the above-mentioned work from Tomizuka et al.[2] was a detailed study made on the characteristics of the isotropic, nongraphitizable carbon fibers obtained in the last steps of Kevlar decomposition.

The essential aim of this work was to get some further insight into the chemistry involved in the pyrolytic transformation of aramid fibers into fibrous carbon residues. For this, we have combined results from thermal analysis and infrared spectroscopy to characterize these residues. Our interest is in the structure of the pyrolyzed fibers and also the solid evolution during thermal treatment, the knowledge of which will allow selection of the optimum conditions for the pyrolysis step prior to ulterior activation of the resulting carbon fibers. These results also are of interest in connection with the thermal stability of aramid fibers, as they are used as a fire-resistant material at moderate temperatures.

Experimental Section

The starting material was commercial Kevlar 29 (low-modulus version, in yarn 1670 dtex), manufactured by DuPont, polymer whose chemical composition corresponds to poly(*p*-phenylene terephthalamide).

TG/DTG/DTA experiments were carried out in a Stanton-Redcroft STA-781 thermobalance provided with a CETA data acquisition and processing system. Samples (15 mg) were placed in Pt crucibles 5 mm in diameter and 5 mm in height. An argon (99.9990% pure by volume) constant flow of 50 cm³ min⁻¹ at atmospheric pressure was used. α-Alumina was used as the reference material for DTA measurements. Temperatures were measured with Pt/Rh thermocouples located at the bottom of the Pt crucibles, in contact with them. A linear heating rate of 10 °C min⁻¹ was used over the 25—1000 °C temperature interval.

Samples pyrolyzed to various carefully controlled extents were prepared in the same thermobalance under the above conditions, by heating at 10 °C min⁻¹ to different selected

temperatures, followed by rapid cooling to room temperature. Elemental analyses were carried out in a Carlo Erba Model EA1108 apparatus, with an estimated precision of ±0.1% for all of the analyzed elements (C, H, N, and S); oxygen was calculated by difference.

Fourier transform infrared (FT-IR) spectra were obtained in a Perkin-Elmer Model 1750 spectrometer. Pellets in KBr with a sample concentration of 1 to 3 × 10⁻² wt %, weighing 120 mg and 13 mm in diameter, were used. Spectra shown are the result of coadding 50 interferograms obtained at a resolution of 1 cm⁻¹ and normalized to 1 mg cm⁻².

Results and Discussion

The equilibrium moisture of virgin Kevlar fibers was determined from their weight loss after heating for 70 min at 110 °C and cooling in a desiccator. An average value of 5.1 wt % of moisture was obtained. It must be pointed out that as received fibers, without drying, were used for all thermal treatments.

The elemental analysis of virgin Kevlar fibers, reported on a dry basis, is given in Table 1. The measured carbon content agrees well with values previously reported in the literature.[10,11] Morgan and Pruneda[11] highlighted the need for correctly drying Kevlar samples prior to elemental analysis is performed, in order to obtain reliable results.

Thermal Analysis Studies. Figure 1 shows TG, DTG and DTA curves obtained during Kevlar pyrolysis under argon. The TG curve first exhibits a weight loss ascribable to release of adsorbed moisture extending from room temperature to 105 °C, this being accompanied by a strong DTA endothermal effect with minimum at 70 °C that coincides with an endothermal minimum in the DTG curve.

No further changes in mass or energy occur between 105 and 350 °C, which is the onset of a new weight loss step that becomes significant above 425 °C and takes place mainly between 520 and 600 °C. The largest weight loss rate occurs at 575 °C (minimum in the DTG curve). This simple weight loss step (note the rather symmetric shape of the DTG peak) is accompanied by a series of overlapping DTA peaks with a well-defined endothermal minimum at 575 °C coincident with the DTG minimum.

A shoulder appearing at a lower temperature (517 °C) might be attributed, according to some authors,[12,13] to partial melting; other authors[14] however, have reported that no melting takes place during Kevlar pyrolysis. Occurrence of fusion phenomena during pyrolysis pro-

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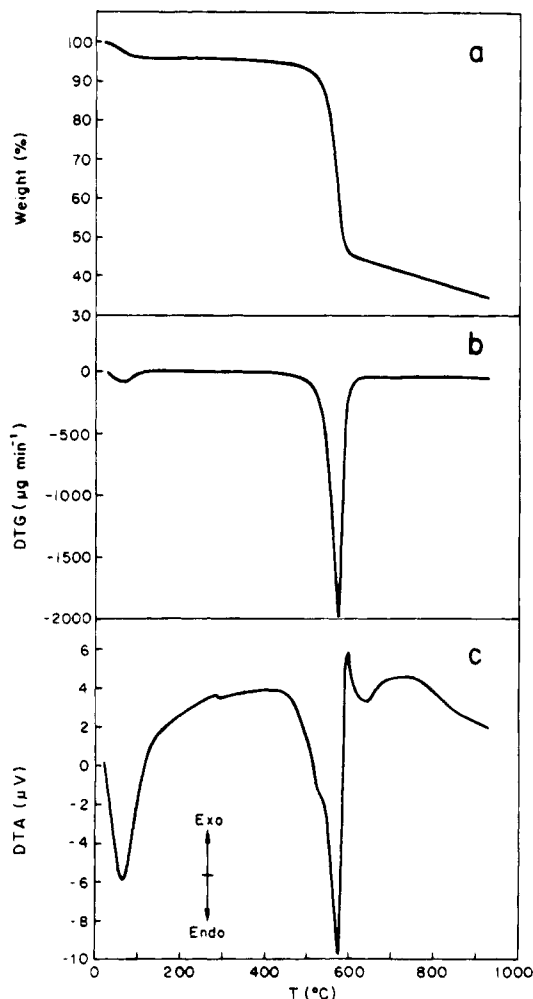
Figure 1. TG (a), DTG (b), and DTA (c) curves for Kevlar under argon.

cesses leading to carbonaceous residues does have important consequences for the structure and behavior of these residues, since the arrangement of parallel layers of polyaromatic molecules in liquid crystal state (mesophase) is well-known to constitute a prerequisite for the formation of graphitizable carbons. Consequently, we carried out a detailed study with a polarized light microscope using a hot stage where Kevlar was pyrolyzed under argon at 10 °C min⁻¹ until 400 °C and then at 5 °C min⁻¹ up to 600 °C. Results (not shown) indicated that no melting at all is detectable, and the fibers thoroughly keep their morphology. This result agrees with Tomizuka et al.'s[2] report that Kevlar pyrolysis gives rise to isotropic carbon fibers.

The DTA minimum at 575 °C is followed by a sudden change in sign of the thermal effect, a sharp DTA exotherm appearing at 600.7 °C. This coincides with a sharp decrease in the slope of the TG curve. Further on, no plateau is attained even at 1000 °C, the continuous, small weight loss in this interval being accompanied by a broad DTA exotherm centered at ca. 733 °C.

Apparent activation energies were calculated from the TG results, using conversion-temperature data and taking a reaction order of 1 for the pyrolysis process; a calculation procedure from auxothermal data described elsewhere[15] was followed. The value of 257 kJ/mol
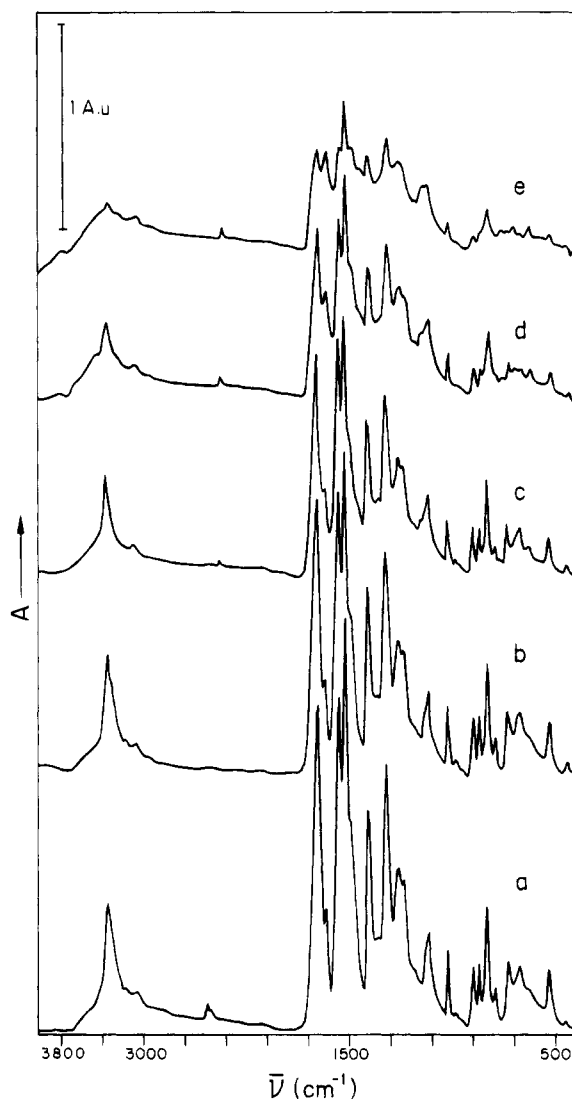
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Figure 2. FT-IR spectra of fresh Kevlar (a) and its solid decomposition products at 311 °C (b) and under the depolymerization regime: 563 (c), 573 (d), and 575 °C (e).

obtained for the temperature range 520–600 °C (conversions between 0.2 and 0.8) decreased to 2.09 kJ/mol for temperatures between 600 and 975 °C (conversions between 0.8 and 0.98). This is a further proof that a sharp change in the mechanism of decomposition takes place at 600 °C; the chemical nature of this change will be later deduced from infrared results.

FT-IR Study of the 20–550 °C Range. FT-IR spectra of Kevlar and its various low-temperature pyrolysis products are presented in Figure 2. As indicated above, poly(*p*-phenylene terephthalamide) is the base polymer for this aramid fiber. According to the chemical formula, the structure of this polymer and the ensuing study on the relative variation of band intensities during the pyrolysis process, the following band assignments for the FT-IR spectrum of fresh Kevlar (Figure 2a) can be made: 3320 cm⁻¹, N–H stretching vibrations in an amide in trans form with a bonded hydrogen; 3054 cm⁻¹, C–H stretching vibrations in an unsaturated compound; 1646 cm⁻¹, amide C=O stretching (usually designated as amide I band) for

hydrogen-bonded amide groups[16] (corresponding to Kevlar's crystal lattice structure[17]); 1543 cm^{-1}, N−H deformation and C−N stretching coupled modes;[18] 1608 and 1515 cm^{-1}, C=C stretching vibrations of aromatic ring; 1018 cm^{-1}, in-plane C−H vibration, characteristic of para-substituted aromatic compounds, particularly polyaramids;[19] 827 cm^{-1}, out-of-plane C−H vibrations of two adjacent hydrogens in an aromatic ring (para substitution of the aromatic); 526, 729, and 865 cm^{-1}, out-of-plane N−H deformation modes.

Assignation of the remaining bands is less conspicuous. A very weak absorption band at 3150 cm^{-1} is ascribable to N−H vibrations, but in an amide in the cis form. The absorption band at 1317 cm^{-1} could be ssigned to Ph−N vibrations.[20] In the 1261−1231 cm^{-1} area, two absorption bands are visible but their assignment is doubtful. The intensities of these bands vary in parallel during the pyrolysis. Thus, they seem to account for the same type of vibration, namely, a coupled mode of C−N and N−H vibrations (amide III band). This assignment is consistent with Raman observations carried out by other authors[21] on poly(*p*-phenylene terephthalamide) in powder form.

The elemental analysis of raw Kevlar (Table 1) shows the presence of sulfur, whereas XPS analysis indicates the occurrence of sodium at the sample's surface. Bands due to inorganic impurities are better identified by studying residues from Kevlar ashing. For this, a Kevlar sample was first ashed in air at 700 °C for 30 min, yielding 1.5 wt % of ash. Figure 3a shows the corresponding FT-IR spectrum, which exhibits characteristic peaks of sodium carbonate (compare with the spectrum of pure Na_2CO_3, Figure 3b), as well as peaks of sulfates, more precisely Na_2SO_4 (compare with the spectrum obtained for pure $Na_2SO_4 \cdot 10H_2O$, Figure 3c). Since carbonates are suspicious to be artifacts formed as a consequence of the ashing process, the Kevlar sample was alternatively submitted to low-temperature (<150 °C) ashing to avoid thermal transformations of inorganic constituents. For this, a cool oxygen plasma generated with microwave radiation was used as the oxidizing agent. The sample was treated under the following conditions: 150 W power, 1 mbar gas pressure, and 4 h treatment time (necessary to attain a constant weight of residue). This treatment led to 2.2 wt % ash, the FT-IR spectrum of which (Figure 3d) exhibits bands close to those found[22] for Na_2SO_4 (1118 and 625 cm^{-1}; see also spectrum 3c). Thus, Na_2CO_3 found in spectrum 3a would be formed from Na_2SO_4 during ashing in air and subsequent exposure to the laboratory atmosphere.

Consequently, the bands detected in the fresh Kevlar spectrum at 1111 and 625 cm^{-1} are due to inorganic impurities and more precisely Na_2SO_4. These bands are detectable in the FT-IR spectra of Kevlar pyrolysis residues until treatment temperatures of about 800 °C
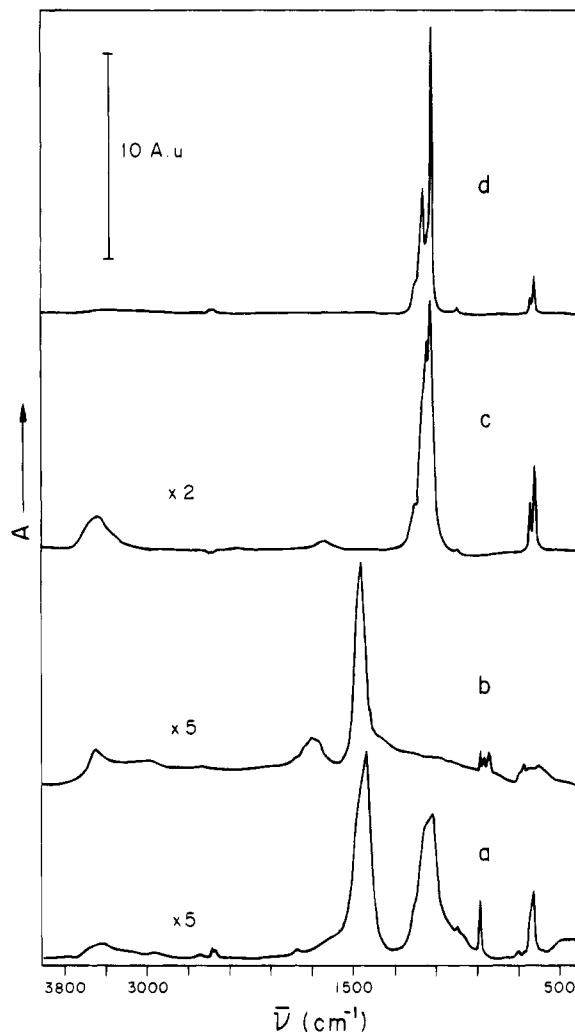

Figure 3. FT-IR spectra of Kevlar high-temperature ash (a), pure Na_2CO_3 (b), pure $Na_2SO_4 \cdot 10H_2O$ (c), and Kevlar low-temperature plasma ash (d).

are reached. Sodium sulfate as an impurity in Kevlar must come from the fiber processing[11,17,23] where sulfuric acid is used to dissolve Kevlar to form an anisotropic liquid-crystal solution prior to spinning, the excess of H_2SO_4 being later neutralized with NaOH.

The FT-IR spectrum obtained after heating Kevlar under argon to 311 °C (Figure 2b) shows the same absorption bands as for fresh Kevlar but with small decreases in their intensities; the decrease in the 1515 cm^{-1} band appears to be slightly greater than the others. For this absorption band, wide variations in intensity can occur depending on the nature and polarity of the aromatic ring substituents.[18] The decrease observed for this band in Kevlar between room temperature and 311 °C suggests that a modification in substituent polarity has occurred due to moisture loss (see DTA curve) and consequent disappearance of some hydrogen bonding.

In the FT-IR spectrum corresponding to a treatment at 523 °C (not shown) an absorption band with a very weak intensity appears at 2224 cm^{-1} which can be assigned to the stretching vibration of C≡N, more specifically in an aryl nitrile.[5] This nitrile should be formed from a radical product assumed by Schulten et

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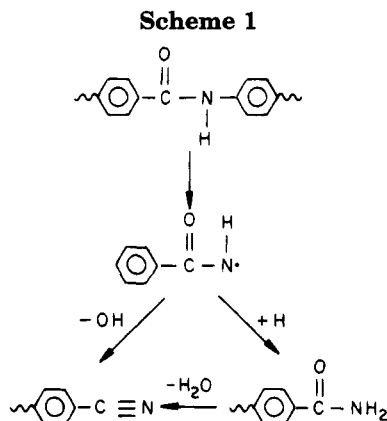
Scheme 1

al.[9] to be one of the products resulting from homolytic decomposition of Kevlar (see Scheme 1). This feature could be related to the shoulder found in the DTA curve at 517 °C. The 2224 cm^{-1} band, which becomes detectable under these low-severity conditions, increases in intensity for higher pyrolysis temperatures as will be later shown; in fact, aryl nitriles constitute the most characteristic intermediate species formed during Kevlar pyrolysis detected by FT-IR spectroscopy.

At 545 °C the weight decrease reaches 17%, while between 311 and 545 °C the intensity of the different bands shows only a very weak decrease (the 3320 cm^{-1} band intensity is nearly constant). That feature suggests that in this temperature range, the decomposition of the polymer takes place along with minor chemical transformations (formation of C≡N), and the fiber framework remains unmodified. As chemical analyses (Table I) show, treatment to 535 °C only results in small decreases in C and N contents as well as some enrichment in S with respect to virgin Kevlar. Schulten et al.,[9] in their study of evolved products during Kevlar thermal degradation by Py-FIMS (heating in high vacuum from 50 to 750 °C at a rate of 1.2 °C s^{-1}), assumed that hydrolysis of amide bonds occurs first with the thus formed carboxylic acids being later involved in decarboxylation reactions. This type of mechanism could allow the above type of transformation of the fiber to take place without any framework change.

FT-IR Study of the 550–575 °C Range. A significant change is evident in the FT-IR spectrum obtained after treatment at 563 °C (Figure 2c). Comparing this spectrum to the 545 °C one, a large drop in absorption intensity for all bands, without any shift, is observed. This evolution follows the same tendency until 573 °C (Figure 2d). The 1640 cm^{-1} (C=O stretching) and 1543 cm^{-1} (N–H bending + C–N stretching) bands both show a relative decrease of their intensity by 40%. Also, in the 545–573 °C temperature range the absorption intensities for these two bands vary in the same ratio (as calculated for various spectra). The 3320 cm^{-1} band (N–H stretching) decreases in the same order of amplitude (by 42%). For the 1317 cm^{-1} band (assigned to Ph–N bond), the observed absorption intensity decrease amounts to 30%. The 1515 cm^{-1} band (C=C stretching) shows a weaker decrease, varying by about 27%. The 1607 cm^{-1} band intensity (C=C stretching) starts increasing in the spectrum at 563 °C, and between this temperature and 573 °C it shows a relative increase of 20%. Furthermore, between 545 and 573 °C the 2224 cm^{-1} band intensity (C≡N stretching) increases by a 3-fold factor.

The study of intensity variations for all of these bands allows to stress the following features:

i. The 1543 cm^{-1} band was ascribed to a coupled mode of N–H bending + C–N stretching, but with a larger contribution of the former mode.[18] In our case, intensity variations for the C=O band (1643 cm^{-1}) are identical to those for 1543 cm^{-1}, and of the same order of amplitude as for 3320 cm^{-1}. This would confirm that the N–H bending vibration mode accounts for most of the 1543 cm^{-1} band intensity. These intensity decreases indicate that amide functional groups are disappearing, with rupture of bonds (C=O, C–N, N–H) via a probably homolytic mechanism[9] leading, on the one hand, to nitrile products. But the 1317 cm^{-1} band (Ph–N) shows a weaker decrease than the amide characteristic bands, suggesting that other types of products with the nitrogen atom still bonded to the aromatic ring (e.g., arylamines) are formed. Either their concentration is low, being undetectable in the FT-IR spectra, or their characteristic bands are hidden behind others.

ii. The intensity of the absorption bands due to the aromatic structure in the 1600–1500 cm^{-1} region varies with changes in the substituents and their relative arrangement. The 1600 cm^{-1} band arises from vibrations where the main dipole moment change is produced by the movements of the substituents on opposite sides of the ring acting in opposition. In case of para disubstitution, with two strong electron donors or two strong electron acceptors, this band will be weak or absent. However, with one strong donor and one strong acceptor, there is a large dipole moment change during the vibration and a very strong band results. The 1500 cm^{-1} band arises from a mode in which the dipole moment change is produced by the relative movements of substituents on opposite sides of the ring, but moving in the same direction. This band therefore appears when both substituents are the same but will vanish if the substituents are an electron donor and an electron acceptor of equal power.[18] The opposite variation of the 1607 and 1515 cm^{-1} bands which is observed is consistent with the change in the aromatic substituents nature due to amide bond cleavage.

iii. Not much change in the chemical composition (Table 1) is observed when the pyrolysis temperature is increased from 535 to 563 °C. However, between 563 and 575 °C, elemental analysis results show a large variation in the relative contents of the different atoms present in the pyrolysis residue (large decrease of O, N, and H concentrations and proportional increase of C). The variation of H/C, H/N, and H/O ratios shows that in this temperature interval, the amount of evolved hydrogen is greater than that corresponding to the disappearance of amide groups. This seems to indicate that there are already modifications in the substitutions (increase of substituent number) on aromatic rings. This feature is in agreement with the intensity decreases (in the same ratio) observed for the 827 cm^{-1} band [characteristic for C–H out-of-plane bending for two adjacent ring hydrogens (para-substitution)] and the 1018 cm^{-1} one (characteristic for C–H in-plane vibration for para-substituted aromatic compounds).

These changes in band intensity and variations of chemical composition coincide with occurrence of the DTA endothermal peak with minimum at 575 °C, which can thus be assigned to depolymerization. Infrared
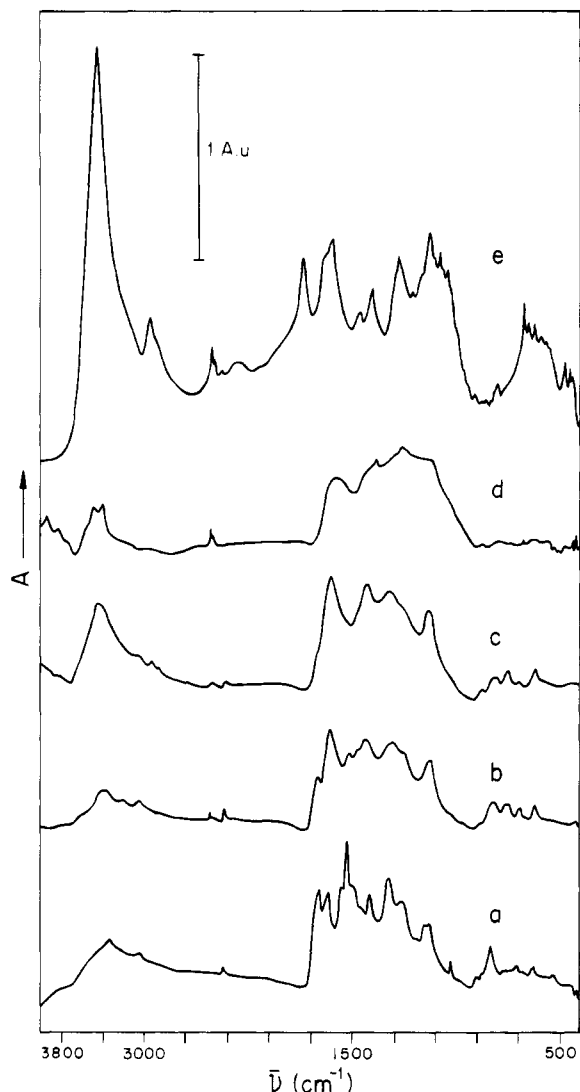
Figure 4. FT-IR spectra of solid decomposition products of Kevlar at 575 °C (a) and under the condensation/aromatization regime: 587 (b), 644 (c), 725 (d), and 960 °C (e).

results seem to show that this process takes place mostly along with the cleavage of the C=O, C—N, and N—H bonds of the amide groups, but the framework of the initial material still exists at the end of the endothermal peak. Indeed, in the spectrum obtained after treating the sample at 575 °C (Figure 2e), corresponding to the minimum of the DTA endothermal peak, the 3320 and 729 cm^{-1} bands have almost disappeared. Although the 1646 and 1543 cm^{-1} bands show a strong decrease, they are still visible. Furthermore, the 1607 cm^{-1} band still increases. These observations are consistent with a process involving random scission leading to small fragments with the same chemical unit as in the raw fiber[5].

FT-IR Study at Temperatures Higher Than 575 °C. As Figure 4 shows, when the treatment temperature exceeded 575 °C the FT-IR spectra were entirely modified, and the absorption bands of amide groups completely disappeared [compare Figures 4a (575 °C) and 4b (587 °C)]. In the spectra corresponding to treatment temperatures between 580 and 640 °C (see, e.g., Figure 4b), four broad bands whose intensities increase with temperature are observed in the 1650–1000 cm^{-1} region; the 1607 and 1436 cm^{-1} bands can be assigned to aromatic compounds. On heating from

575 to 644 °C the H/C, H/N, and H/O ratios progressively decrease (Table 1), with the most significant change being the strong nitrogen loss between 594 and 644 °C.

Sulfur, which was rather constant between 535 and 594 °C, significantly decreases after heating to 644 °C. Since sodium sulfate is known to be stable at these temperatures, S-containing species other than this should be decomposing in this temperature interval. Morgan and Pruneda[11] have shown that benzenesulfonic acid groups are formed during the fabrication process, most likely during the spinning step where the sulfonating power of H_2SO_4 is at a maximum. However, no direct evidence for the presence of sulfonic groups, either in acidic form or neutralized as sodium salts, can be obtained from FT-IR spectra, as the position of their FT-IR bands would coincide with bands characteristic for the polymer (see above).

In this temperature range, the 2224 cm^{-1} band (C≡N) decreases due to the decomposition of the products formed at lower temperatures. (Note that decomposition of these products leads to release of toxic HCN, which was indeed detected by Fitzer et al.[3] Consequently, care must be taken to avoid inhalating the evolved gases.) Furthermore, a band arises at 1660 cm^{-1}. This band seems to become detectable because of the disappearance of the intense one at 1646 cm^{-1}. The 1660 cm^{-1} band still exists until a treatment temperature of 640 °C, and its assignment is doubtful. Different hypotheses can be made:

i. This band could be due to C=O vibrations in quinone species. Quinones can be formed by oxidation of the benzene ring. Formation of these products seems to be difficult under our reaction conditions. Results of elemental analysis cannot provide additional information, as the oxygen concentration, obtained by difference, exhibits in this temperature range an increase (Table 1) larger than expected according to the experimental conditions in the pyrolysis treatment.

ii. This band could account[24] for C=N stretching in imine species (—CH=N—). Nevertheless, some doubt remains as this type of product is not likely to be stable at these temperatures.

iii. This band could be ascribed to ring stretching vibrations for either polynuclear aromatic hydrocarbons [for this type of products, a shift of the 1600 cm^{-1} band of the aromatic ring towards shorter wavelengths (1650–1600 cm^{-1}) has been observed], or aromatic compounds substituted by functional groups with heteroatoms inducing a shift to a higher frequency. This latter hypothesis is consistent with other observations in the FT-IR spectra corresponding to thermal treatments performed in the above-mentioned temperature range: (a) The intensity of the 1607 cm^{-1} band varies, indicating a change in the substituent polarity. (b) The 825 cm^{-1} band, assigned to out-of-plane C—H vibration of two adjacent ring hydrogen atoms, and the 1018 cm^{-1} band, assigned to in-plane C—H vibration in a para substitution, decrease whereas a band at 877 cm^{-1} arises. This band occurs in the infrared region characteristic for C—H out-of-plane deformation vibrations for one isolated hydrogen atom (900–860 cm^{-1}), sug-

(24) Colthup, B. N.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1975.

gesting that the substituent number on the aromatic ring increases.

In parallel with the above findings, the intensities of the 752 and 697 cm^{-1} bands increase after thermal treatment above 580 °C (Figure 4b). Rao[25] has ascribed these bands to out-of-plane C—H vibrations of adjacent hydrogen atoms in substituted polynuclear aromatic compounds. This suggests the occurrence of condensation reactions. Alternatively, these bands can be assigned to out-of-plane C—H vibrations of five adjacent ring hydrogen atoms, i.e., for a monosubstituted benzene.[9] Consequently, competitive reactions for free-radical stabilization, such as recombination of radical compounds like —Ph• (which can come, e.g., from the cleavage of Ph—C≡N products) with a H• (coming from hydroaromatic compounds), or disproportionation reactions[26] could take place, as it has been assumed in modeling coal pyrolysis.[27]

All of the above findings show that at temperatures >600 °C a great modification of the chemical structure has occurred, this observation being in agreement with the slope change in the TG curve (Figure 1a), a carbonaceous material with progressively increasing aromaticity being formed above this temperature.

Between 644 and 725 °C (compare respectively c and d spectra from Figure 4) a decrease of the 1600 cm^{-1} band and increase of the 1313 cm^{-1} band versus the 1436 cm^{-1} one is observed. At the same time, these bands broaden. The 2240 cm^{-1} band disappears at 700 °C. Chemical analysis results (Table 1) follow a trend similar to that noticed between 594 and 644 °C (see above).

The FT-IR spectra corresponding to pyrolysis temperatures above 725 °C (onset temperature of the broad DTA exothermal peak, Figure 1c), exhibit a strong infrared radiation absorption. Figure 4e shows the spectrum corresponding to a thermal treatment at 960 °C, where broad bands at 1590, 1400, 1270, and 1120 cm^{-1} (characteristic of aromatic species) can still be distinguished; the absorption bands in the 900—600 cm^{-1} range have, however, disappeared.

The concomitant DTA exothermal peak (centered at ca. 733 °C) extends over a wide temperature interval and its intensity is weak; in parallel, the TG curve indicates that a continuous weight loss is still taking place at these high temperatures. In agreement with previous studies on the carbonization of pitches[28] and polycyclic aromatic hydrocarbons,[29] these effects can be ascribed to polycondensation and aromatization reactions transforming the semicoke into coke. Note the large decrease in hydrogen concentration and corresponding increase for carbon and, especially, oxygen (Table 1). Nevertheless, oxygen-by-difference data are known to accumulate many experimental and calculation errors and should be viewed with caution.

Finally, although the nitrogen content strongly decreased when the temperature was increased from 725 to 960 °C, a significant amount of this element is still present in samples treated at temperatures as high as 960 °C (see Table 1). This element must occur in the form of heterocyclic aromatic compounds (e.g., quinolines), these products exhibiting characteristic frequencies close to those of benzene and condensed aromatic rings and, consequently, difficult to be distinguished from the unsubstituted aromatic hydrocarbons.

Conclusions

The characterization of Kevlar pyrolysis residues by combined thermal analysis—infrared spectroscopy shows the chemical evolution of these fibers during thermal treatment. Kevlar appears to be chemically stable up to about 545 °C. Below this temperature only minor changes associated to loss of hydrogen bonds are detected. Above 500 °C a significant weight loss takes place; however, no significant framework destruction occurs until ca. 550 °C.

The main chemical transformation during Kevlar pyrolysis takes place over a narrow temperature range (550—575 °C) where the maximum rate of weight loss and a DTA endotherm (attributable to depolymerization) coincide at 575 °C. This process leads to collapse of the initial framework, which proceeds mainly through the progressive decomposition of amide groups by C=O and C—N bonds cleavage. Intermediate aryl nitrile species are formed during this process.

Above ca. 600 °C a significant change in the pyrolysis mechanism takes place. As DTA and infrared results show, progressive aromatization/ring condensation occurs leading to polyaromatic compounds. As usual for carbonization processes, the degree of condensation of the network increases with increasing temperature giving rise to strong infrared-absorbing carbonaceous solids.

(25) Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic Press: New York, 1963.

(26) Stein, S. E. in *Chemistry of Coal Conversion*; Schlosberg, R. H., Ed.; Plenum Press: New York, 1985; Chapter 2, p 13.

(27) Solomon, P. R.; Hamblen, D. G. In *Chemistry of Coal Conversion*; Schlosberg, R. H., Ed.; Plenum Press: New York, 1985; Chapter 5, p 121.

(28) Martínez-Alonso, A.; Bermejo, J.; Granda, M.; Tascón, J. M. D. *Fuel* **1992**, *71*, 611.

(29) Martínez-Alonso, A.; Bermejo, J.; Tascón, J. M. D. *J. Therm. Anal.* **1992**, *38*, 811.