

Effect of an Acidic Comonomer on Thermooxidative Stabilization of Polyacrylonitrile

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SYNOPSIS

This paper presents a study of the reactions involved in stabilization of polyacrylonitrile (PAN) through the effect of various experimental variables on the differential scanning calorimetry (DSC) exotherm and thermogravimetric measurements coupled with Fourier transform infrared (FTIR) spectroscopy, i.e., DSC-FTIR and TG-FTIR. The experimental variables used were the environment of heat treatment (viz. oxidative and inert) and incorporation of an acidic comonomer (viz. itaconic acid). The essential findings include the broadening of the exotherm in an air atmosphere over that in a nitrogen (i.e., inert) atmosphere. This broadening of the exotherm was further enhanced in the presence of the acidic comonomer. Furthermore, the exotherm revealed a doublet character with greater separation of the peaks in case of the copolymer than the homopolymer. Possible explanations of these observations are discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Understanding structural changes and optimization of parameters during stabilization of acrylic precursors is essential for the development of carbon fibers with desired properties.^{1,2} The environment of heat treatment is also reported^{3,4} to have its effect on the stabilization of polyacrylonitrile (PAN), which should yield the highest degree of cyclization with a minimum of adverse effects such as chain scission and defect structures. Although the main reaction involved in the process of stabilization is cyclization, some other reactions occur, such as oxidation, which are highly exothermic, hence the heat evolved may produce adverse effects which need to be checked.

DSC measurements during stabilization of the acrylic fibers show a distinct exotherm. The width and temperature ranges of the exotherm reported by various authors⁵⁻¹¹ differ for reasons unknown, since it is difficult to interpret these differences by just comparing the experimental conditions and the specifi-

cations of samples used by them. The sample specifications are difficult to match, hence in this work we have carried out a study of the effects of the experimental conditions, viz. the atmosphere of heat treatment and heating rate, on the DSC exotherm of the sample of polyacrylonitrile synthesized by us. During this study we have observed systematic variation in the DSC exotherm in the temperature range for the stabilization process. These systematic changes and their accompanying changes in FTIR spectra and TG data are studied and analyzed to obtain insight into the reactions occurring during stabilization as well as to the role of the acidic comonomer in the stabilization of PAN. Moreover, for the explanation of the observed effect, an attempt is made to invoke the reaction schemes suggested by previous authors¹¹⁻²⁹ for the reactions occurring during thermooxidative stabilization to account for the observed variation in the DSC exotherm by using additional data obtained by differential scanning calorimetry coupled with the Fourier transform infrared spectroscopy (DSC-FTIR) technique.

EXPERIMENTAL

Synthesis and Characterization

Polyacrylonitrile homopolymer (PAN) and the random copolymer P(AN-IA) of acrylonitrile (AN)

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with itaconic acid (IA) were prepared by aqueous suspension polymerization. Details of the polymerization process are described elsewhere.³⁰ The copolymer P(AN-IA) was prepared by using 5% by weight of comonomer in the initial feed, and the mole fraction of the comonomer in the final product, determined by Perkin-Elmer 240C elemental analyzer, was 2.5 mol %, which was smaller than the predicted value.³⁰ Intrinsic viscosities of the sample in *N*:*N*-dimethylformamide at 25°C were 2.87 and 2.58 dL/g for the homopolymer and the copolymer, respectively.

Measurements

DSC thermograms were recorded on a Perkin-Elmer Delta series thermal analyzer DSC-7 module at heating rates of 10 and 20°C/min in air and nitrogen atmosphere.

DSC-FTIR spectra of heat-treated and untreated samples were recorded on Jansen (X16) + DSC system. The samples were placed in KBr pellets and then scanned for DSC measurements under air atmosphere at 10°C/min. The FTIR spectra of these samples were recorded simultaneously at intervals of 1 min.

The thermogravimetric curve of the P(AN-IA) copolymer was recorded on a Perkin-Elmer TGA-7 thermal analyzer at a heating rate of 20°C/min in air atmosphere. FTIR spectra of evolved gases were recorded on a 1725 × FTIR spectrometer.

RESULTS AND DISCUSSION

DSC Studies

DSC exotherms of the homopolymer PAN and the copolymer P(AN-IA) under nitrogen and air atmosphere are shown in Figures 1(a) and 1(b) and 2(a) and 2(b), respectively. These exotherms are characteristic of the chemical changes in AN sequence of the homopolymer and the copolymer studied.²¹ Some parameters distinguishing these exotherms in nitrogen and air atmosphere, viz. the temperature of initiation (T_i), finish (T_f), and their difference or the width of the exotherm ($\Delta T = T_f - T_i$), the peak temperature (T_{pk}), and the heat evolved (ΔH), are shown in Table I.

PAN Homopolymer

The DSC exotherm of the PAN homopolymer under nitrogen atmosphere is distinctly narrower than that under air atmosphere and the temperature of initiation is higher under nitrogen (282°C) than in air

(250°C). The lower onset of the exotherm and higher value of ΔH (3681 J/g) in air atmosphere may be attributed to the occurrence of some additional exothermic reactions in an oxidative atmosphere, probably starting at a lower temperature, which do not occur under nitrogen (inert) atmosphere. Another distinguishable feature of the exotherm recorded under air atmosphere is its doublet character, which may be due to the occurrence of a variety of reactions in two different temperature ranges.

P(AN-IA) Copolymer

In nitrogen atmosphere, the DSC exotherm for the P(AN-IA) copolymer, recorded at the same heating rate, is very narrow and small [Fig. 2(a)], whereas, in air atmosphere it appears as a broad doublet [Fig. 2(b)]. This doublet character is more distinct in the case of the copolymer than the homopolymer. Furthermore, as seen from the data given in Table I, the exotherm starts at a higher temperature in nitrogen ($T_i = 272^\circ\text{C}$) than in air ($T_i = 208^\circ\text{C}$) and the width of the exotherm is much smaller in nitrogen atmosphere ($\Delta T = 37^\circ\text{C}$) than that of the exotherm in air atmosphere ($\Delta T = 217^\circ\text{C}$). The heat of reaction corresponding to the total exotherm area is lower for the nitrogen atmosphere than the air atmosphere by a factor 15. All this difference between air and nitrogen is qualitatively similar to those found for the PAN homopolymer, and thus the same interpretation is valid here too, i.e., the virtual simultaneous occurrence of some reactions and/or absence of some reactions in the inert atmosphere.

The higher values of T_i of the exotherms for PAN homopolymer than P(AN-IA) copolymer, in both nitrogen and air atmospheres, indicate that the acidic comonomer, viz. itaconic acid induces some exothermic reactions at a lower temperature through an ionic mechanism of initiation.²¹ The considerable difference (42°C) in the values of T_i for PAN and P(AN-IA) in air atmosphere, suggests a great ease of initiation of the exothermic process by the comonomer under air atmosphere, which indicates that the acidic comonomer also facilitates the additional exothermic reactions which occur under air atmosphere (and not under inert atmosphere).

Furthermore, the acidic comonomer (itaconic acid) slows down the exothermic reaction in both nitrogen and in air atmosphere, as seen from the width of the exotherm (ΔT) of the PAN and P(AN-IA) recorded under nitrogen and air atmosphere (see Table I).

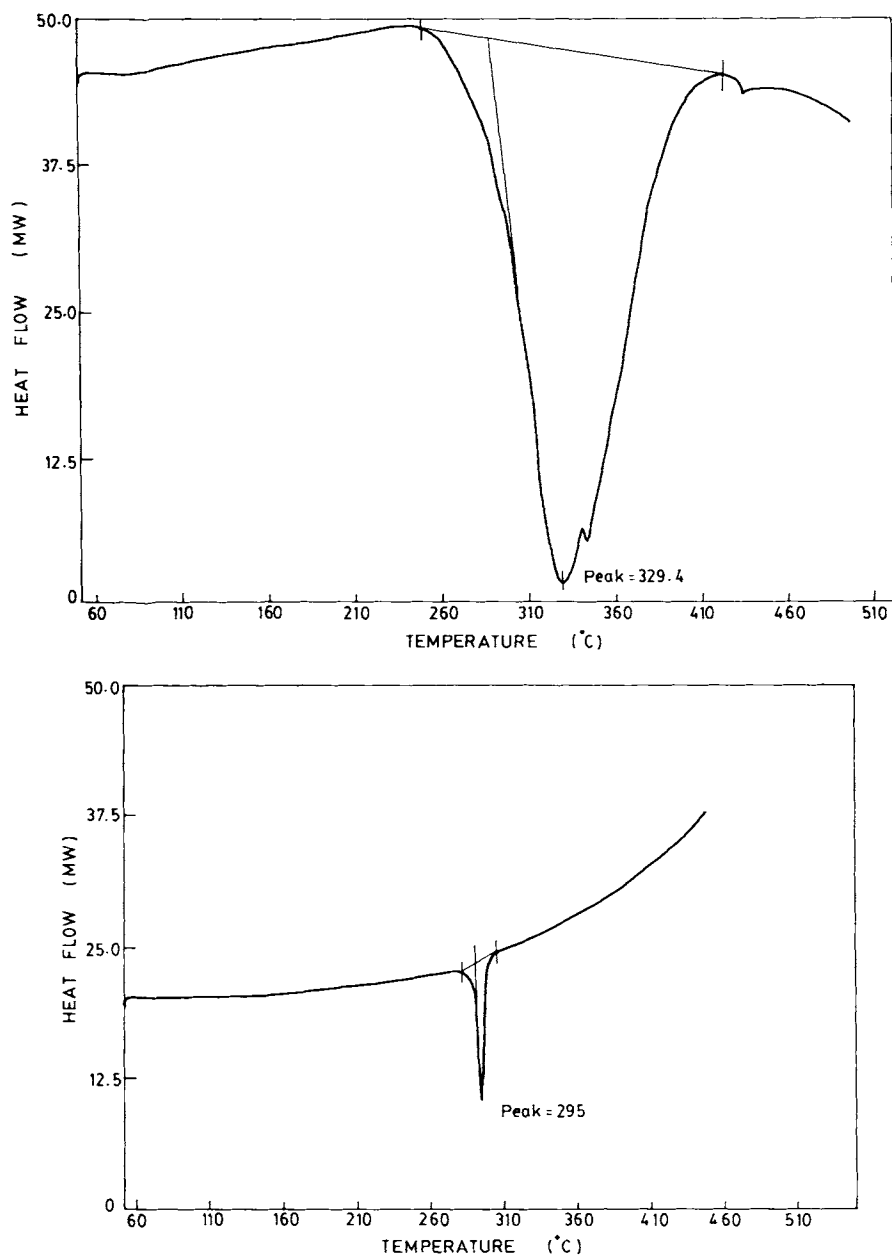


Figure 1 (a) DSC exotherms of PAN homopolymer scanned at 10°C/min under air atmosphere. (b) DSC exotherms of PAN homopolymer scanned at 10°C/min under nitrogen atmosphere.

Exothermic Reactions and the Exotherm

The differences in the DSC exotherm and parameters obtained from them, as will be discussed later in this paper, provide information about the relative magnitude, rapidity, and predominance of the various reactions occurring in the temperature range of the exotherm. The sequence of the various reactions occurring during stabilization is proposed, as shown in Figure 3, on the basis of reports in the literature¹¹⁻²⁹ on various individual steps of the reactions. These may be classified as

1. oxidation reactions and
2. cyclization reactions.

Polyacrylonitrile on heat treatment under air (oxidative atmosphere) may undergo certain reactions such as elimination of hydrogen (dehydrogenation) and addition of oxygen. These reactions may be referred to as oxidative reactions and could lead to the formation of structures such as $-\text{C}=\text{C}-$, $-\text{C}-\text{H}$, $>\text{C}=\text{O}$, $\text{N} \rightarrow \text{O}$ in the polyacrylonitrile molecule.

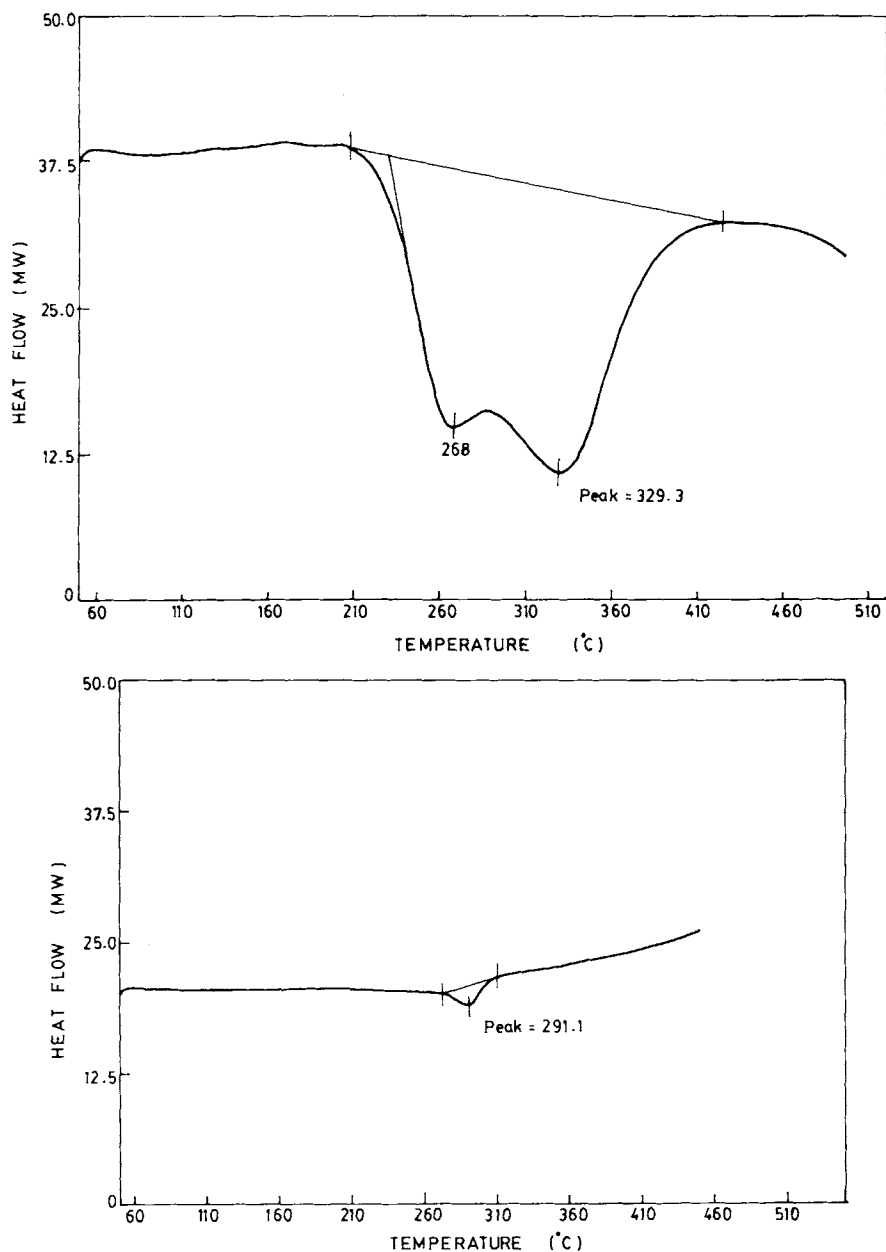


Figure 2 (a) DSC exotherms of P(AN-IA) copolymer scanned at 10°C/min under air atmosphere. (b) DSC exotherms of P(AN-IA) copolymer scanned at 10°C/min under nitrogen atmosphere.

The formation of a ladder structure in the polyacrylonitrile molecule as a result of oligomerization of nitrile groups of the PAN molecular chain is often known as cyclization. The cyclization in PAN is believed²⁴ to be initiated through different mechanisms in the absence and presence of the acidic comonomer. In the PAN homopolymer, it occurs through a radical mechanism which initiates at a higher temperature and proceeds at a faster rate, whereas in the case of the AN copolymers, the cyclization starts at a lower temperature, propagates

at a slower rate, and is initiated through an ionic mechanism.

The oxidation as well as cyclization reactions are exothermic, hence both of them contribute to the DSC exotherm. The calculations (see Appendix 1) based on bond energy data³¹ suggest that heat of oxidative reactions is greater than cyclization reactions and if it is assumed that only oxidative and cyclization reactions occurred during the heat treatment and the heat-treated polymer has acquired the structure of a stabilized fiber as suggested by Tak-

Table I Parameters Obtained from DSC Exotherms of PAN Homopolymer and P(AN-IA) Copolymers

Polymer	Atmosphere	T_i (°C)	T_f (°C)	ΔT (°C)	T_{pk} (°C)	H (J/g)
PAN	Nitrogen	282	305	23	295	436
	Air	250	424	174	329	3681
P(AN-IA)	Nitrogen	272	309	37	291	189
	Air	208	425	217	329	2971

ahagi et al.³² (Fig. 4), the oxidation and cyclization reactions may contribute 75.8 and 24.2%, respectively, to the DSC exotherm.

All these reactions, i.e., oxidation and cyclization, may occur more or less simultaneously in the temperature range 180–350°C,³³ i.e., the temperature range of the DSC exotherm. However, an attempt has been made to invoke the sequence of these reactions and to explain the doublet character of the DSC exotherms recorded under air atmosphere by using DSC-FTIR and TG-FTIR techniques.

DSC-FTIR Studies

The DSC-FTIR spectra of the PAN homopolymer and P(AN-IA) copolymer are presented in Figures 5 and 6, respectively, in three parts to cover the total studied range. The spectra are placed over each other in a three-dimensional expression. Wave number and absorbance are at X- and Y-axes, respectively, whereas, the Z-axis represents the temperature at which the spectrum was recorded.

As reported in the literature,^{34–38} the major absorption bands in PAN are C≡N stretching at 2240 cm⁻¹, C—H stretching at 2938 cm⁻¹, C—H bending at 1458 and 1260 cm⁻¹, and C—H in-plane deformation at 1368 cm⁻¹ [Fig. 7(a)]. The FTIR spectra of the P(AN-IA) copolymer [Fig. 8(a)] shows, in addition to these bands, an absorption band at 1722 cm⁻¹ due to stretching mode of C=O bond present in the comonomer.

PAN Homopolymer

DSC-FTIR studies on the PAN homopolymer reveal that, it does not undergo any significant chemical change on heating up to 250°C as may be seen from Figure 5(a) to (c). However, some changes observed in these FTIR spectra in the region 1650–1500 cm⁻¹ at 268°C are attributable to the initiation of oxidation reactions. Similarly, the changes in the spectra in the range of 3500–2900 and 2250–2000 cm⁻¹ at 288°C probably indicate the oxidation and begin-

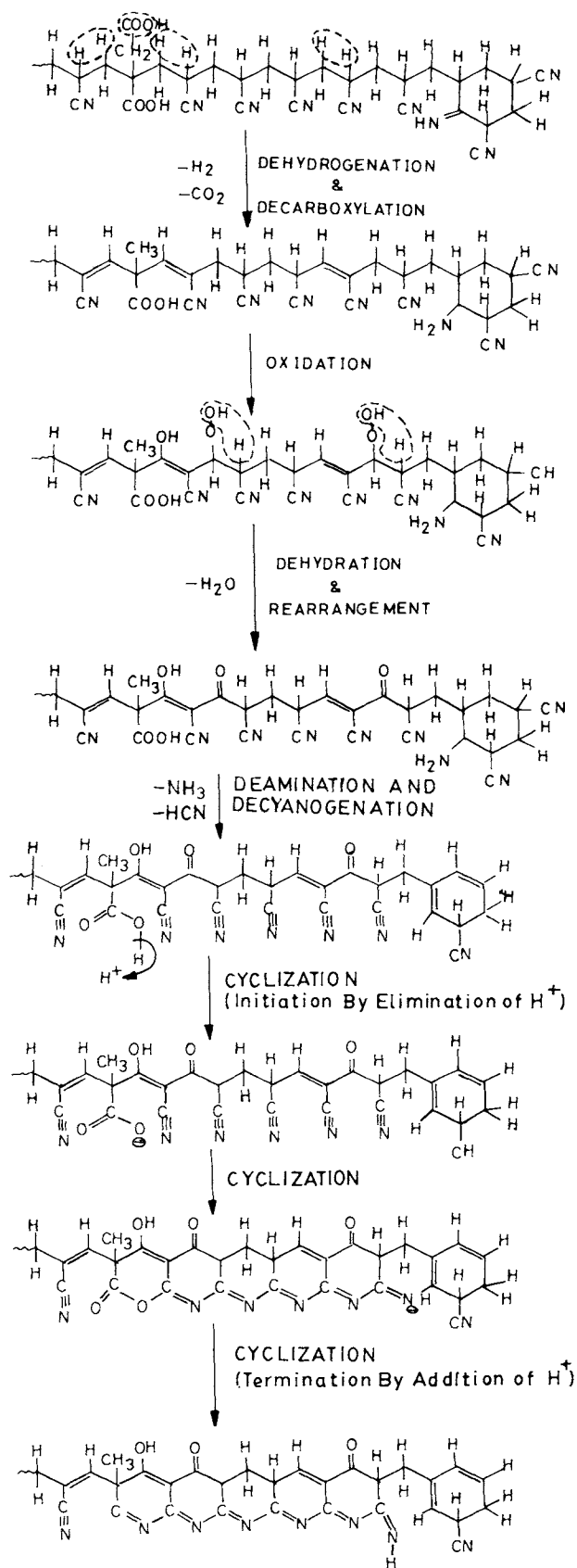


Figure 3 Reaction scheme of thermal stabilization of acrylonitrile polymers.

ning of cyclization reactions, respectively. In order to more clearly illustrate these changes, the FTIR spectra of PAN at 268, 288, and 308°C were laid over the spectrum of non-heat-treated PAN, which are shown in Figure 7. The emergence of new absorption bands at 1610 and 1575 cm^{-1} at 268°C (Fig. 5 as well as Fig. 7) may be an indication of dehydrogenation reactions of the reaction scheme shown in Figure 3, as these bands are attributed to $-\text{C}=\text{C}-$ and $=\text{NH}$ structures.^{18-20,39} Further rise in temperature leads to the development of some new absorption bands in the range of 3500–2900 and 1400–1100 cm^{-1} , and to the increase in the intensity of the bands that emerged at 1610 and 1575 cm^{-1} (see Fig. 5). These bands become more prominent in the spectra recorded at 288°C, where the bands at 1368 and 1260 cm^{-1} also broaden and some new absorptions at 3240 cm^{-1} (in the form of triplet) and 1140 cm^{-1} generate. These absorptions are assigned to the intermolecularly bonded $-\text{OH}$ groups and $\text{C}-\text{O}$ stretch in aliphatic alcohols.⁴⁰ Such structures may be generated in the polymer chain at this stage of heat treatment as a result of oxidative reactions indicated in Figure 3. The broadening of the absorption bands at 1368 and 1260 cm^{-1} could be due to the $-\text{OH}$ in-plane bending vibrations. These bands grow in intensity with the rise in the temperature of heat treatment.

The FTIR spectrum of PAN recorded at 288°C (Fig. 7) shows the considerable increase in the intensity of the absorption band at 2200 cm^{-1} . This band is assigned by Usami et al.²⁰ to the $=\text{NH}$ structure and is reported to occur as a result of the cyclization of nitrile groups (Fig. 3) present in the polymer chain. They also estimated the conjugated nitrile content (formed as a result of cyclization reaction) from the ratio of the relative height of absorption bands at 2200 and 2240 cm^{-1} . This band increases in intensity with increase in temperature, as evident from the spectra recorded at 308°C, whereas, the intensity of absorption band at 2240 cm^{-1} (characteristic of $\text{C}\equiv\text{N}$ group) decreases. This implies that cyclization of nitrile groups (Fig. 3) has started at 288°C and is further enhanced with the increase in the temperature of heat treatment.

P(AN-IA) Copolymer

The stacked FTIR spectra of the P(AN-IA) copolymer (Fig. 6) also depicts types of changes similar to those observed for the PAN homopolymer, however, they start at lower temperature, e.g., the change in the region 1650–1500 cm^{-1} occurs at 238°C, while in the PAN homopolymer they start at 268°C. Since the stacked spectra (Fig. 6) show significantly new

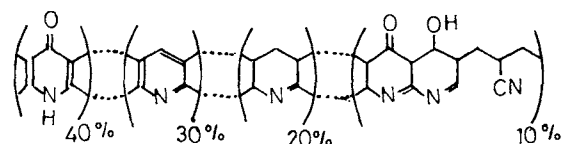


Figure 4 Chemical structure of stabilized PAN in air.

developments at 238, 268, and 307°C, the FTIR spectra of the copolymer at these temperatures were overlaid on the spectra of the non-heat-treated copolymer and are shown in Figure 8.

In addition to the various characteristic absorption bands in the FTIR spectra of the PAN homopolymer, the spectra of the P(AN-IA) copolymer show absorption bands at 3410 and 1732 cm^{-1} due to the $\text{O}-\text{H}$ and $\text{C}=\text{O}$ stretching in $-\text{COOH}$ groups of the comonomer, i.e., itaconic acid. Like the homopolymer, the copolymer also experiences the appearance of a much stronger (as compared to homopolymer) absorption band at 1610 and 1575 cm^{-1} (due to $-\text{C}=\text{C}-$ and $=\text{NH}$ stretching) but at a lower temperature, i.e., 238°C. This suggests that in the copolymer the dehydrogenation and oxidation reactions [which lead to the formation of structures containing $-\text{C}=\text{C}-$ and $=\text{NH}$ (Fig. 8)] are facilitated and occur at lower temperature, due to the presence of the acidic comonomer (itaconic acid). Takahagi et al.³² also reported that comonomer accelerates the dehydrogenation reaction in the stabilization process of PAN precursors. Moreover, the broad band at 3410 cm^{-1} (due to the $-\text{OH}$ stretching in $-\text{COOH}$) decreased in intensity, thereby suggesting the disappearance of some $-\text{COOH}$ groups, probably due to the decarboxylation reaction. On further increasing the temperature of heat treatment to 268°C, the newly generated absorption bands at 1610 and 1575 cm^{-1} increase in intensity, suggesting the increase in the number of $-\text{C}=\text{C}-$ and $=\text{NH}$ structures. Furthermore, as in the case of the homopolymer, the emergence of new absorption bands at 3240 (as a broad multiplet) and 1140 cm^{-1} and the broadening of bands at 1368 and 1260 cm^{-1} indicate the occurrence of oxidation reactions leading to the development of structures containing $-\text{OH}$ group. The spectra of P(AN-IA) copolymer at 268°C [Fig. 8(b)] show the decrease in the intensity of absorption band at 2240 cm^{-1} (due to $-\text{C}\equiv\text{N}$), thus indicating the initiation of cyclization of nitrile groups which is enhanced with the increase in the temperature of heat treatment. At 307°C, the appearance of an IR band at 2200 cm^{-1} further supports the occurrence of cyclization reaction.

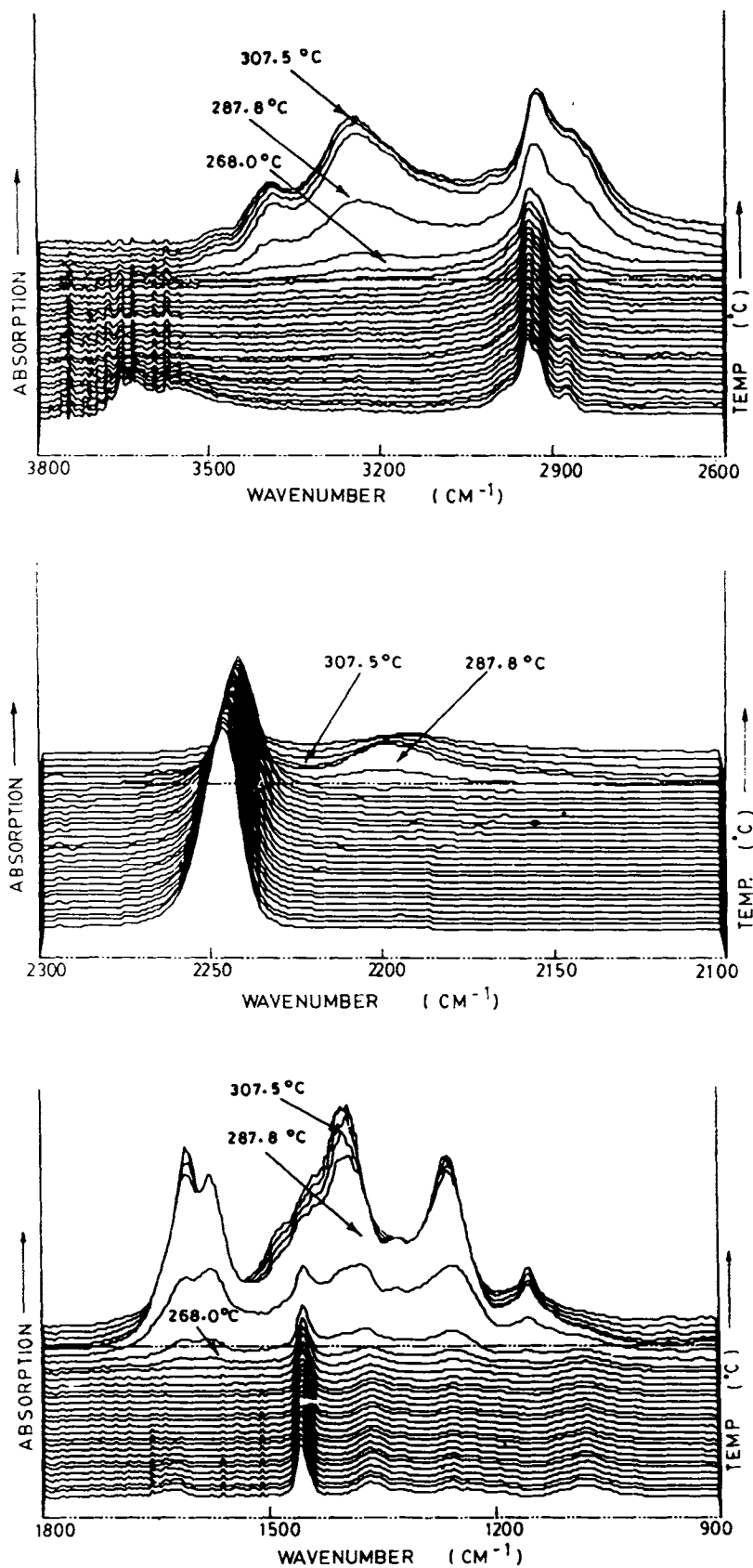


Figure 5 DSC-FTIR of PAN homopolymer recorded during DSC run at 10°C/min at an interval of 1 min in the range (a) 3800–2600, (b) 2300–2100, and (c) 1800–900 cm⁻¹.

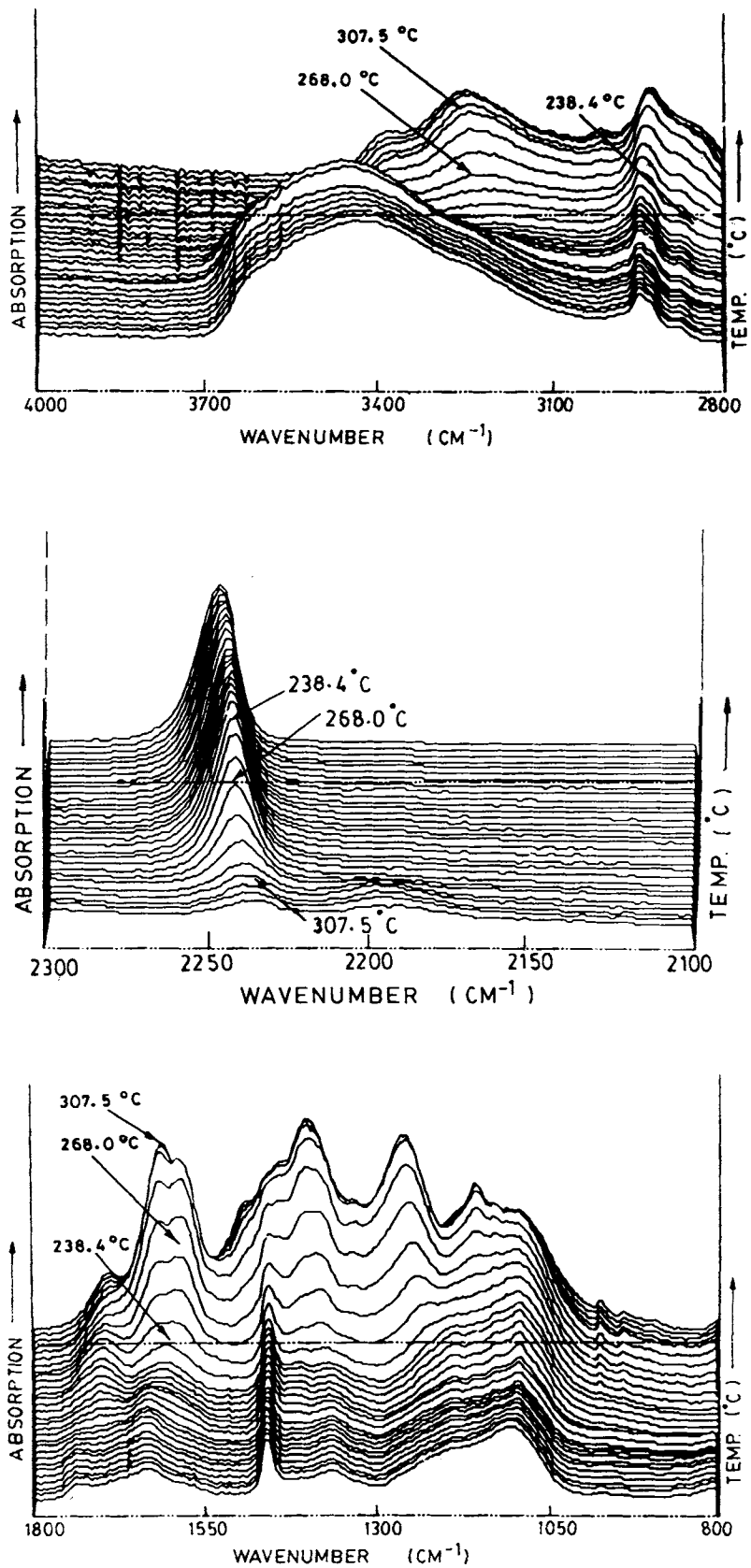


Figure 6 DSC-FTIR spectra of P(AN-IA) copolymer recorded during DSC run at 10°C/min at an interval of 1 min in the range (a) 4000–2800, (b) 2300–2100, and (c) 1800–800 cm⁻¹.

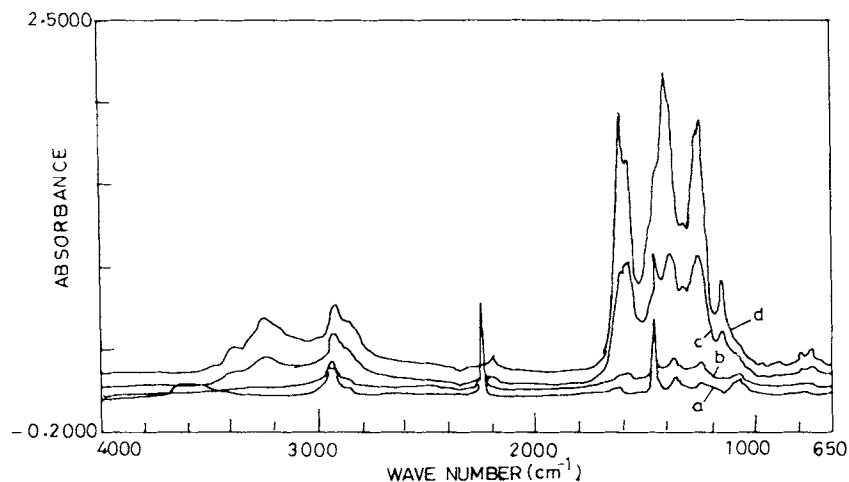


Figure 7 FTIR spectra of (a) non-heat-treated PAN homopolymer and heat-treated PAN up to (b) 268°C, (c) 288°C, and (d) 308°C.

The above discussion suggests that the onset of oxidative reactions seems to precede the onset of cyclization reactions in the homopolymer as well as in the copolymer. Therefore there is greater overlap of these two categories of reactions in the case of the homopolymer than the copolymer.

TG-FTIR Studies

The P(AN-IA) copolymer was heated in the pan of the thermal analyzer from 50 to 600°C at a heating rate of 20°C/min. The evolved gases were swept through a heated transfer line at 200°C by an air purge into a heated gas cell (temperature 200°C) mounted on the external bench of an FTIR spectrometer. The weight loss curve and the variation of first derivative are shown in Figure 9. The stacked

FTIR spectra in three-dimensional expression of the evolved gases, 5.22 min after the start of TGA, run up to 21.85 min is shown in Figure 10. The wave number and the extent of absorption are at the *X*- and *Y*-axes, respectively, whereas, the time is shown at the *Z*-axis. The FTIR spectra of the evolved gases at 240°C (where the rate of weight loss is maximum) and also at 320°C (where the weight loss again starts), i.e., 9.5 and 14 min after the start of run, respectively, are shown in Figure 11).

An attempt has been made to correlate the thermogravimetric curve (Fig. 9) with the DSC exotherm of the P(AN-IA) copolymer, which is also recorded at a heating rate of 20°C/min under air atmosphere and is shown in Figure 12. This exotherm appears as a doublet with superimposition of two exotherms.

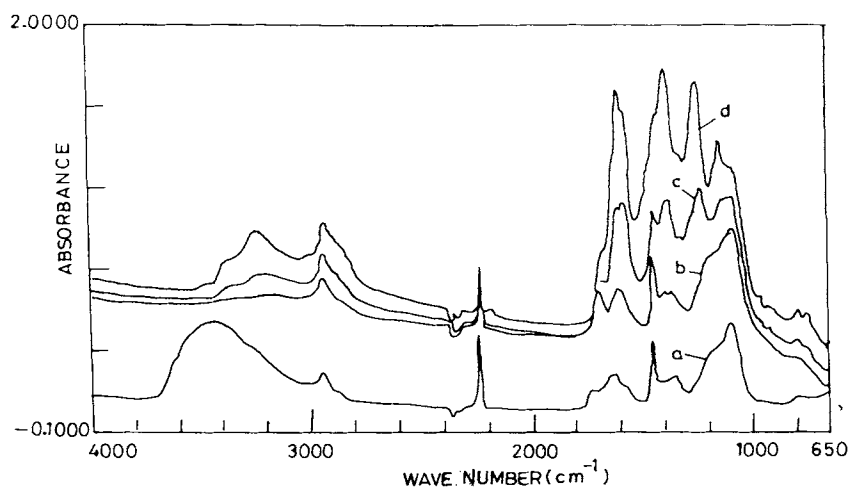


Figure 8 FTIR spectra of (a) non-heat-treated P(AN-IA) copolymer and heat-treated P(AN-IA) copolymer up to (b) 238°C, (c) 268°C, and (d) 307°C.

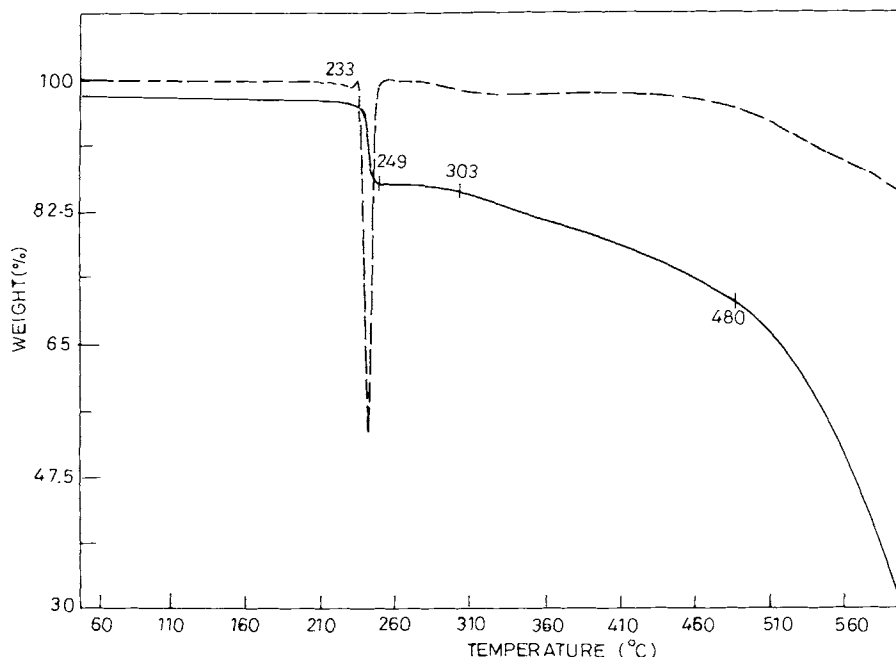


Figure 9 Thermogravimetric curve of P(AN-IA) copolymer recorded under air atmosphere at a heating rate of 20°C/min.

In the thermogravimetric curve of the P(AN-IA) copolymer (Fig. 9), five zones, i.e., up to 233°C, 233–249°C, 249–303°C, 303–480°C, and above 480°C, are apparent. There is no substantial weight loss in the first and third zones. The rate of weight loss is maximum in the second zone, followed by the fifth and

fourth zone. Interestingly, the rate of weight loss is highest in that temperature range, which also shows the highest heat flow (in the DSC exotherm—Fig. 12), thereby suggesting that this high heat flow also

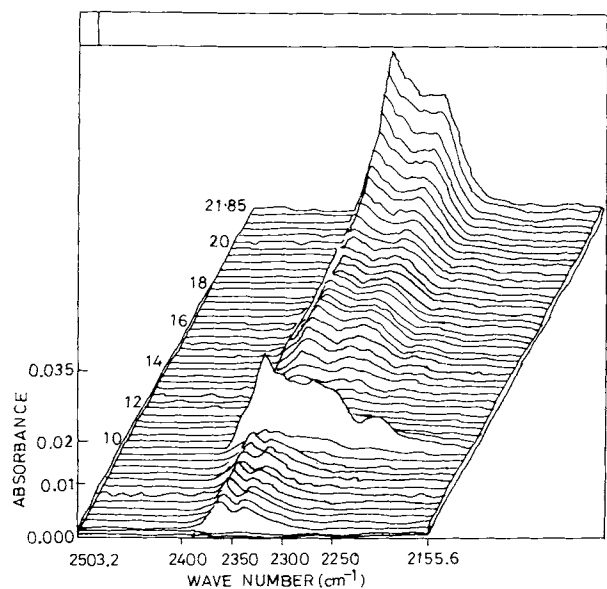
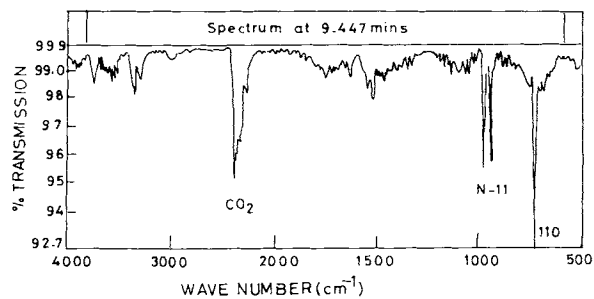
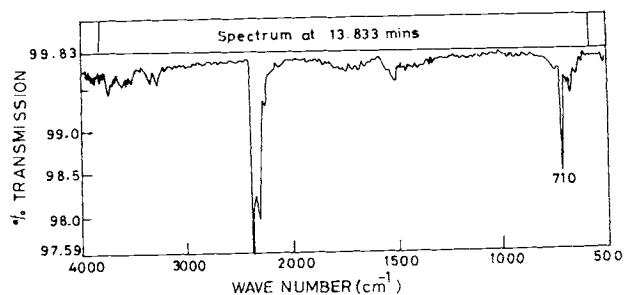


Figure 10 Stacked FTIR spectra in three-dimensional expression with time (min) as a parameter of the gases evolved during heating of P(AN-IA) copolymer in air at a heating rate of 20°C/min.



(a)



(b)

Figure 11 FTIR spectra of the gases evolved during heating of P(AN-IA) copolymer in air at a heating rate of 20°C/min at (a) 240°C and (b) 320°C.

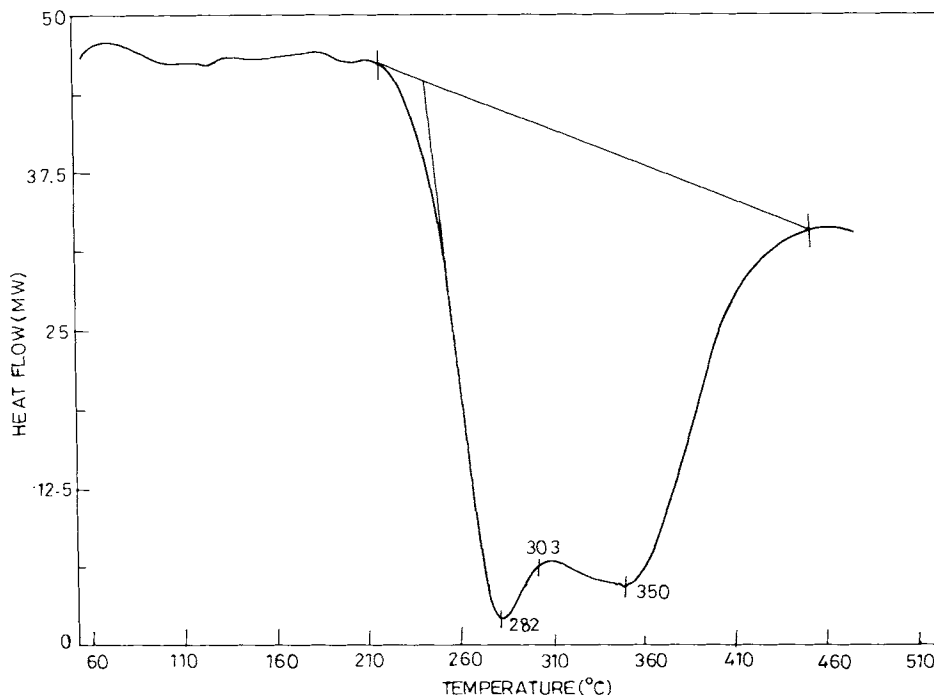


Figure 12 DSC exotherm of P(AN-IA) copolymer scanned at 20°C/min under air atmosphere.

contributes to the observed rate of the weight loss in the second zone. There is negligible weight loss in the third zone falling under the temperature range 249–303°C (Fig. 12), which shows a decrease in heat flow. The weight loss in the fourth and fifth zones of the TG curve could be attributed to the higher temperature of the sample, also under air atmosphere, which is conducive to the oxidation reactions (probably leading to the chain scission reactions) as may be seen from FTIR spectra of the evolved gases (Fig. 11).

A study of the FTIR spectrum of the evolved gases at 240°C when the rate of weight loss is highest suggests that ammonia (NH₃), hydrogencyanide (HCN), aliphatic species, and the moieties containing —C≡N or N≡C structures are present in the evolved gases. The IR absorption bands in the spectrum at 950–900 and 3300–3200 cm⁻¹ as well as at 710 cm⁻¹ may be due to the presence of NH₃ and HCN, respectively, as the bands at 950–900 and 3300–3200 cm⁻¹ are attributed to N—H and H—C stretching vibrations in ammonia and HCN, respectively.⁴⁰ Another band due to C≡N or N≡C stretch at 2090 cm⁻¹⁴⁰ may also be seen as a shoulder on the absorption band at 2360 cm⁻¹. The presence of aliphatic species in the evolved gases may be evident from the absorption band at 2900 cm⁻¹, which could be assigned to the C—H aliphatic stretch.⁴⁰

These species could have formed as a result of chain scission and oxidation reactions.

The small weight loss in the fourth zone could be attributed to the evolution of HCN, CO₂, and CO, as may be seen from the presence of IR absorption bands at 3300–3200 cm⁻¹ (HCN) and 2360 cm⁻¹ (CO₂). The IR band at 2210–2190 cm⁻¹ has been assigned to CO stretch in carbon monoxide.⁴⁰ At this temperature, HCN might have evolved due to the fragmentation of the PAN chain at the places where —CN groups could not undergo cyclization, whereas the cleavage of the chain at the site of oxygen-containing groups such as >C=O and C—OH followed by oxidation probably led to the formation of CO and CO₂. Thus DSC exotherm (Fig. 12) from 320°C and onward could be attributed to the oxidative reactions, which lead to the chain scission and the oxidation of products of such chain scission reactions. In other words, it may be said that the peak of the doublet (of DSC exotherm) with higher onset temperature, i.e., peak 2, could be assigned to the occurrence of oxidative reactions. Also in DSC-FTIR studies it was observed that peak 2 of the doublet of the DSC exotherm could be assigned to the oxidative reactions, e.g., secondary oxidation reactions, causing chain scission and the initiation of oxidative reactions precedes the onset of cyclization reactions, however, both cat-

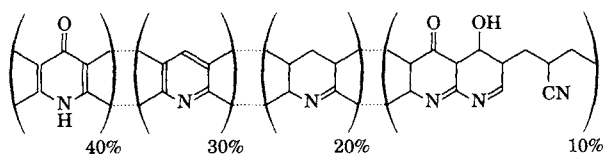
egories of reactions proceed more or less simultaneously.

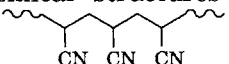
CONCLUSION

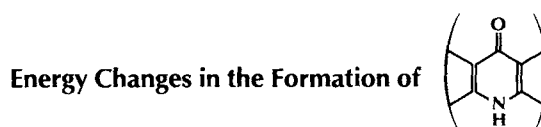
The acidic comonomer (itaconic acid) not only initiates the cyclization of nitrile groups in polyacrylonitrile at lower temperature (as compared to the homopolymer) but also facilitates the additional oxidative reactions in air atmosphere. The DSC exotherms of the PAN homopolymer as well as of the P(AN-IA) copolymer appear as a doublet with superimposition of two peaks, in air atmosphere. These doublets may be attributed to the exothermic cyclization and oxidative reactions, which may proceed more or less simultaneously, however, initiation of the oxidation reaction precedes the onset of cyclization. The first peak of these doublets could be assigned to the oxidative and cyclization reactions and the second peak to the secondary oxidative reactions, leading to the chain scission, which causes evolution of HCN, CO₂, and CO. The calculations on the basis of bond energy data suggest that oxidative and cyclization reactions may contribute 76 and 24% to the exotherm, respectively.

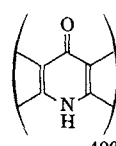
APPENDIX 1: CALCULATION OF ENERGY CHANGES DURING THERMOOXIDATIVE STABILIZATION OF POLYACRYLONITRILE

The energy change during a chemical reaction may be defined as the difference in the energy of the reactants and products and may be estimated by their bond energies. We have attempted to estimate the energy change during the thermooxidative stabilization of the polyacrylonitrile (PAN) precursor considering the following chemical structure for stabilized PAN:



During the process of thermooxidative stabilization of PAN, the occurrence of two reactions, oxidation and cyclization, has been reported. The energy changes in these reactions may be estimated by summing up the energy changes in the formation of different chemical structures in stabilized PAN from PAN  in their respective proportion as illustrated below.

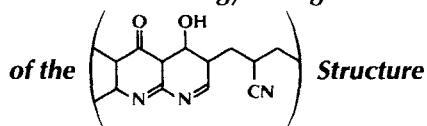


The formation of the  structure may involve the following transformations:

	Energy Required (+) or Released (-) (kJ/mol)
(a) Dissociation of 4 C—H bonds	4 (+80.6) = +322.4
(b) Dissociation of $\frac{1}{2}$ O ₂ (O=O)	$\frac{1}{2}$ (+118) = + 59.0
(c) Dissociation of $\frac{1}{2}$ H ₂ (H—H)	$\frac{1}{2}$ (+104) = + 52.0
(d) Formation of 2, H—H bonds	2(-104) = -208.0
(e) Formation of 1 C=O bond	1(-257.3) = -257.3
(f) Formation of 1 C—N bond	1(-147) = -147.0
(g) Formation of 1 N—H bond	1(-81) = - 81.0
(h) Conversion of C—C to C=C bonds	2(145 - 200) = -110.0
(i) Conversion of 1 C≡N to C—N bond	1(213 - 147) = + 66.0
Total	-303.6

Since this structure constitutes 40% of the stabilized structure, its contribution to total energy change would be $-303.6 \times 0.4 = -121.4$ kJ/mol.

Estimation of Energy Changes in the Formation



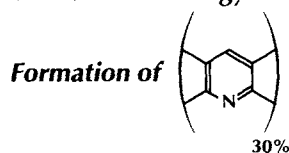
The generation of the above structure may occur due to the following changes:

	Energy Required (+) or Released (-) (kJ/mol)
(a) Dissociation of 3 C—H bonds	3(+80.6) = +241.8
(b) Dissociation of 1 O=O bond	1(+118) = +118.0
(c) Formation of 1½ H—H bonds	1½ (-104) = -156.0
(d) Formation of 1 C=O bond	1(-257.3) = -257.3
(e) Formation of 1 C—O bond	1(-174) = -174.0
(f) Formation of 1 O—H bond	1(-102) = -102.0
(g) Formation of 2 C=N bonds	2(-160) = -320.0
(h) Conversion of 2 C≡N to C—N bonds	2(213 - 147) = +132.0
Total	-517.5

Since this structure constitutes 10% of the stabilized structure, its contribution to total energy change would be $-517.5 \times 0.1 = -51.7$ kJ/mol.

Energy Changes in the Cyclization Reaction

Estimation of Energy Changes in the



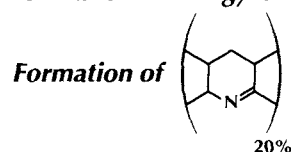
This structure may form as a result of the following changes:

	Energy Required (+) or Released (-) (kJ/mol)
(a) Dissociation of 3 C—H bonds	3(+80.6) = +241.8
(b) Formation of 1½ H—H bonds	1½ (-104) = -156.0
(c) Formation of 1 C=N bond	1(-160) = -160

(d) Conversion of 2 C—C to C=C bonds	2(145 - 200) = -110.0
(e) Conversion of 1 C≡N to C—N bond	1(213 - 147) = + 66
Total	-118.2

Since stabilized PAN has 30% of this structure, its contribution of energy change by this step would be $-118.2 \times 0.3 = -35.4$ kJ/mol.

Estimation of Energy Changes in the



The following changes in the chemical structure of PAN may be anticipated during the formation of this structure:

	Energy Required (+) or Released (-) (kJ/mol)
(a) Conversion of 1 —C≡N to C—N bond	1(213 - 147) = + 66
(b) Formation of 1 C=N bond	1(-160) = -160
Total	- 94

The contribution of this step in the total energy change during stabilization would be $-94 \times 0.2 = -19.8$ kJ/mol, considering that 20% of this structure remains present in the stabilized PAN.

Now the total energy change during thermooxidative stabilization due to oxidative reactions is

$$(-121.4) + (-51.7) = -173.1 \text{ kJ/mol}$$

and to cyclization reactions is

$$(-35.4) + (-19.8) = -55.2 \text{ kJ/mol}$$

Thus the total energy change would be -228.4 kJ/mol.

This shows that 75.80% of the total heat released in these reactions is due to oxidative reactions. The remaining 24.2% of the total heat released may thus be attributed to the cyclization reactions.

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