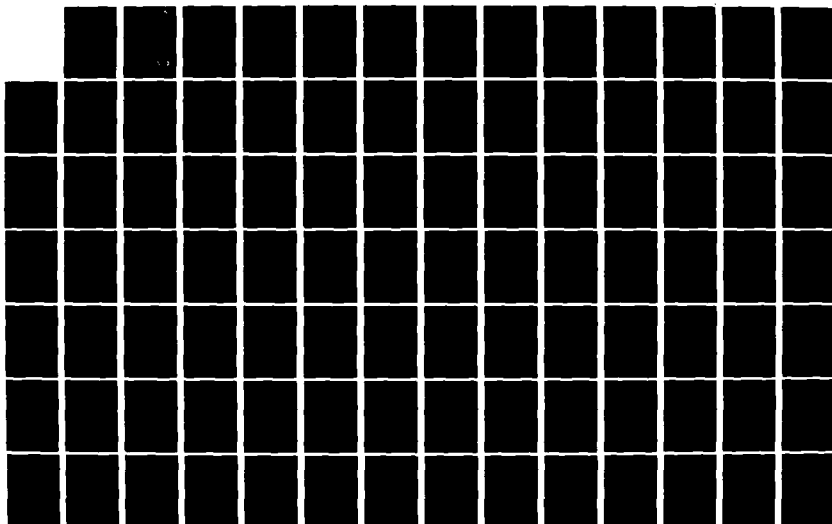AD-A121 021   STUDIES OF THE INITIAL STAGES OF THE DEGRADATION OF
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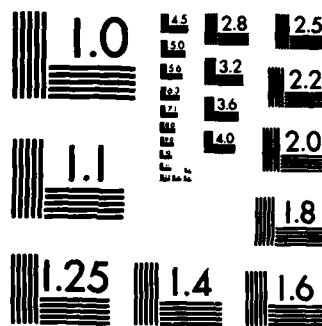   UNIVERSITY PARK APPLIED RESEARCH LAB..   G T SIVY
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STUDIES OF THE INITIAL STAGES OF THE DEGRADATION OF
POLYMERIC PRECURSORS USED IN THE PREPARATION OF
CARBON/GRAPHITE FIBERS

George T. Sivy

The Pennsylvania State University
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George T. Sivy

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

   The thermal degradation of Polyacrylonitrile (PAN) copolymers as a function of composition and temperature under reduced pressure and in air has been studied by Fourier transform infrared spectroscopy. Three PAN copolymers containing varying concentrations of the comonomers acrylamide (AM), Acrylic acid (AA) and itaconic acid (IA) have been examined.

   The results obtained for the copolymers containing AM units, degraded under reduced pressure are somewhat surprising and indicate that above a certain threshold of comonomer concentration the fraction of available nitrile groups

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that undergo reaction is limited and falls within a remarkably narrow range. From a consideration of the copolymer and stereochemical sequence distribution, the stereochemistry of ring formation and intermolecular crosslinking, a "step-ladder" model for the degraded product may be applicable. Additionally, it is concluded that the distribution of tactic placements in the copolymer chains is indeed a factor limiting the degree of cyclization of the available nitrile groups. A computer program has been developed for calculating the extent of reaction of the acrylonitrile units based upon the above model and the results are in good agreement with the experimental observations.

The results obtained for these AN copolymers degraded at $200^{\circ}C$ in air suggest that reaction other than ring formation and intermolecular crosslinking predominate. These reactions are similar to the well known autoxidation proposed for many other polymeric materials. It has been concluded that reaction with oxygen leads to a series of elimination reactions which result in the formation of polyenes. These polyenes have the potential to form a fused ring system via a Diels-Alder addition reaction. A degradation scheme based on the infrared results is advanced.

In an analogous fashion to the AN copolymers, the results obtained for copolymers containing AA units also suggest a limited amount of nitrile groups will undergo cyclization above a threshold of comonomer concentration. From results obtained at $200^{\circ}C$ under reduced pressure, it is concluded that these AA copolymers follow a similar trend of degradation to that of the AN copolymers. However at $160^{\circ}C$ under reduced pressure, the rate at which the AA copolymers degrade is slower than the corresponding AN copolymers. It appears that at this temperature factors such as AA units condensing to anhydrides and the kinetics of acid-nitrile reactions are playing a major role in determining the rate of degradation.

Interpretation of the preliminary results of studies undertaken on two copolymers containing IA units is made complicated by the presence of amide and ester groups in the AN/IA copolymer chain. These additional functional groups result from the ability of the IA monomer to provide conditions suitable for acid catalysed hydration of the AN groups and esterification of the acid groups during polymerization. Therefore, continued work dealing with these copolymers is probably unwarranted.

ABSTRACT

The thermal degradation of polyacrylonitrile (PAN)
copolymers as a function of composition and temperature under
reduced pressure and in air has been studied by Fourier
transform infrared spectroscopy. Three PAN copolymers
containing varying concentrations of the comonomers
acrylamide (AM), acrylic acid (AA) and itaconic acid (IA)
have been examined.

The results obtained for the copolymers containing AM
units, degraded under reduced pressure, are somewhat
surprising and indicate that above a certain threshold of
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groups that undergo reaction is limited and falls within a
remarkably narrow range. From a consideration of the
copolymer and stereochemical sequence distribution, the
stereochemistry of ring formation and intermolecular
crosslinking, a "step-ladder" model for the degraded product
may be applicable. Additionally, it is concluded that the
distribution of tactic placements in the copolymer chains is
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results are in good agreement with the experimental
observations.

The results obtained for these AM copolymers degraded at

200°C in air suggest that reactions other than ring formation and intermolecular crosslinking predominate. These reactions are similar to the well-known autoxidation proposed for many other polymeric materials. It has been concluded that reaction with oxygen leads to a series of elimination reactions which result in the formation of polyenes. These polyenes have the potential to form a fused ring system via a Diels-Alder addition reaction. A degradation scheme based on the infrared results is advanced.

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groups and esterification of the acid groups during
polymerization. Therefore, continued work dealing with these
copolymers is probably unwarranted.

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CHAPTER 1

INTRODUCTION

1.1 Structure and Properties of PAN

Typically, polyacrylonitrile (PAN) is polymerized by
solution or suspension polymerization techniques with the
former offering the advantage of direct fiber spinning. As
with most acrylic polymers, PAN has a predominantly
head-to-tail structure and an essentially random (atactic)
configuration of the nitrile groups (1). Despite the lack of
order along the polymer chain, wide angle X-ray diffraction
analysis of oriented fibers and solution grown crystals
reveals sharp reflections on the equator and diffuse
scattering on the quadrants (2). From this data, it has been
suggested that repulsion of neighboring nitrile groups causes
each chain to assume a stiff extended and randomly kinked
conformation such that, on average, each chain occupies a
cylindrical space about $6\text{\AA}$ in diameter. These cylinders are
then packed into a pseudo-hexagonal array (3) as shown in
Figure 1. Such a model will be used later in this thesis to
account for the degradation of PAN copolymers. This type of
imperfect crystal structure is sufficiently disordered to
incorporate large amounts of comonomer without a change in
the pseudo-hexagonal array (3).

Because of the strong intermolecular interactions that
would arise from this type of structure, PAN is soluble only
in highly polar solvents such as dimethylsulfoxide (DMSO) and
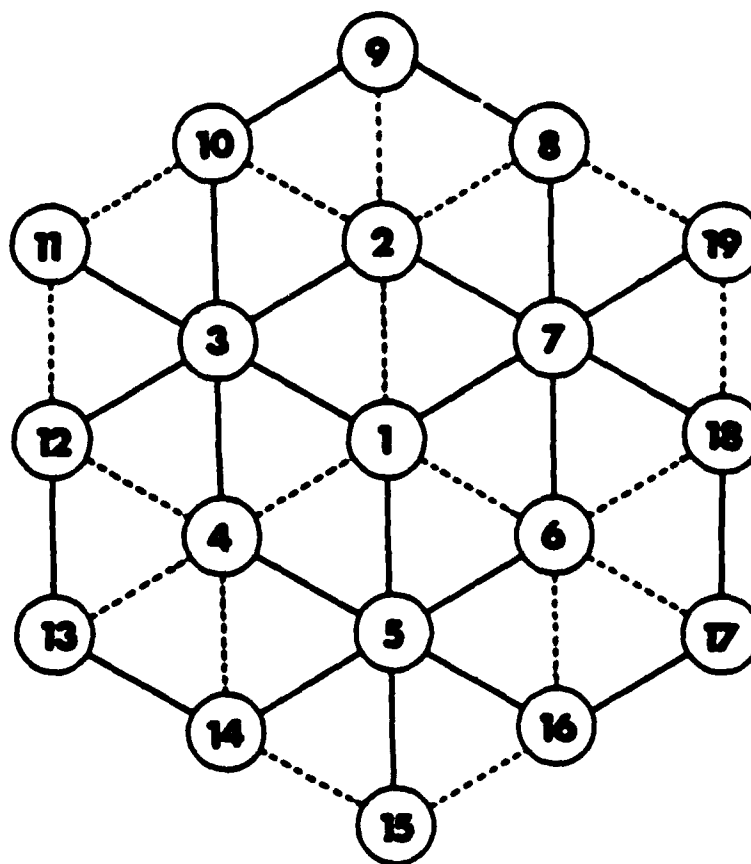
Figure 1. Schematic representation of the
pseudo-hexagonal packing of PAN chains.

dimethylacetamide (DMA), and must be copolymerized with small
amounts (5-15%) of other monomers to aid in dyeability as
well as solubility. These polymers also exhibit very high
crystalline melting points of about $320^{\circ}C$ (3,4). However,
this melting point can only be observed at heating rates in
excess of $1000^{\circ}C/min$ (4). At normal processing rates and
temperatures the polymer does not melt but instead undergoes
extensive discoloration and increased insolubilization.
Continued heating ($3000^{\circ}C$) yields a material with a graphite
type crystal structure of very high strength. This type of
thermal behavior has made PAN one of the principle precursors
for the production of high strength carbon and graphite (C/G)
fibers. This subject will be dealt with in greater detail in
the following section. Along with its limited solubility,
PAN and PAN copolymers are relativily unaffected by most
common solvents, oils, greases, water and most acids. High
nitrile containing fibers have good resistance to stretch,
heat, microorganisms, insects, and many chemicals (1).
Fibers also show good resistance to washing and cleaning,
have good flex life, low moisture absorption and good bulking
properties (1). Nitrile-containing plastics exhibit good
dielectric properties, light stability, high tensile and
impact strength, good resistance to solvents and heat, and
low gas transmission.

1.2 Uses

1.2.1 General

The above properties provide for a wide variety of uses

for PAN as a textile fiber. These uses include knitwear, pile fabrics, carpets, blankets, shirts, cushions and commercial filters. Acrylonitrile-containing plastics such as acrylonitrile-butadiene-styrene (ABS) may be molded and machined for such end uses as decorative panels and luggage. Other PAN copolymers such as PAN/methacrylonitrile are used to form soft drink bottles and plastic domes (1).

1.2.2 As a Precursor for C/G Fibers

Carbon and graphite fibers have long been recognized as outstanding reinforcing materials for various polymeric resins. Aside from the common uses of these fibers (golf clubs, tennis racquets), many components used in the aerospace industry utilize C/G fibers. For example, the payload bay doors of the space shuttle are composed of a mixture of C/G tape and fabric in an epoxy resin. The properties of these fibers, which give them such wide variety of uses, include high modulus (typically 50.0×10^{4} psi), high tensile strength (300,000psi), high strength-to-weight ratio and resistance to heat and flame.

C/G fibers may be prepared from several precursor materials. These include rayon, cellulose, pitches and PAN. To date, a majority of the primary producers of C/G fibers utilize PAN as the principle precursor. The reasons for this being, that the PAN fibers allow for continuous production (not possible with pitch) and yield superior fibers compared to those from rayon or cellulose.

Briefly the steps involved in C/G fiber production from

PAN are: 1) Oxidation of PAN fiber in tension at 200-220°C; 2) carbonization at 1200°C and 3) graphitization at 2900°C. During the first step, polymerization of the nitrile groups followed by reaction with oxygen yields a cyclized ladder polymer with sufficient rigidity to maintain a structure favorable for formation of a graphite structure with high 3-dimensional order. In the second step, elimination of most of the nitrogen and hydrogen results in a structure with high 2-dimensional order but low 3-dimensional order. Finally, graphitization yields a graphitic type crystal structure with high 3-dimensional order.

Although C/G fibers from PAN were first discovered in the late 1950's, it was not until 1966 that Shindo [5] demonstrated that the preoxidation step plays a major role in determining properties of the final product. Since that time a vast amount of work has been done to elucidate the chemistry and final product of this preoxidation step. The generally accepted cyclization of the pendant nitrile groups in groups of 3-4 has been supported by a variety of analysis techniques such as Differential Scanning Calorimetry (DSC), Thermal Volatilization Analysis (TVA), Thermal Gravimetric Analysis (TGA), and electronic and vibrational spectroscopy. However, the exact role of oxygen during this step remains unclear. Under normal production conditions, the carbon yield from PAN precursor fibers is usually only 50% or so. The reason for this low yield is believed to result from side reactions such as chain scission and oxidative degradation

that compete with the nitrile polymerization during the
preoxidation. To overcome this problem two alternatives may
be examined. First, reducing the amount of oxygen present
during preoxidation would decrease the amount of oxidative
side reactions. However Shindo [5] has shown that decreasing
the amount of oxygen results in poor performance C/G fibers
with a brittle low strength product resulting from total
exclusion of oxygen. The second alternative is to induce
cyclization of the nitrile groups at a lower temperature and
increase the number of units that cyclize before a
significant amount of detrimental degradation occurs. This
may be accomplished by the inclusion of comonomers into the
PAN chains.

It has been shown by numerous authors that inclusion of
comonomers such as acrylic acid (AA), acrylamide (AM) or
itaconic acid (IA) does lower the temperature at which
cyclization occurs. However, the number of nitriles cyclized
for each initiation site remains at or .y 3-4 as for pure PAN
at higher temperatures. To overcome this problem copolymers
of varying comonomer concentration may be prepared to at
least maximize cyclization. The major problem here is the
increasing probability of chain scission with increasing
comonomer content. Furthermore, if chain scission was
negligible, and the comonomers did initiate cyclization, most
likely they would initiate only in one direction thereby
leaving weak gaps between cyclized blocks. Ideally, a
comonomer capable of two-sided initiation would be in

order. As will be shown in the next section AN is one such
monomer.

1.3 Summary of Previous Work

1.3.1 The Thermal Degradation of PAN and PAN Copolymers

As previously mentioned, numerous authors have suggested
mechanisms by which PAN degrades. An excellent review of the
many proposed mechanisms has been presented by Peteavien (6)
and will not be presented in this thesis. The basic feature
common to all these schemes is the cyclization of the nitrile
groups to form a ladder type structure. However, the
incorporation of oxygen into the stabilized product is still
debatable. Coleman and Peteavien (7,8) have suggested from
Fourier transform infrared (FT-IR) studies that oxygen is
present in the ladder polymer as pyridone carbonyls formed
via the mechanism shown in Figure 2. Infrared bands at 1500
and 1610 cm^{-1} which appear and steadily increase in the
spectra of degrading PAN (shown in Figure 3) may confidently
be assigned to the pyridone structure shown in Figure 2.
These spectra were recorded at 200°C and under a reduced
pressure of 5 x 10^{-2} torr. By performing the degradation
studies at a reduced pressure the detrimental oxidative side
reactions previously mentioned may be reduced thus giving an
uncomplicated spectrum of the cyclized product.

This author (9) has previously presented the results
obtained from Fourier transform infrared (FT-IR) studies of
the degradation of three copolymers of acrylonitrile (AN),
containing approximately 4 wt% of the comonomers methacrylic
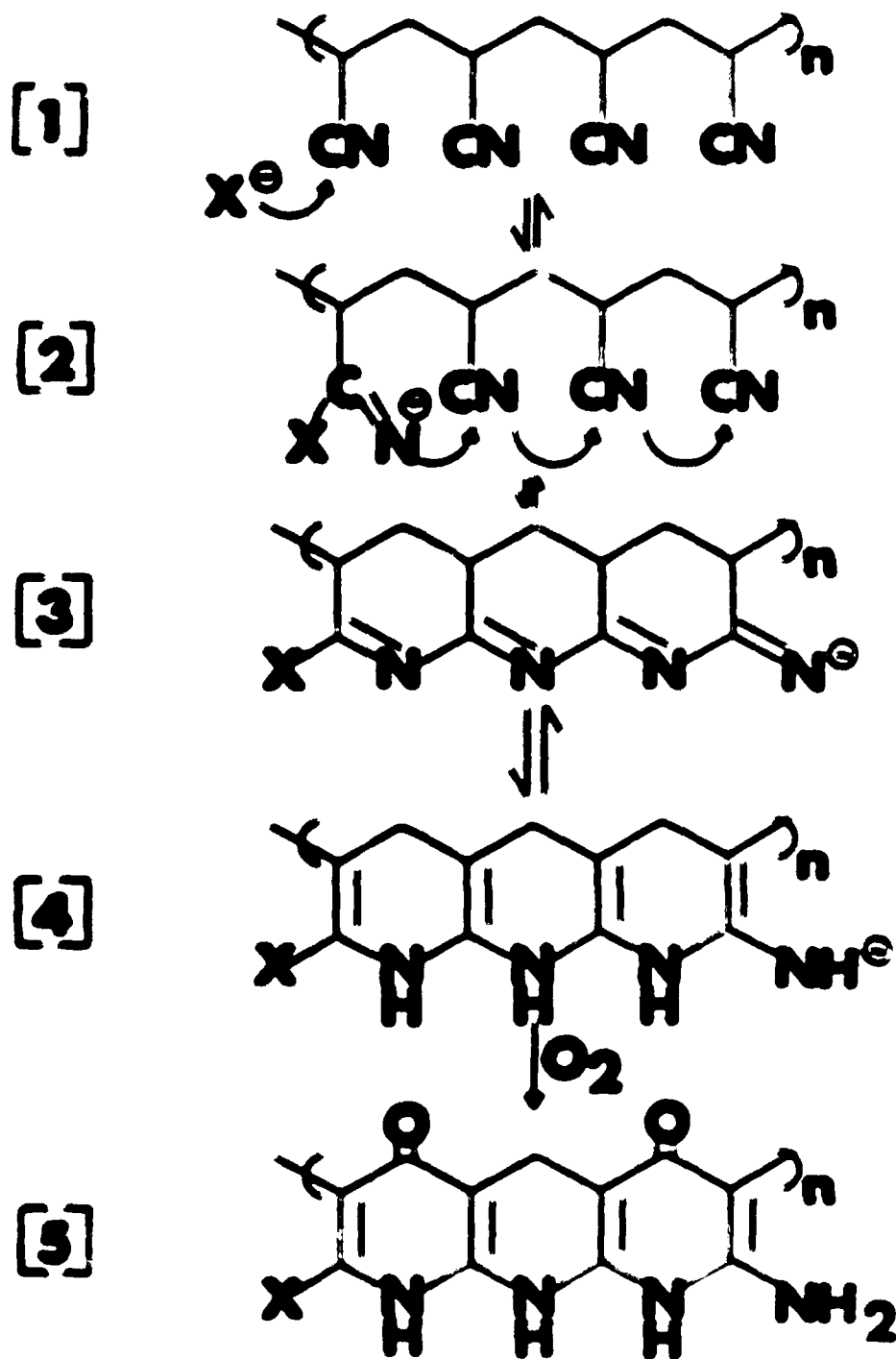
Figure 2   Scheme depicting the proposed chemical reactions occurring during the degradation of PAN at 2000°C under reduced pressure
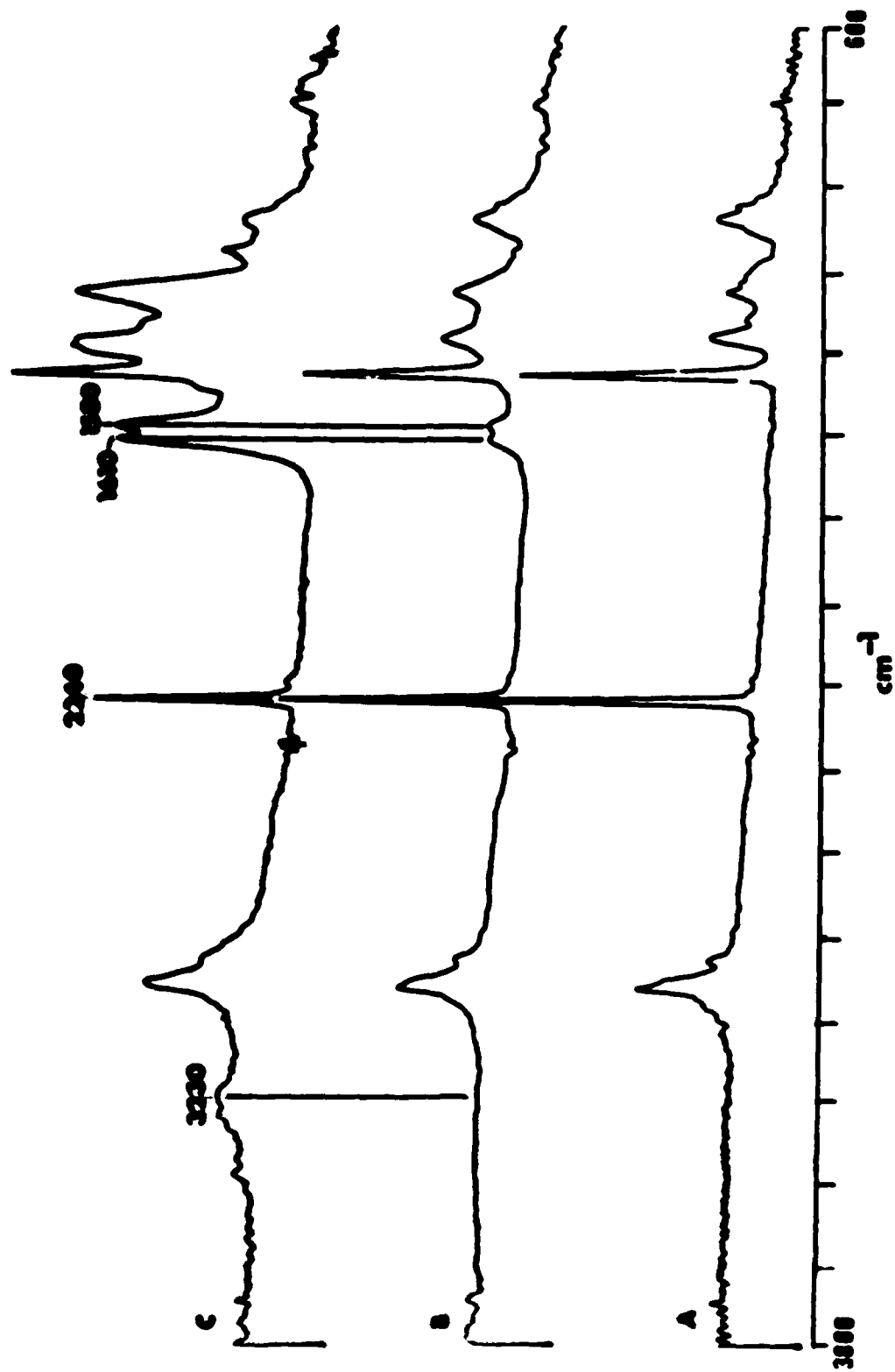
Figure 3. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of a PAN polymer recorded at 200°C under reduced pressure. A) initial spectrum; B) 4 hours and C) 8 hours.

acid (MAA), acrylamide (AM) and vinyl acetate (VAc)
respectively. The rate of degradation in the temperature
range of 130 to 200°C and under reduced pressure was observed
to be markedly dependent upon the chemical nature of the
comonomer. Figure 4 shows the initial absorbance infrared
spectra of PAN and the three copolymers at 200°C under a
reduced pressure of 5 X 10^{-2} torr. Of immediate interest is
the presence of the bands at 1580 and 1610 cm^{-1} in the
spectrum of the MAA and AM copolymers indicative of the
pyridone formation. These bands are not present in the
spectrum of the PAN homopolymer or the PAN/VAc copolymer
indicating that very little if any degradation has occurred.
After 4 hours, these bands appear in the spectrum of PAN,
however they are still relatively weak when compared to the
spectra of the copolymers. Monitoring of the decrease in the
C≡N stretching absorbance at 2240 cm^{-1} (loss of nitrile) as a
function of time and temperature, as plotted in Figure 5,
further demonstrates that inclusion of MAA and AM units into
the predominantly polyacrylonitrile (PAN) chain had the
greatest effect on the rate of degradation. In essence, it
was concluded that MAA or AM units act as initiation sites
for the cyclization of adjacent AN units. Both of these
comonomers are themselves converted into cyclic species and
are incorporated into the block of cyclized AN units. It was
determined, however, that there were significant differences
in the degradation mechanisms of the AN/MAA and AN/AM
copolymers. In the former, initiation of the cyclization
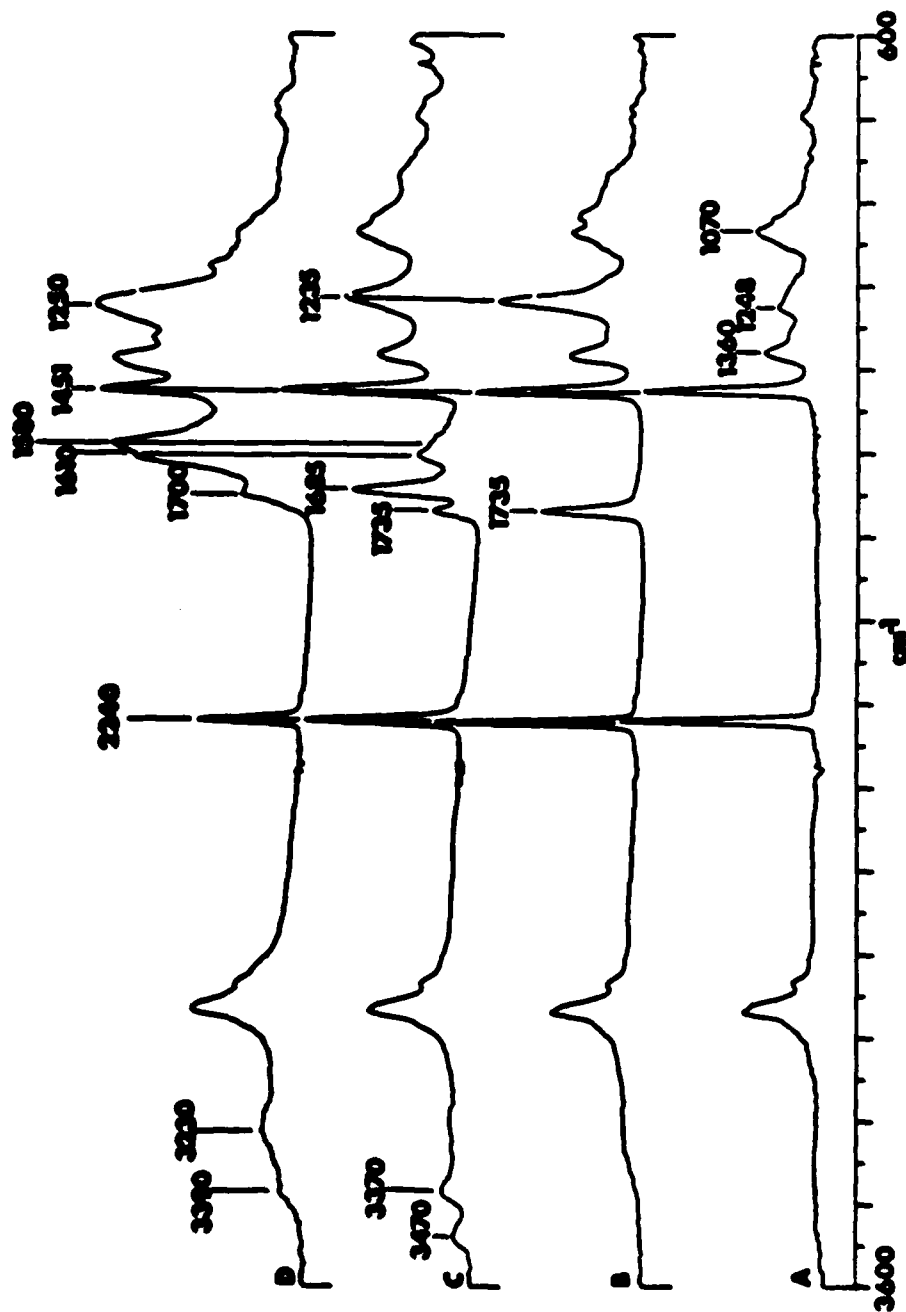
Figure 4. FT-IR absorbance spectra in the range 600-3800 cm^{-1} recorded when the samples attained 200°C under reduced pressure. A) PAN; B) PAN/VAc copolymer; C) PAN/AM copolymer and D) PAN/AA copolymer.
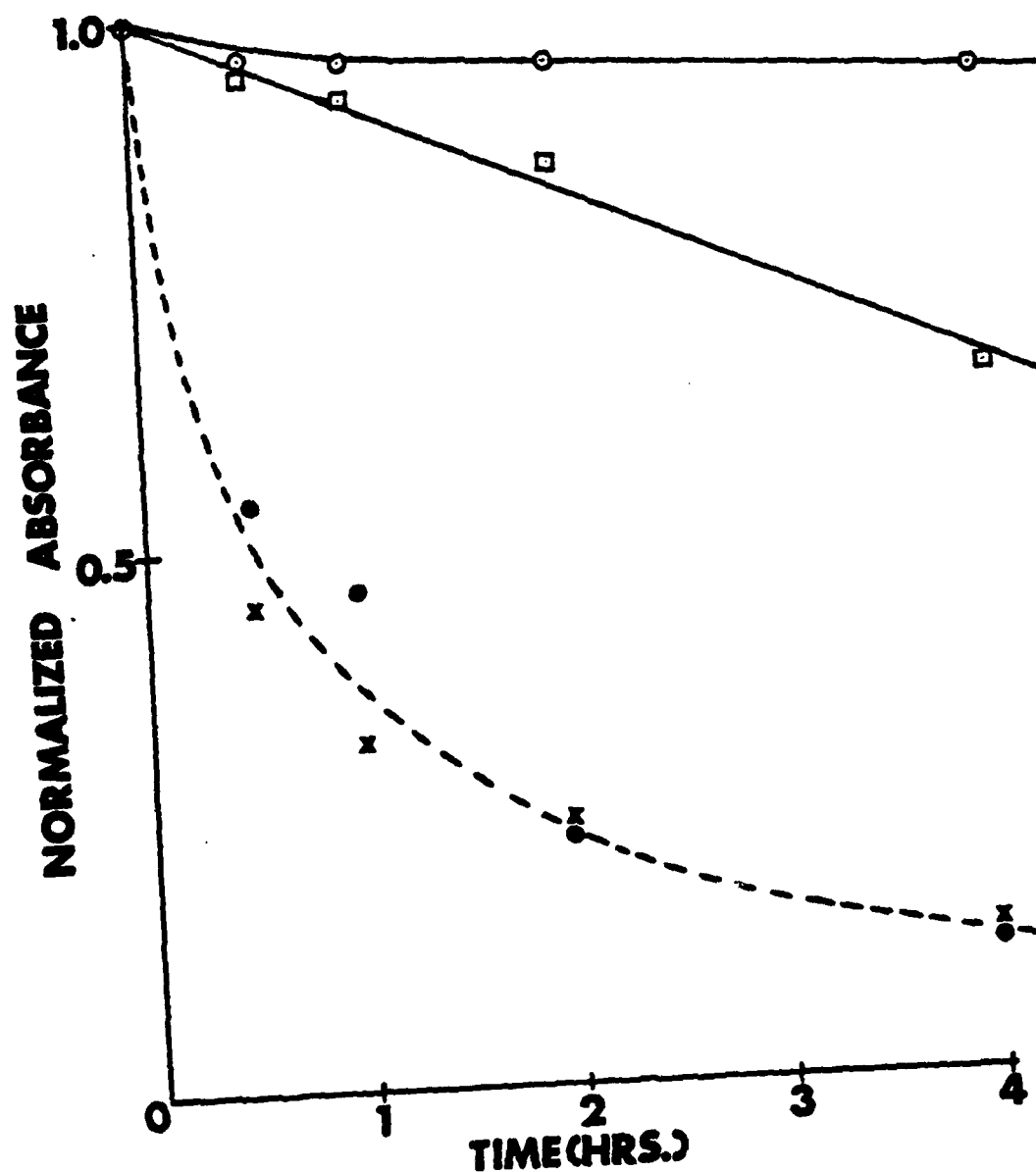
Figure 5. Normalized C≡N stretching absorption as a function of time at 200°C under reduced pressure. ○ PAN homopolymer; ▢ PAN/VAc; ✗ PAN/AM and ● PAN/AA.

reaction occurs without an apparent inhibition period, at least in the temperature range of 130 to 200°C. Conversely, for the AN/AM copolymers an inhibition period is observed, but this is offset by a more rapid rate of cyclization compared to the analogous AN/MAA copolymers, once the inhibition period has been exceeded. In addition, mechanisms were suggested in which the AN/AM copolymer could initiate intramolecular cyclization in both directions from the initiation site while the AN/MAA was restricted to initiation in one direction. For expository purposes, these mechanisms are reproduced in Figure 6. From inspection of the mechanisms, it can be seen that a two-way initiation by the AM comonomer is made possible by the tautomerism of the exocyclic carbonyl of structure IIa to form a conjugated ring structure. Continued cyclization by the resulting exocyclic hydroxyl would eliminate the presence of voids between cyclized blocks. In the case of the MAA copolymer, tautomerism of the exocyclic carbonyl is blocked by the presence of the α-methyl group. It was initially thought that such tautomerism would take place with a copolymer of PAN/acrylic acid (AA). However, it will later be shown that such a reaction does not take place.

1.4 Objectives of this Work

Given the enhanced rate of degradation exhibited by the PAN/MAA and PAN/AM copolymers the next logical step in this study is to vary the concentration of the comonomers. The underlying rational for this is based on the following
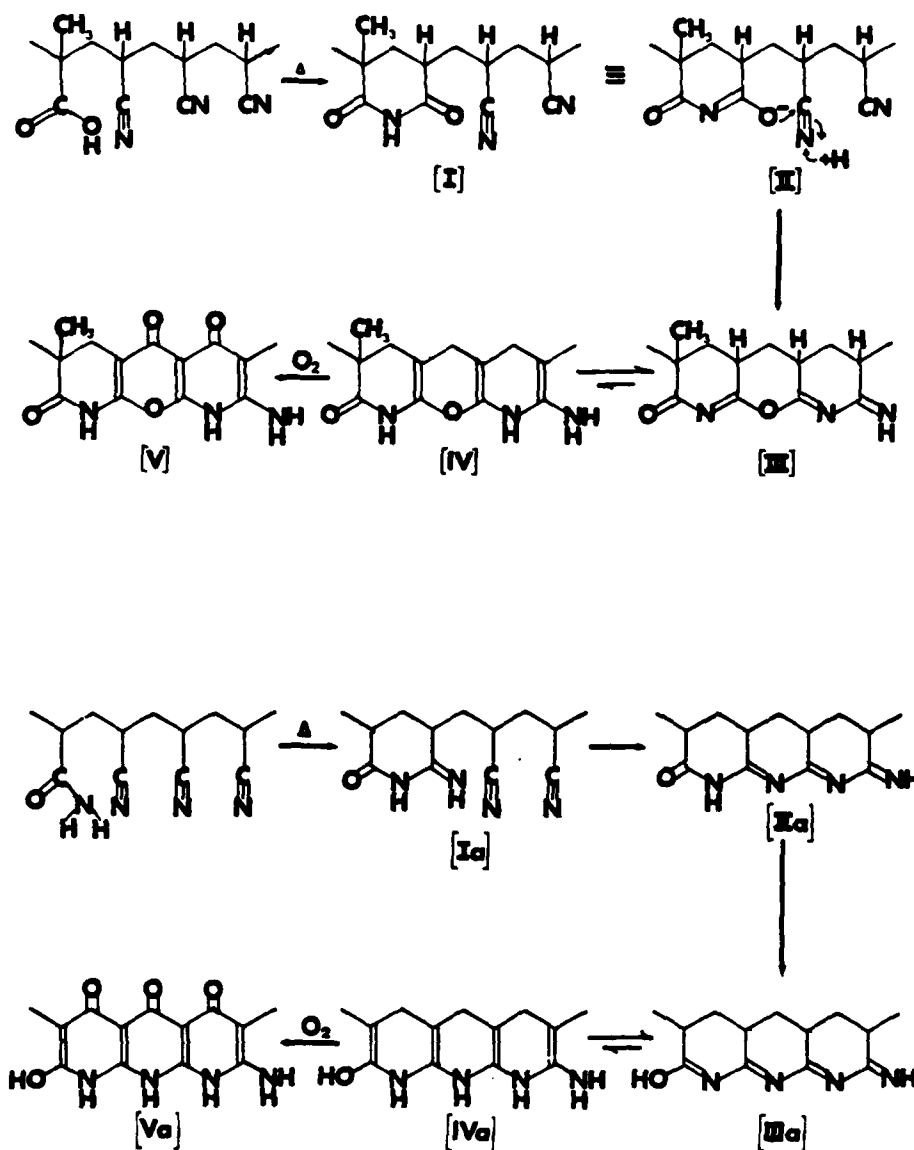
Figure 6. Schemes depicting the proposed chemical react-
ions during the thermal degradation of: (top)
PAN/MAA and (bottom) PAN/AM copolymers.

argument. If one particular concentration of comonomer increases the number of AN units that cyclize, perhaps incorporation of more initiation sites would result in even a greater amount of nitrile cyclizations. Furthermore, if the number of cyclized blocks formed during cyclization can be maximized and the number of oxidative side reactions minimized, it is feasible that the properties of the resulting C/G fibers could be significantly modified.

The majority of this thesis deals with this question of concentration dependance. Three copolymers of varying comonomer concentrations were thermally investigated using FT-IR spectroscopy. To re-emphsize, the original intent of this study was to maximize the amount of AN units that cyclize after a given period of time by varying the type and amount of comonomer present.

CHAPTER 2

EXPERIMENTAL

2.1 Synthesis of Copolymers

The PAN/AM, AA and IA copolymers in this study were
synthesized by free-radical polymerization in aqueous
solution at $50^\circ C$ using potassium persulfate initiator. A
small amount of methanol was also added as a chain transfer
agent. At the onset of this study, copolymer compositions
ranging from 2 to 40 mole % were desired and the
corresponding molar feed ratios were calculated using
reactivity ratios found in the literature (10). It should be
noted that these reactivity ratios are questionable in that
the precise experimental details are lacking in the
references. In order to ensure a narrow distribution of
polymer chains in terms of copolymer composition, the
copolymers were isolated before 10% conversion. The
copolymers were purified by multiple reprecipitation from
DMSO into methanol, dried under vacuum and stored at $0^\circ C$ in
the absence of light.

For reasons that will be discussed in the following
chapters, the composition of the AM copolymers was determined
by ^{13}C NMR spectroscopy while elemental analysis was employed
for the AA and IA copolymers.

Table 1 lists the copolymer designation, molar feed
ratios, yield and the results of elemental or ^{13}C NMR
analysis.

TABLE 1

POLYMERIZATION DATA AND COPOLYMER COMPOSITION.

Copolymer AN/acrylamide	Molar Feed Ratio AN/comonomer	Analysis 13C Nmr $^*C\equiv N$	$^*C=O$	Composition %AN	%comonomer
I	.273/.009	147	4	97.1	2.9
II	.273/.024	104	6	94.8	5.2
III	.273/.054	139	14	89.4	10.6
IV	.273/.141	123	25	81.8	18.2

AN/acrylic acid		Elemental %C	%N	%H		
IA	.273/.006	67.4	25.6	5.65	97.7	2.3
IIA	.273/.013	64.6	25.6	5.51	94.0	6.0
IIIA	.273/.023	63.2	23.3	5.40	91.0	9.0
IVA	.273/.012	66.4	25.0	5.65	96.4	4.0

AN/itaconic acid		Elemental %C	%N	%H	**	**
1b	.273/.009	60.8	20.9	5.40	90.0	10.0
2b	.273/.002	65.8	19.3	6.30	87.0	13.0

* Integral NMR peak hieghts
** Contains units other than itaconic acid. See Chapter 5
for discussion.

2.2 Sample preparation

Thin films (<0.5 mil) used for the FT-IR degradation studies were prepared by evaporation of a 3% DMSO solution. The solvent was removed by stirring in water for several days and the films were then dried under vacuum at ambient temperature. The films were subsequently transferred to KBr discs and placed into a specially designed cell contained in the sample compartment of the spectrometer. This cell allows continuous monitoring while under reduced pressure at elevated temperatures. Temperature control ($+2^{\circ}C$) was attained using a Specac automatic temperature controller.

Solutions of the copolymers in deuterated DMSO (3 % w/v) were used for ^{13}C NMR analysis. A small amount of chromium acetylacetonate (0.6 % w/v of polymer) was added as a relaxation agent.

2.3 Instrumental

The infrared spectra were recorded on a Digilab model FTS-15/B FT-IR spectrometer. Each spectrum was recorded at a resolution of 2 cm^{-1} using 128 scans. The frequency scale is accurate to 0.02 cm^{-1}. Particular care was made to ensure that the films were sufficiently thin enough for the Beer-Lambert law (7,8).

The ^{13}C NMR spectra were recorded on a Brucker WP-200 NMR spectrometer in the pulsed Fourier transform mode. Instrumental conditions for quantitative measurements were as follows: relaxation delay, 2 secs.; aquisition time, 1.3 secs.; number of transients co-added, 6660. All spectra were

obtained at $25^{\circ}C$ in a solution of DMSO-d_6 using 10mm O.D. sample tubes.

A Carlo Erba model 1106 Elemental Analyzer was used for the determination of the acid copolymer compositions. Nitrogen was determined as nitrous oxide, carbon as carbon dioxide and hydrogen as water. Approximately 1mg of sample was used for the determinations.

CHAPTER 3

THERMAL DEGRADATION OF ACRYLONITRILE/ACRYLAMIDE COPOLYMERS

3.1 Original Objectives

The apparent ability of the acrylamide (AM) comonomer to initiate cyclization in two directions as shown in Figure 6, made this copolymer a most attractive system for potential use as a C/G fiber precursor. This type of initiation would exclude weak gaps between blocks of cyclized AN units and therefore could lead to a superior C/G fiber. Intuitively it was hoped that by simply increasing the amount of AM units incorpor. ~d into a predominantly PAN chain the concentration of cyclized blocks would increase and ultimately cyclize all available AM units.

3.2 Analysis of Copolymers

The analysis of the copolymer composition of the AN/AM samples presents a difficult problem. If it can be assumed that the literature values of the respective reactivity ratios are correct (not necessarily a good assumption given the generally wide variation of reactivity ratios reported in the literature for numerous monomer pairs), one can calculate a copolymer composition based on the instaneous copolymer equation if the degree of conversion is less than 10%. Nevertheless, this procedure is fraught with difficulties and is most unsatisfactory. Elemental analysis is also unsuitable for the AN/AM copolymers. Both monomer units contain carbon, hydrogen and nitrogen and the only major

difference between the AN and AM units is the presence of oxygen, which is notoriously difficult to accurately determine .

Potentially, the copolymer composition could be determined from the infrared spectra. The infrared bands associated with the nitrile group at 2240 cm^{-1} (AN unit) and the carbonyl group at 1685 cm^{-1} (AM unit) are isolated well-established group frequencies and relatively easy to measure. Room temperature infrared spectra of four copolymers are shown in Figure 7. It is immediately apparent that there are marked differences in the relative intensities of the 2240 and 1685 cm^{-1} bands in the copolymers. However, for quantitative analysis it is necessary to prepare a calibration curve from known standards or to have a knowledge of the respective absorptivity coefficients. This information was not available. An obvious approach to the quantitative analysis of the AN/AM copolymers is to employ ^{13}C NMR spectroscopy. The carbon atom associated with a carbonyl group has a chemical shift in the range of 160 - 180 ppm while a nitrile carbon occurs between 115 - 125 ppm (11). All other carbons present in the AN/AM copolymers occur at a much higher field. However, for quantitative analysis, ^{13}C NMR spectroscopy is not without inherent problems associated with nuclear Overhauser enhancement (NOE) and variations in spin relaxation times. Fortunately, Mr. A. Preyer, of the Chemistry Department at Penn State (12) has studied similar materials and was able to provide optimum instrumental ^{13}C
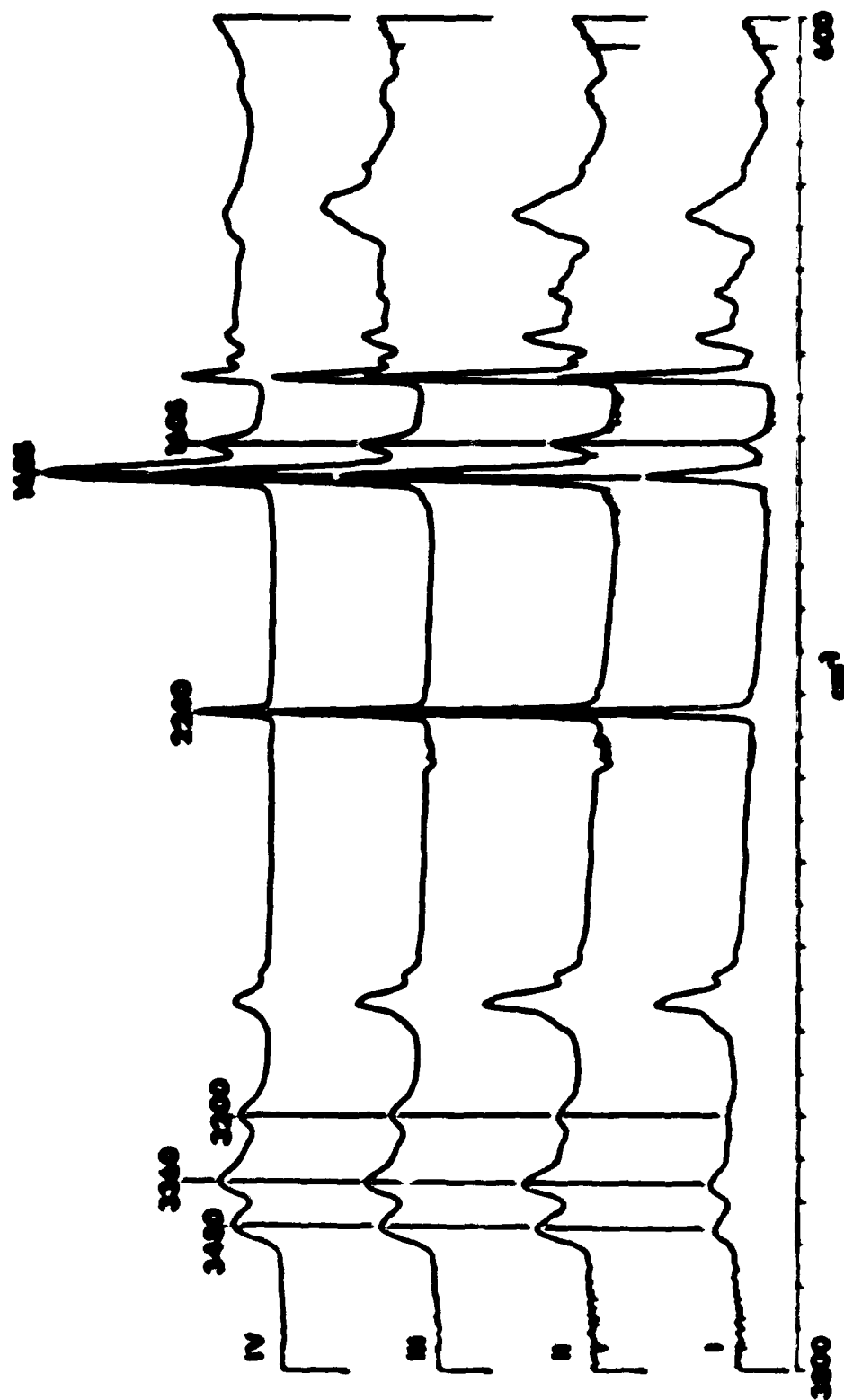
Figure 7. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/AM copolymers recorded at room temperature. (i) 2.9. (ii) 5.2. (iii) 10.6 and (iv) 18.2 mole% AM.

NMR parameters for the quantitative analysis of the copolymers. These are described in the instrumental section. In the ^{13}C NMR spectra of two representative copolymer samples, shown in Figures 8 and 9, a line observed at 174 ppm is assigned to the carbonyl carbon of the AM unit. The lines associated with the nitrile carbon are observed at 120.2, 119.9 and 119.6 ppm and presumably reflect stereochemical triads of the AN units. From a determination of the relative areas of the two regions of the spectra the copolymer composition can readily be calculated. These results are summarized in Table 1.

Now knowing the copolymer composition of these four copolymers and given the fact that the copolymers were isolated at conversions below 10%, a calibration curve for the infrared spectrum was prepared and the reactivity ratios determined from a Fineman - Ross plot. Figure 10 shows a plot of the copolymer composition determined by NMR versus the ratio of the intensities of the infrared bands at 2240 and 1685 cm^{-1}. An essentially linear relationship is observed in the range of compositions examined. Accordingly, it is now possible to use the infrared results to calculate copolymer composition in this range.

From a knowledge of the copolymer composition and the monomer feed ratios the reactivity ratios of AN and AM can be determined by assuming a terminal copolymerization model (13). The Fineman - Ross equation may be expressed as:

$$x/y(y-1) = r_a(x^2/y) - r_b$$
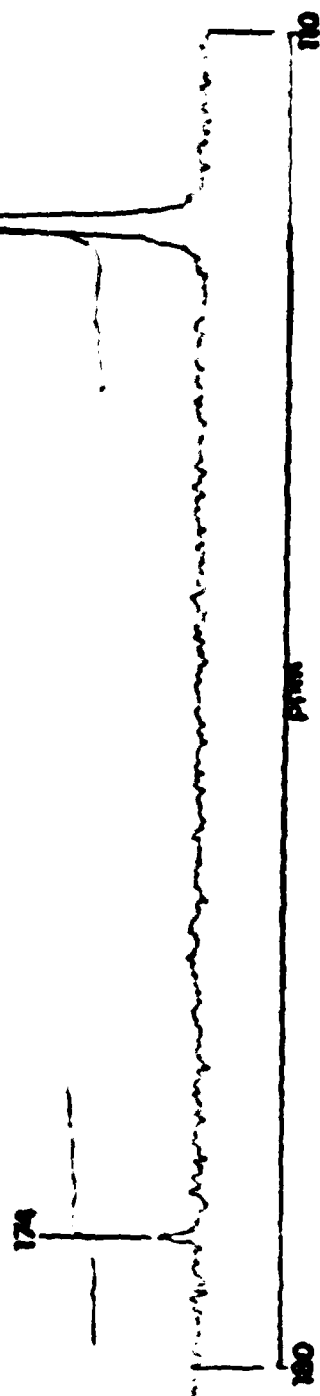
Figure 8. ^{13}C NMR spectrum of the AN/AM copolymer containing 5.2 mole% AM.
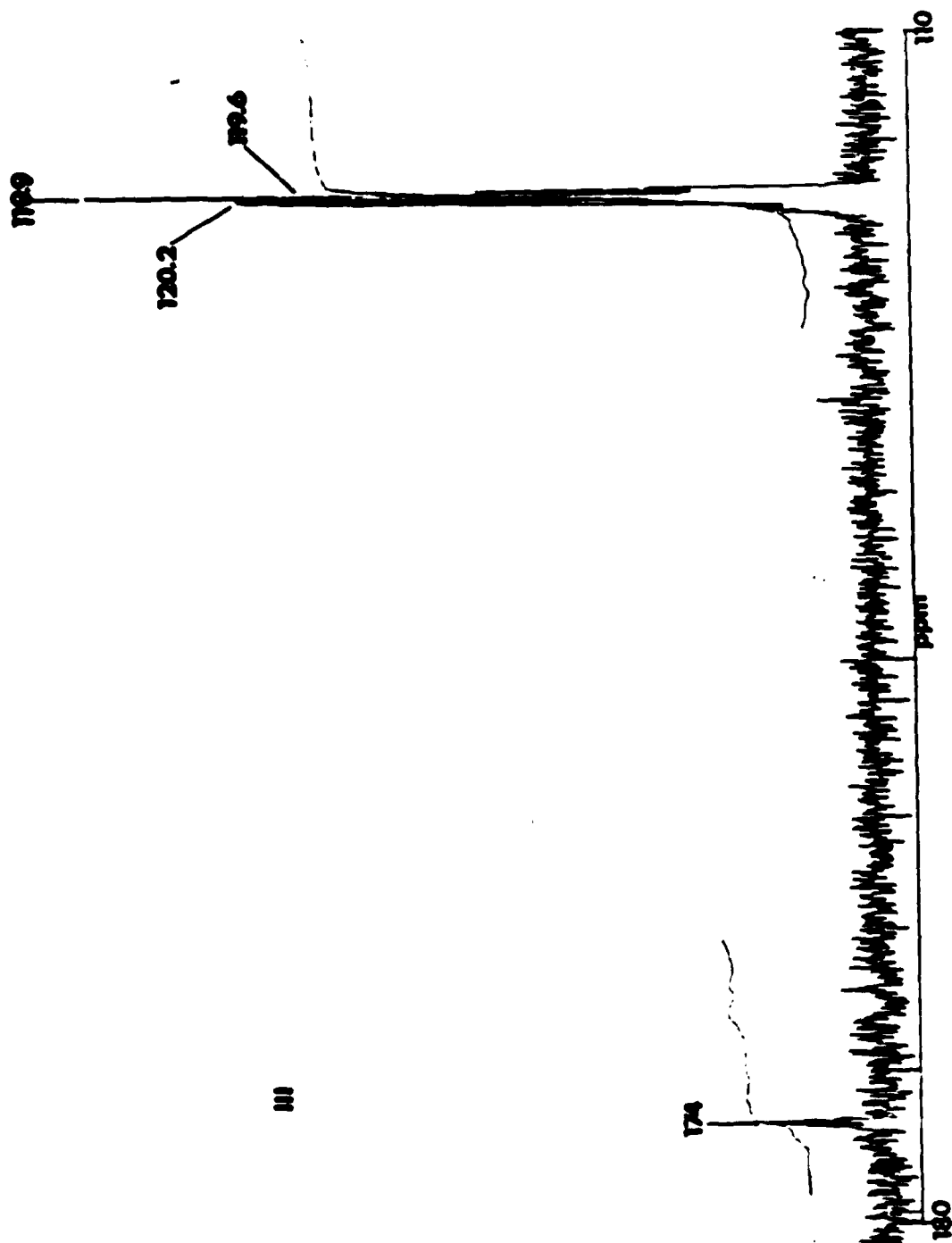
Figure 9. 13C NMR spectrum of the AN/AM copolymer containing 10.6 mole% AM.
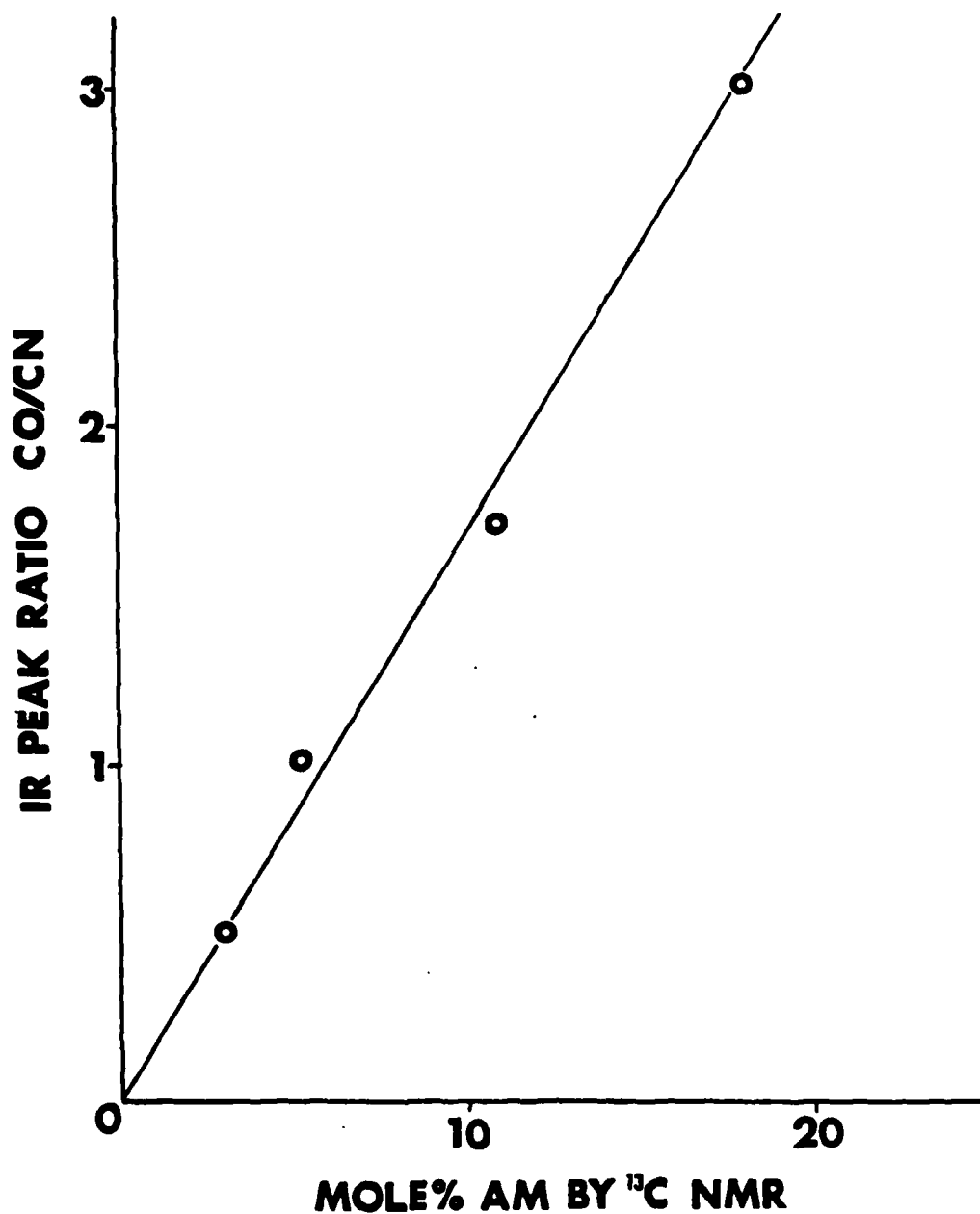
Figure 10. Infrared/^{13}C NMR calibration curve for AN/AM copolymer composition.

where x is the molar feed ratio and y is the copolymer molar
composition ratio.

A plot of $x/y(y-1)$ versus x^2/y should yield a straight
line with the intercept equal to $-r_b$ and the slope equal to r_a.
By defining the AN and AM monomers to r_a and r_b respectively
and then switching the definitions, two plots may be obtained
(Figure 11). From a least squares fit of the data, values of
1.5 and 0.3 for the reactivity ratios of AN and AM were
obtained. These results are very different from those
reported in the literature (0.8 and 1.3) (14), but as
previously mentioned, the precise experimental details used
to determine these literature values could not be found.
Therefore, the variance of the two sets of results is not
alarming. Furthermore, AN is only sparingly soluble in water
whereas AM is very soluble. Accordingly, the apparent
reactivity ratios will be sensitive to the precise
experimental polymerizaon conditions. In this study,
polymerization was carried out in dilute aqueous solution to
ensure complete solubility of the AN monomer.

3.3. Results

3.3.1 Thermal Degradation at 160 and 200°C Under Reduced
Pressure.

Figure 7 shows the FT-IR absorbance spectra of films of
the four AN/AM copolymers containing approximately 2.9, 5.2,
10.6 and 18.2 mole % AM (denoted I thru IV respectively)
recorded at room temperature. Of immediate interest to this
study are the infrared bands at 1685 and 2240 cm^{-1}. The
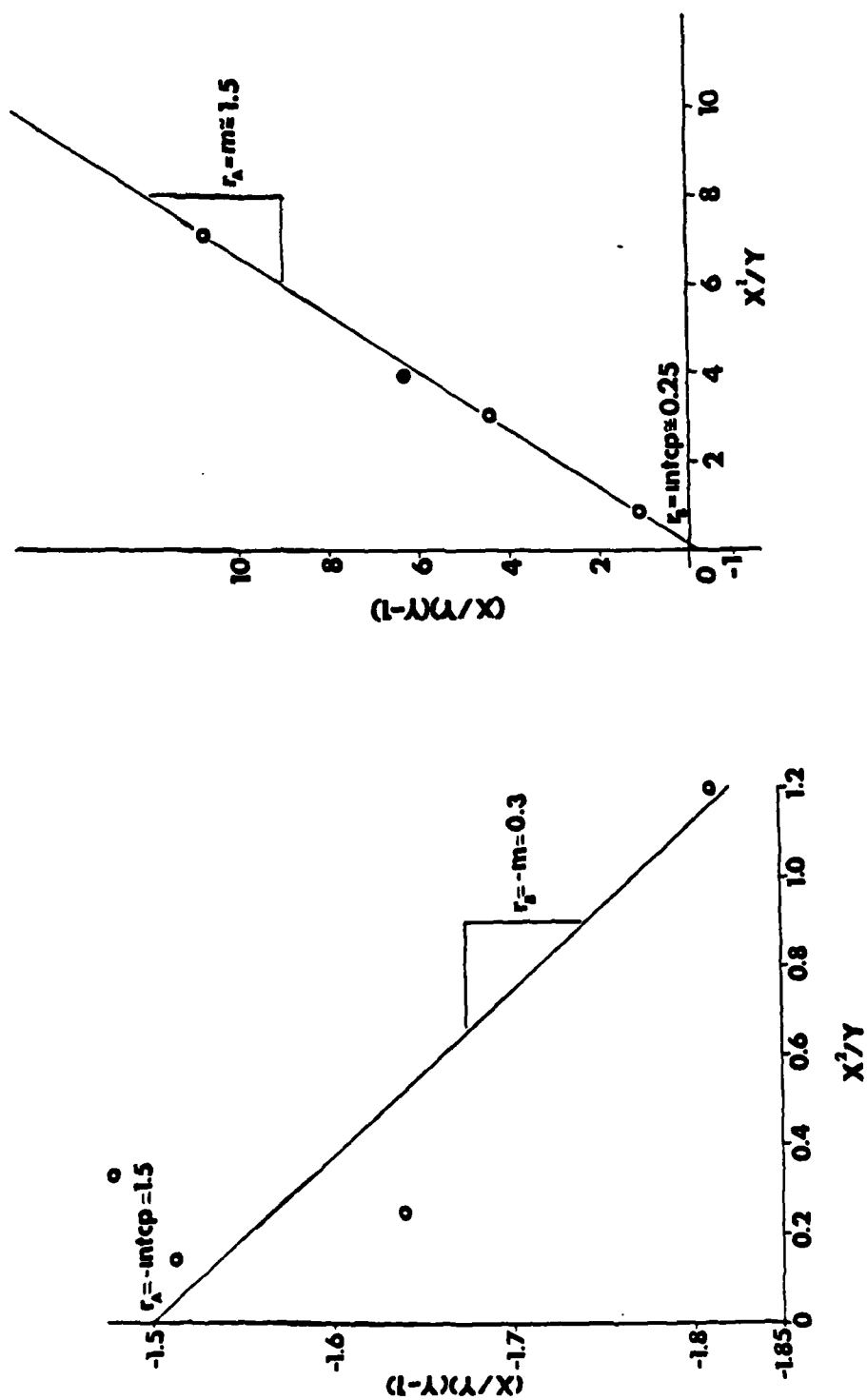
Figure 11. Fineman-Ross plots for the determination of reactivity ratios for the AN/AM copolymers. Plot on left results from defining AN to r_a and AM to r_b. Right plot results from switching the definitions.

former is associated with the stretching vibration of the carbonyl bond of the amide group (AM unit) while the latter corresponds to the stretching vibration of the nitrile bond (AN unit). Another band which will be of significance to this study is that occuring at 3480 cm^{-1}. Actually, this mode is one of a pair of bands observed at 3480 and 3360 cm^{-1} which are characteristic of the symmetric and assymetric stretching vibrations of the amine group of the amide unit.

Figure 12 shows the IR spectra of the 5.2 mole % AM copolymer recorded at 160°C as soon as the film had attained this temperature (denoted A) and after 1, 3 and 10 hours at 160°C (denoted B thru D respectively). These spectra were chosen as a function of degradation at 160°C rather than at 200°C because the reaction is much slower. As degradation proceeds there is a reduction in the absolute intensities of the nitrile bands at 2240 cm^{-1} and the amine bands at 3480 cm^{-1}. By measuring the absorbance of these bands as a function of time at the degradation temperature one can obtain an estimate of the fraction of AN and AM units that have reacted. Concurrently, bands at 1580 and 1610 cm^{-1}, which have been assigned to pyridone type structures, increase in intensity as the degradation reaction proceeds. New bands in the NH_2 stretching region of the spectrum are also observed but fortunately they do not overlap seriously with the 3480 cm^{-1} band.

At 200°C under reduced pressure, the spectral changes are, as expected, much faster than at 160°C. Figure 13 shows
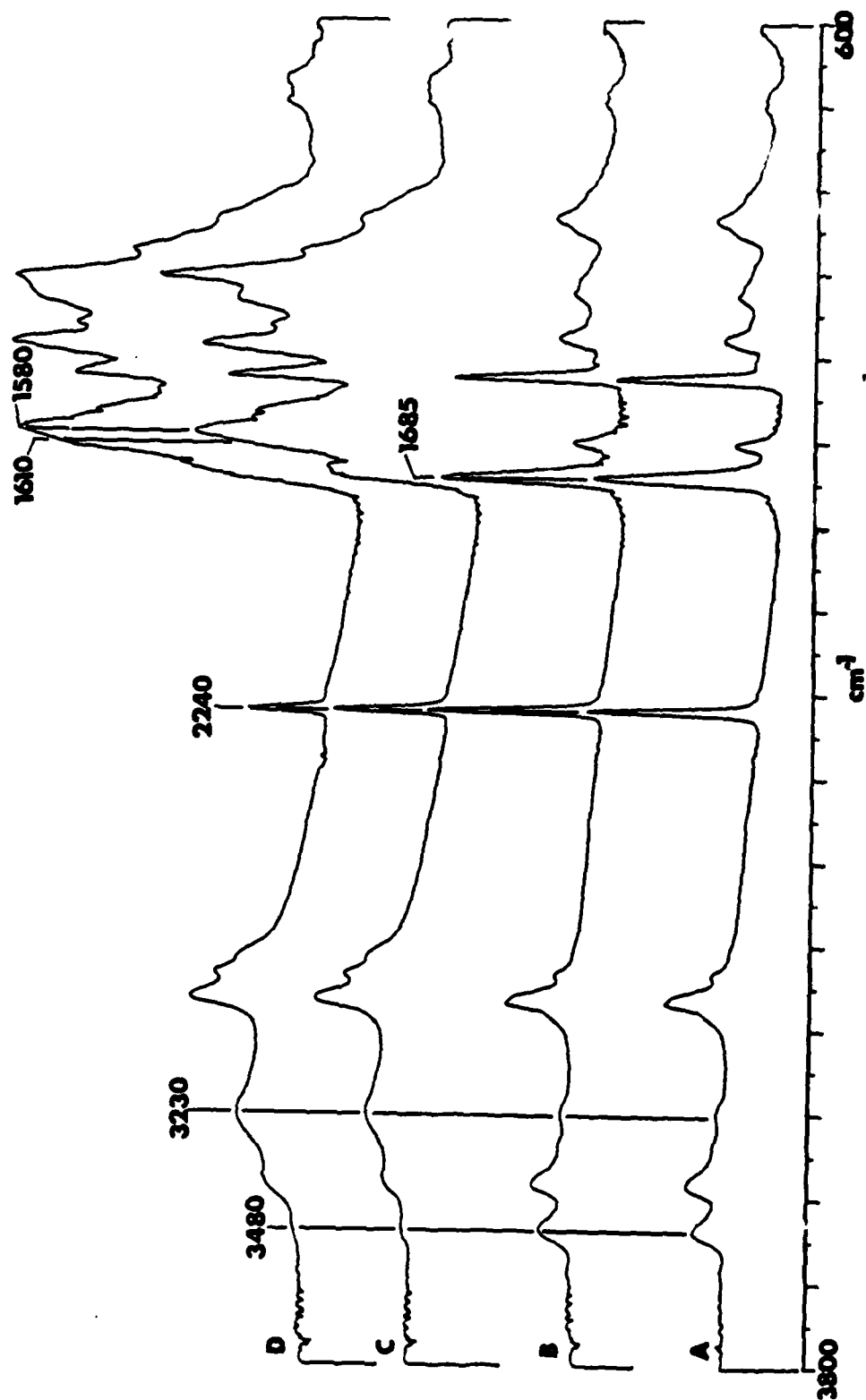
Figure 12. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/AM copolymer containing 5.2 mole% AM recorded at 160°C under reduced pressure. A) initial; B) 1 hour; C) 3 hours and D) 10 hours.

the FT-IR spectra of the 5.2 mole% AM copolymer recorded at room temperature, initially at 200°C and after 15 minutes at this temperature. Note the intense $1580/1610$ cm^{-1} bands and the sharp reduction of the nitrile absorbance at 2240 cm^{-1} in the spectrum recorded initially at 200°C. This greatly enhanced rate of degradation at 200°C is further demonstrated by the close resemblence of the spectrum recorded at 15 minutes at 200°C to that recorded at 10 hours at 160°C. Figure 14 shows a graph of the normalized nitrile absorbance plotted against degradation time at 200°C and under reduced pressure for the four copolymers containing 2.9, 5.2, 10.6 and 18.2 mole % AM, respectively. Suprisingly, the rate curves for the 5.2, 10.6 and 18.2 mole % AM copolymers are very similar and probably superimposable within experimental error. If anything, after four hours at 200°C the fraction of available nitrile groups that have reacted is greatest in the case of the 5.2 mole % AM copolymer and somewhat less for the 10.6 and 18.2 mole % AM copolymers. In contrast, the degradation rate curve for the 2.9 mole % AM copolymer is distinctly different in that the fraction of available nitriles that have reacted after four hours is considerably less than in the case of the other copolymers. The rate curves shown in Figure 14 may be considered to be made up of two components; an initial rapid reaction of the nitrile groups which occurs within 30 minutes, followed by a relatively slow reaction of further nitrile groups. After four hours at 200°C the rate of reaction of the nitrile
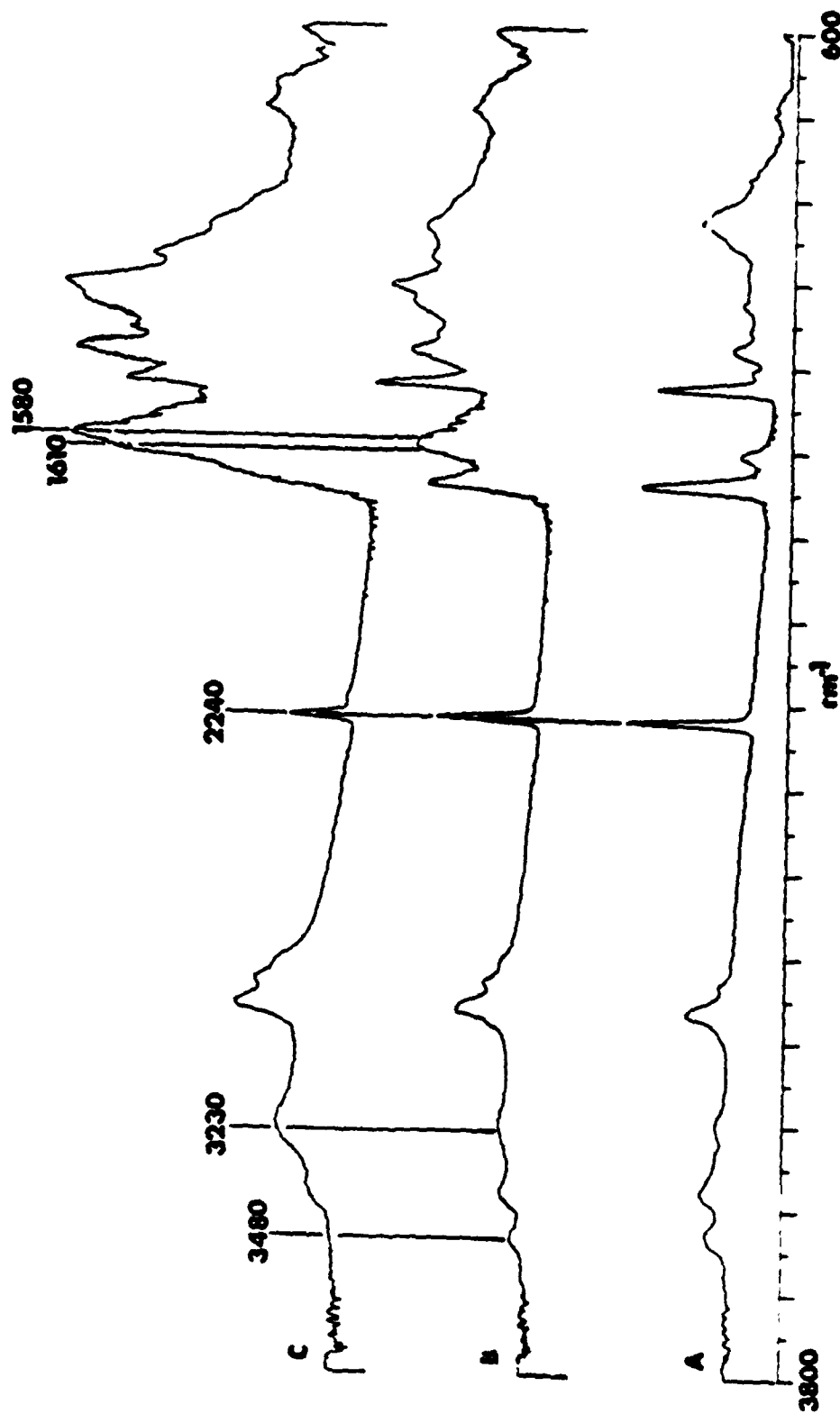
Figure 13. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/AM copolymer containing 5.2 mole% AM recorded under reduced pressure. A) room temperature; B) initial at 200°C and C) after 15 minutes at 200°C.
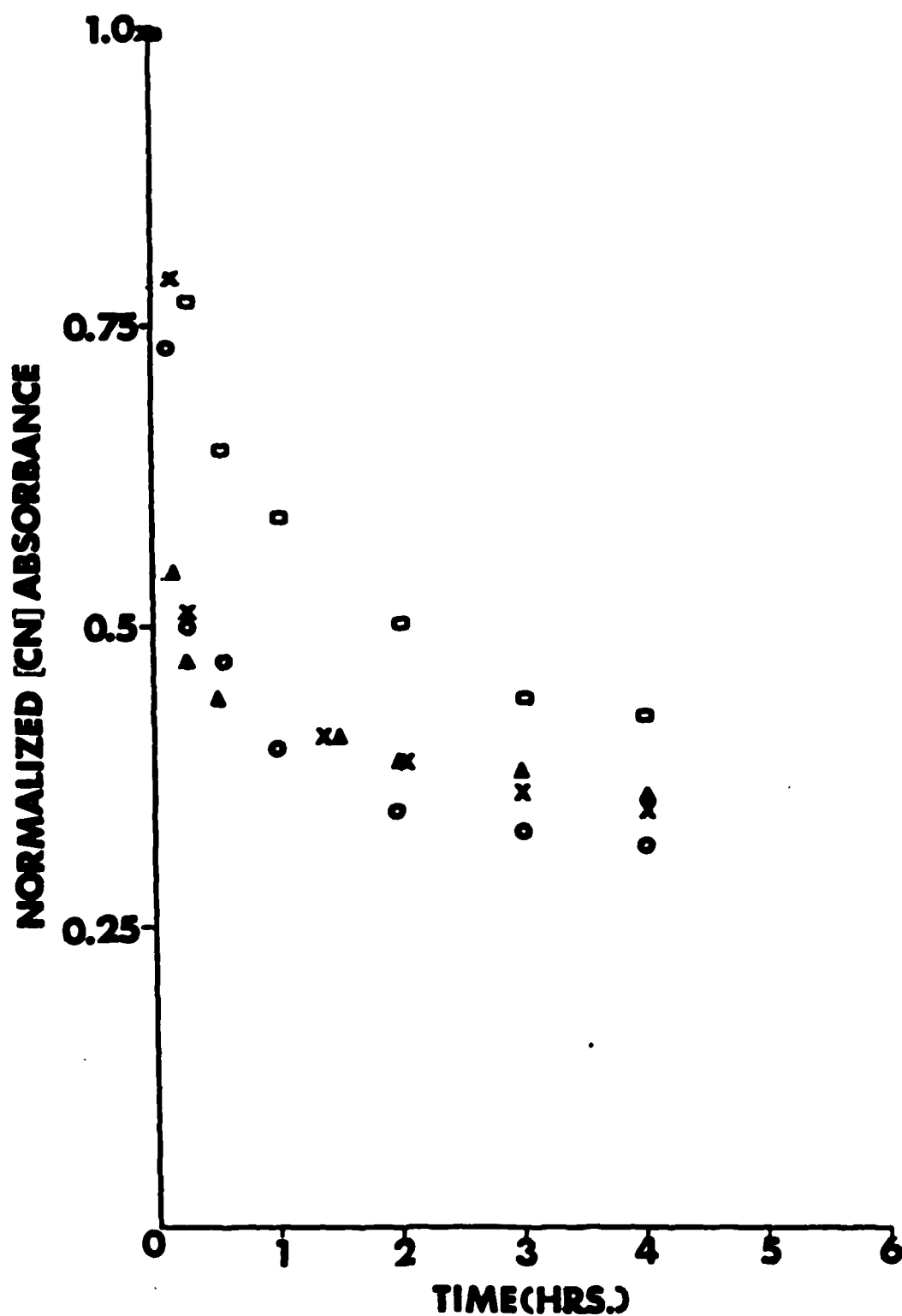
Figure 14. Normalized C≡N absorption of the AN/AM copolymers plotted as a function of time at 200°C under reduced pressure. (◻) 2.9; (⦿) 5.2; (✕) 10.6 and (▲) 18.2 mole% AM.

groups appears to have reached a plateau and any additional reaction is extremely slow.

In order to examine more closely the rapid part of the degradation rate curves, the study for the 5.2 and 18.2 mole % AM copolymers was repeated. However, in this experiment single interferograms (obtained approximately every two seconds) were stored sequentially on the disc system over a period of 30 minutes. By signal averaging blocks of interferograms and subsequently performing the Fourier transform spectral data at approximately one minute intervals was obtained. The results are displayed in Figure 15. It is readily apparent that the two rate curves are identical within experimental error and that the rapid part of the degradation reaction occurs within six minutes at $200^{\circ}C$. Significantly, this is also the point at which the large majority of the AM units have reacted, as determined by the relative absorbance of the amine band at 3480 cm^{-1}.

Figure 16 shows a plot of the normalized absorbance of the nitrile band versus degradation time at $160^{\circ}C$ under reduced pressure. In this particular case it was possible to monitor the extent of reaction of the amide group and this is depicted in the insert in Figure 16. The rate curves for both the nitrile and amide groups as a function of degradation time for the 5.2, 10.6 and 18.2 mole% AM copolymers are again remarkably similar. In other words, the fraction of available nitrile and amide groups that have reacted at any given time is the same for all three of these
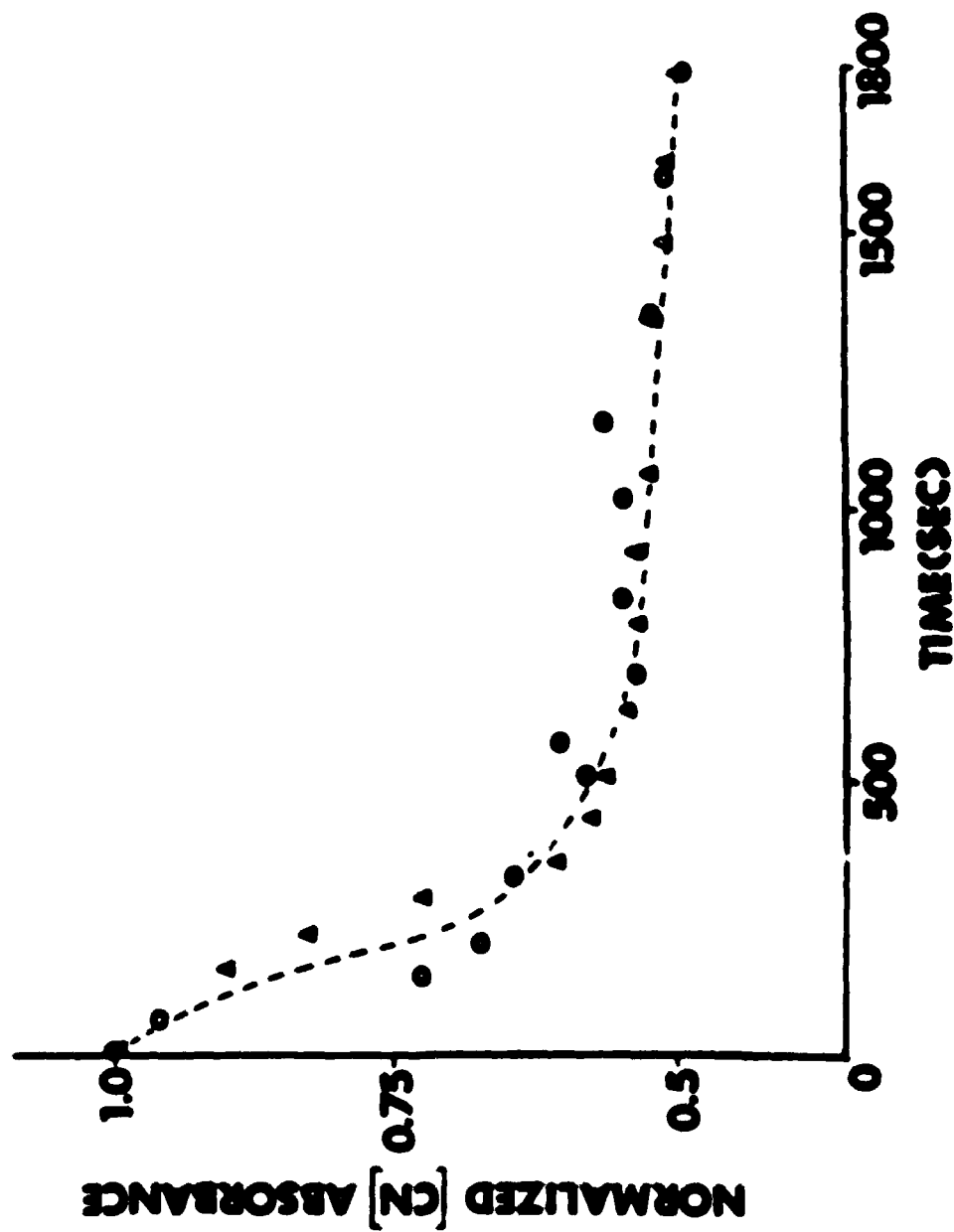
Figure 15. Normalized C≡N absorption of the AN/AM copolymers plotted as a function of time at 200°C under reduced pressure. (●) 5.2 and (▲) 18.2 mole% AM.
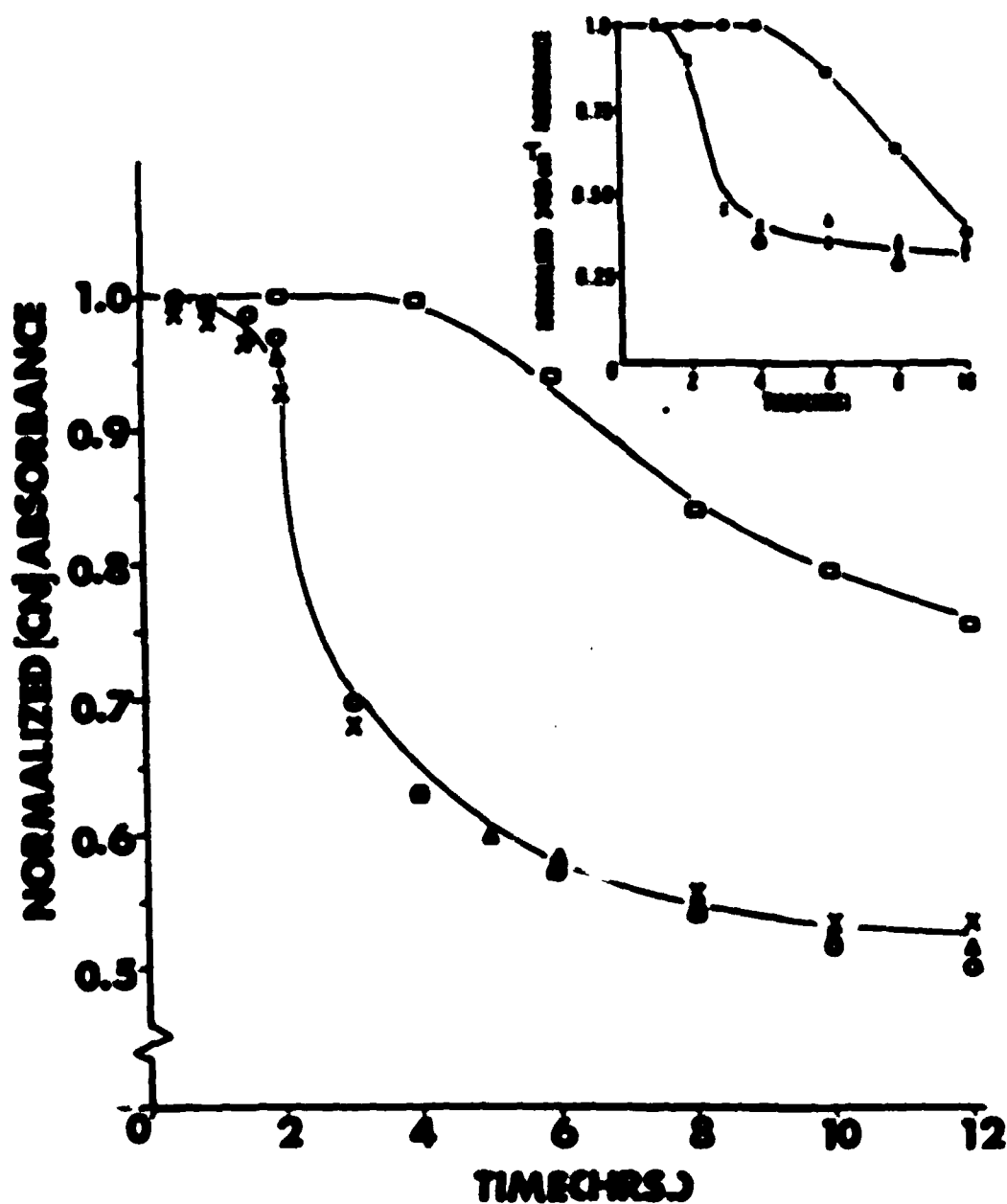
Figure 16. Normalized C≡N absorption of the AN/AM copolymers plotted as a function of time at 200°C under reduced pressure. (□) 2.9, (●) 5.2, (×) 10.6 and (▲) 18.2 mole%. Insert: Analogous plot of the normalized absorbance of the 3480 cm⁻¹ band.

copolymers. For example, at four hours approximately 60% of the available AM units and 35% of the available AN units have reacted. Accordingly, the ratios of AN:AM units reacted is roughly 3:1, 5:1 and 10:1 for the 18.2, 10.6 and 5.2 mole % AM copolymers, respectively. Furthermore, the rate curves for the 2.9 mole % AM copolymer are again distinctly different from those of the other three copolymers. It can also be seen in Figure 16 that an induction period of approximately one hour is observed at 160°C for the three copolymers containing the higher concentration of AM, whereas a four hour induction period is seen for the 2.9 mole% AM copolymer. In common with the experiments performed at 200°C, the onset and rapid reaction of the nitrile groups occurs simultaneously with the reaction of the amide groups.

One final observation concerning the extent of coloration of the degraded copolymer films is relevant. A comparison of the films of the four copolymers after four hours at 200°C under reduced pressure shows that the sample which initially contained the least amount of AM (i.e. 2.9 mole% AM) yields the most highly colored product (deep red). Conversely, the copolymer initially containing the highest concentration of AM (i.e. 18.2 mole% AM) yields the least colored product (pale yellow). The intermediate copolymer compositions gave products intermediate coloration and it is evident that the extent of coloration was inversely proportional to the concentration of AM units in the copolymers. This suggests that the extent of conjugation

(average cyclized block length) decreases as the
concentration of AM increases in the copolymers. This
subject will be dealt with later in this chapter.

3.4 Discussion

3.4.1 Thermal Degradation at 200°C Under Reduced Pressure.

There are several important questions that must be
addressed if one is to rationalize the results of these
degradation studies. The most intriguing are:

1. "Once initiation of the cyclization of the first AN
unit is achieved, why does the reaction not continue
indefinitely down the chain (or at least until it meets
another AM unit or a cyclized block propagating in the
opposite direction) ?"

2. "What prevents all or the vast majority of the AN
units from undergoing reaction by cyclization or
intermolecular crosslinking at 200°C especially in the case
of the 18.2 mole % AM copolymer ?"

3. "Why are the degradation rate curves of the three
copolymers containing 5.2, 10.6 and 18.2 mole % AM very
similar at 200°C ?" A marked similarity is also observed in
the rate curves of the same copolymers at 160°C.

4. "why are the rate curves significantly different for
the 2.9 mole % AM copolymer ?"

To attempt to answer these questions it is necessary to
consider a number of factors, the most important of which are
sequence distribution, tacticity, stereochemistry of
intramolecular ring formation and intermolecular

crosslinking.

The first factor that will be discussed is the effect of sequence distribution. Intuitively, one would expect variations in the distribution of the comonomers in the copolymer and the distribution of tactic placements to play a role in limiting the number of AN units that can react. Whether or not the additional factor of isotactic placements of AN units is necessary for intramolecular cyclization remains at this point open to debate. Henrici-Olive and Olive (15) have recently summarized the different viewpoints presented in the literature and from their own results conclude that intermolecular crosslinking is of greater importance than intramolecular reactions in the degradation of PAN polymers at temperatures of 200°C and higher. At this stage all possibilities will be considered. The type of sequence information that could be useful includes a measure of the randomness of the comonomers incorporated into the polymer chain; an estimation of the average length of AN and AM runs, and the number and weight fraction of sequences of a specific length. Fortunately, these parameters are readily calculated from a knowledge of the reactivity ratios, monomer feed ratio and the assumption that the copolymerization obeys the terminal model (13,16).

For convenience, the sequence information for four hypothetical copolymers containing 2.5, 5, 10 and 20 mole% AM was calculated and these results are summarized in Table 2. Calculations were performed using the experimentally

TABLE 2

AN/AM COPOLYMERS

COPOLYMER COMPOSITION AND SEQUENCE INFORMATION

	Composition						
Number	Monomer		Polymer		Chi	La	Lb
	AN	AM	AN	AM			
I	.97	.03	.975	.025	1.01	40.4	1.01
II	.93	.07	.95	.05	1.03	18.9	1.02
III	.85	.15	.90	.10	1.06	9.35	1.05
IV	.71	.29	.80	.20	1.10	4.50	1.12

COPOLYMER I

NA(1)=.02	WA(1)=0.0	NB(1)=.98	WB(1)=.97
(2)=.02	(2)=0.0	(2)=.01	(2)=.02
(3)=.02	(3)=0.0	(3)=0.0	(3)=0.0
(4)=.02	(4)=0.0	(4)=0.0	(4)=0.0
(5)=.02	(5)=0.0	(5)=0.0	(5)=0.0

COPOLYMER II

NA(1)=.05	WA(1)=0.0	NB(1)=.97	WB(1)=.95
(2)=.05	(2)=0.0	(2)=.02	(2)=.04
(3)=.04	(3)=0.0	(3)=0.0	(3)=0.0
(4)=.04	(4)=0.0	(4)=0.0	(4)=0.0
(5)=.04	(5)=.01	(5)=0.0	(5)=0.0

COPOLYMER III

NA(1)=.10	WA(1)=.01	NB(1)=.94	WB(1)=.90
(2)=.09	(2)=.02	(2)=.04	(2)=.09
(3)=.08	(3)=.02	(3)=0.0	(3)=0.0
(4)=.07	(4)=.03	(4)=0.0	(4)=0.0
(5)=.06	(5)=.03	(5)=0.0	(5)=0.0

COPOLYMER IV

NA(1)=.22	WA(1)=.04	NB(1)=.88	WB(1)=.78
(2)=.17	(2)=.07	(2)=.10	(2)=.17
(3)=.13	(3)=.08	(3)=.01	(3)=.03
(4)=.10	(4)=.09	(4)=0.0	(4)=0.0
(5)=.08	(5)=.09	(5)=0.0	(5)=0.0

determined reactivity ratios of 1.5 and 0.3 for AN and AM,
respectively. A simple computational method for calculating
the parameters shown in Table 2, has recently been described
(16) but a brief comment on the definitions is in order. The
parameter Chi, which may have values in the range from 0 to
2, is a measure of the deviation from random placement of the
monomer units incorporated into the copolymer chain. For a
completely random placement, Chi has a value of unity while
values approaching 0 or 2 represent a tendency towards block
or alternating copolymers, respectively. It is apparent from
the values of Chi listed in Table 2 that all of the
copolymers contain essentially random placements of the AN
and AM units.

The parameters La and Lb are defined as the number
average length of sequences of AN and AM units in the
copolymers respectively. The values of La for the four
copolymers are approximately 40, 19, 9 and 5 respectively for
the 2.5, 5, 10 and 20 mole % AM copolymers. Similarly, the
Lb values give the number average sequence length of AM runs
which range from 1.01 to 1.12 and indicate that the majority
of the AM units are isolated.

The number fraction of AN and AM sequences of length n=1
to 5 are given by the NA(n) and NB(n) values shown in Table
2. For example, a value for NA(3) of 0.13 (see copolymer IV
in Table 2) means that 13% of the sequences (based on the
total number of sequences) in the copolymer chain exist as
AM-AN-AN-AN-AM runs. The weight fraction of AN and AM

sequences of length n=1 to 5 are given by WA(n) and WB(n),
respectively. In the case of WA(3)=0.08, 8% of the sequences
(based on the total weight) exist as AM-AN-AN-AN-AM runs.

The information contained in Table 2 can be used in
conjunction with the experimental observations to test a
number of different models of the degradation of the AN/AM
copolymers. In essence, specific assumptions will be made
for each proposed model and the sequence information used to
calculate the fraction of the total number of AN units that
can react. These results will then be compared to those
observed experimentally.

The first model (MODEL I) is trivial but serves to
illustrate the type of calculations performed. This model
contains the following assumptions:

(i) Each AM unit which is adjacent to an AN unit
initiates cyclization of the AN unit regardless of the
stereochemical configuration (i.e. whether or not the
nitrile group is isotactic or syndiotactic to the adjacent
amide group).

(ii) No intermolecular crosslinking reactions occur.

(iii) Propagation of the cyclization reaction to
adjacent AN units down the chain also occurs without regard
to stereochemistry.

(iv) The AM units can initiate in both directions down
the chain (4).

Consider a polymer chain containing 1000 units composed

of 800 AN and 200 AM units (i.e. a 80/20 mole % AN/AM
copolymer). The Chi value of 1.10 (see Table 2) immediately
indicates that the distribution of AN and AM units in the
copolymer is essentially random. The weight fraction, WB(1),
of AN-AM-AN sequences equals 0.78. Therefore, the number of
AM units in such sequences is 0.78 x 200 = 156. Initially,
each AM unit initiates the cyclization of both adjacent AN
units. Hence 312 AN units are involved in initial
cyclization.

Similarily, the weight fraction, WB(2), of AN-AM-AM-AN
sequences is 0.17. Thus 0.17 x 200 = 34 AM units are
contained in such sequences. Again in this case, each AM
unit can initiate cyclization of adjacent AN units on either
side of the sequence and initially 34 AN units are involved.
(A complication might arise where the two adjacent AM units
cyclize to form a cyclic imide with elimination of ammonia.
However, no evidence for such a reaction was seen during the
FT-IR studies at temperatures of 200°C and below).

For the AN-(AM)3-AN sequences the weight fraction is
0.03 and 6 AM units are involved in such sequences. Only two
thirds of the AM units can initiate cyclization of adjacent
AN units and consequently 4 AN units are initially cyclized.
At this stage, 196 of the 200 AM units (98%) have been
considered. The remaining few AM units are contained in
sequences of greater than 3 and for simplicity will be
ignored.

The total number of AN units involved in this initial

stage of cyclization is 312 + 34 +4 = 350 or 44% of the available AN units. Note that the La value for this polymer is 4.5 and having reacted 44% of the available AN units on the first cyclization, it is now only necessary to further react, on average, less than two adjacent AN units to cyclize the vast majority of the available AN units.

A similar exercise for the 10, 5 and 2.5 mole % AM copolymers leads to the following conclusions: For the 10 mole % copolymer approximately 99% of the AM units initiate cyclization of an adjacent AN unit which represents 22% of the available AN units. The corresponding figures for the 5 and 2.5 mole % AM copolymers are 99 and 10% and 100 and 5%, respectively.

In this simple case, given the La values presented in Table 2, there is no reason why the large majority of the AN units should not react. Certainly, it is difficult to rationalize the experimental results obtained for the 20 and 10 mole % AM copolymers based on this model, where a 65% reaction of the AN units is observed after four hours at $200^{o}C$ under reduced pressure.

The assumptions in a second model (MODEL II) are similar to those of MODEL I with the following exceptions.

(i) Following the initial cyclization of the AM and AN units, propagation of the cyclization reaction to the next adjacent AN unit requires an isotactic placement.

(ii) the probability of an isotactic or syndiotactic AN

placement is equal and entirely random.

The calculation of the number of AN units initially cyclized by the AM units is identical to Model I. However, further propagation is now limited by the stereochemistry of the adjacent AN unit. One half of these AN units will be isotactic to the initially formed ring.

It was previously shown that 350 AN units were initially cyclized by the AM units in the hypothetical 1000 unit chain of the 20 mole % AM copolymer. Given that the La value is 4.5, one now has average sequences that may be depicted as follows:
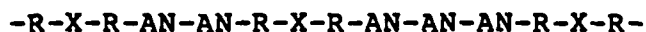
-R-X-R-AN-AN-R-X-R-AN-AN-AN-R-X-R-

where X denotes the reacted AM unit; R (ring) denotes a cyclized AN unit and AN denotes an unreacted AN unit which may be either isotactic or syndiotactic to the R unit.

However, at any given point in the sequence of AN runs only half of the AN units will be isotactic to the preceeding unit. Therefore, the maximum number of AN units that can cyclize is 350 + 175 + 0.5(88) = 569 or 71% of the available AN units.

Using a similar approach, with due regard for the calculated La values, one can readily determine that the maximum extents of reaction of the AN units for the 10, 5 and 2.5 mole % AM copolymers are 42, 21 and 10%, respectively.

It is immediately apparent that the calculations based on this model do not correlate with the experimental observations.

The assumptions in a third model (MODEL III) are similar to those of MODEL II with the following exception.

(i) The initial cyclization of AM and the adjacent AN unit requires that the AN unit is isotactic to the AM unit.

For the hypothetical chain of 1000 units it was previously shown for the 20 mole % AM copolymer that 156 AM units are involved in AN-AM-AN sequences. If one now consider the stereochemistry of the AN units relative to the adjacent AM unit there are four possible sequences of equal probability, i.e.:

(AN)i-AM-(AN)i

(AN)i-AM-(AN)s   i=isotactic

(AN)s-AM-(AN)i   s=syndiotactic

(AN)s-AM-(AN)s

The bottom sequence cannot initiate cyclization under the assumptions above and consequently only 0.50 x 156 = 78 AN units are cyclized initially.

In a similar fashion, for the AN-AM-AM-AN sequences which contain 34 of the AM units there are again four possible sequences,of equal probability, to consider:

(AN)i-(AM)-(AM)-(AN)i

(AN)i-(AM)-(AM)-(AN)s

(AN)s-(AM)-(AM)-(AN)i

(AN)s-(AM)-(AM)-(AN)s

Now the number of AM units adjacent to an isotactic AN unit is again one half of the total. Thus 0.5 x 34 = 17 of

the AN units are initially cyclized.

Continuing this exercise for the remaining higher sequences leads to the conclusion that a total of 97 AN units are initially cyclized. Now if the restrictions that further intramolecular cyclization can only occur for isotactic placements adjacent to the propagating ring structure and that the average length of AN runs is given by La (as in Model II) are imposed, then a maximum extent of reaction of AN units of 23% is caculated.

Identical calculations for the 10, 5 and 2.5 mole % AM copolymers yield maximum extents of reaction of the AN units of 11, 5 and 2.5%, respectively. Once more, the calculated results do not resemble those observed experimentally. Nevertheless, an important conclusion arises from these initial calculations. If tacticity does not play a role, there is no apparent reason why the vast majority of AN units should not cyclize. However, models based on simple stereochemical requirements alone are not capable of predicting the observed degree of reaction. An additional factor, intermolecular crosslinking, has so far been neglected. Incorporation of this factor leads to a model that is both intuitively satisfying and in remarkable agreement with the experimental results.

The final model (MODEL 4) contains the following assumptions:

(i) Initial intramolecular cyclization of the AM unit to

an adjacent AN unit requires an isotactic placement. This
can occur in either or both chain directions.

(ii) Subsequent intramolecular cyclization of AN units
adjacent to the propagating ring structure also requires an
isotactic placement.

(iii) Intermolecular crosslinking, of the type depicted
schematically in Figure 17, will be presumed to occur. This
is considered to be a non-stereospecific reaction. Either
unreacted AM units, (e.g. those AM units in sequences such as
-(AN)s-AM-(AN)s or -(AN)s-AM-AM-(AN)i- etc.), or cyclized AN
units in blocks that are adjacent to syndiotactic AN units
are considered as potential crosslinking sites to AN units on
neighbouring chains.

(iv) As shown in section 1.1, the polymer chains are
presumed to pack as rods in a pseudo-hexagonal fashion.

(v) Once the intermolecular crosslinking reaction has
occured, the crosslinked site may initiate further
intramolecular cyclization in one direction down the chain.
This also requires that the AN unit adjacent to the
crosslinked site is in an isotactic configuration.

In contrast to the previous models, and after numerous
fruitless and frustrating attempts, it was concluded, that in
this case, it is practically impossible to calculate, by
simple arguments, the extents of reaction of the AN units
upon degradation, given the assumptions mentioned above and
using the sequence information generated thus far.
Accordingly, a 'brute force' computer method was applied to
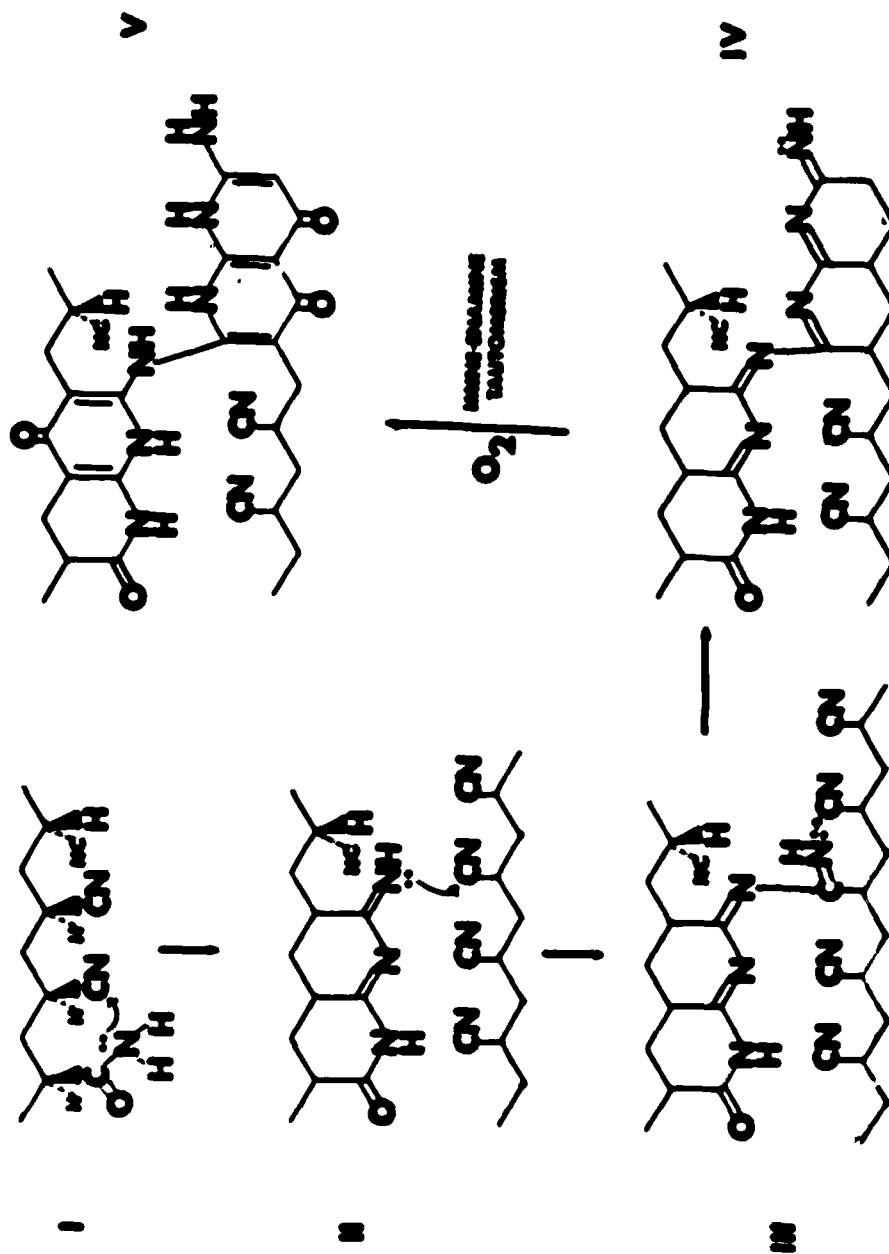
Figure 17. "Step-ladder" degradation scheme showing intramolecular cyclization and intermolecular crosslinking.

attempt to solve this problem. The results obtained from this computer application are in close agreement with the experimental results. A full description of the computer program is given in the Appendix but for expository convenience, a brief description is given below.

The computer generates a primary chain composed of random placements of AN, isotactic and syndiotactic AN units (justified by the Chi values noted in Table 2). The relative number of AN units is based on the copolymer composition and the probabilities of isotactic and syndiotactic AN units are taken as 0.48 and 0.52, respectively (17).

The computer now performs the initial intramolecular cyclization (steps (i) and (ii)) upon the primary chain and six secondary chains (which represent the nearest neighbors in hexagonal packing). Intermolecular crosslinking from these secondary chains to the primary chain is then considered (steps (iii) and (iv)) followed by subsequent intramolecular cyclization of the primary chain (step (v)). At this stage, effects of tertiary chains operating on the secondary chains which, in turn, operate on the primary chain, are considered in an analogous fashion. Finally, the fraction of AN units reacted in the primary chain is calculated.

The results are summarized in Table 3. Ten computations were performed for each copolymer composition. The average calculated extents of reaction of the AN units were determined to be 46, 55, 63 and 66% for the 2.9, 5.2, 10.6

and 18.2 mole % AM copolymers, respectively. These
calculated results compare very favorably with the
experimental results shown in Figure 14. After four hours at
200 C and under reduced pressure, the rate curves for the
four copolymers have essentially reached a plateau and the
extent of reaction of the AN units is 56% for the 2.9 mole %
AM copolymer and between 64 and 67% for the other three
copolymers.

It is now pertinent to summarize the results obtained
from this study of the effect of sequence distribution on the
degradation of the AN/AM copolymers. The calculated extents
of reaction from each model are shown Table 4. The
implications of the calculations based on Model IV are as
follows. Initiation by AM units of intramolecular
cyclization of adjacent isotactic AN units at 200°C is a
relatively rapid reaction, as is the propagation of
subsequent isotactic AN units down the chain. Intermolecular
crosslinking is presumably followed by rapid intramolecular
cyclization of isotactic AN units along the chain. Factors
that appear to limit the extent of reaction of the AN units
are the stereochemical distribution of AN and AM units in the
copolymer chain and spacial considerations. It is fully
realized that the model is somewhat simplistic.
Nevertheless, the assumptions are reasonable and the unusual
experimental results may be explained on the basis of this
model. Incidentally, the "step ladder" model of degraded PAN
attributed to Mueller et al. (18) proposes that short

TABLE 3

COMPUTER CALCULATIONS OF THE EXTENT OF REACTION OF AN UNITS BASED ON MODEL IV

COPOLYMER COMPOSITION (MOLE %AM)	%AN REACTED INITIAL INTRAMOLECULAR CYCLIZATION	FINAL EXTENT OF REACTION*
2.9	5.3 , 5.7	47.5 , 44.5
	4.6 , 4.6	46.1 , 44.9
	3.7 , 5.3	44.5 , 47.5
	4.8 , 3.4	46.3 , 43.4
	3.7 , 5.7	45.9 , 44.1
	Ave: 5 + 2	Ave: 46 + 2
5.2	10.0 , 7.9	52.1 , 57.5
	9.3 , 9.6	52.8 , 55.8
	10.7 , 5.1	51.4 , 56.1
	8.6 , 9.1	57.7 , 54.0
	5.4 , 5.1	54.9 , 52.8
	Ave: 8 + 3	Ave: 55 + 3
10.6	19.3 , 16.1	63.1 , 64.1
	14.9 , 16.8	61.4 , 63.1
	16.0 , 14.6	63.9 , 62.1
	14.6 , 15.6	62.1 , 62.1
	18.5 , 14.5	62.6 , 60.2
	Ave: 16 + 3	Ave: 63 + 3
18.2	23.8 , 25.1	65.7 , 67.3
	19.1 , 25.4	66.8 , 67.3
	21.6 , 20.8	68.1 , 67.3
	19.5 , 25.9	64.6 , 64.9
	26.5 , 28.1	67.6 , 65.1
	Ave: 24 + 5	Ave: 66 + 2

* After initial intramolecular cyclization followed by intermolecular crosslinking and subsequent intramolecular cyclization.

TABLE 4

CALCULATED EXTENTS OF REACTION FOR DEGRADATION MODELS

Model	Composition (Mole% AN/AM)			
	·80/20	90/10	95/5	97.5/2.5
	%AN Reacted			
I	100	100	100	100
II	46	21	11	4
III	34	16	7.5	3.6
IV*	66	63	55	46
Experimental	65	65	65	56

* Based on computer program

sequences of intramolecular reactions (1 to 3 steps) are followed by a jump to an AN unit of another chain and is thus similar to the mechanism proposed here. Another important observation that serves to support the model is that the FT-IR spectra indicate that those AM units that do react do so in the first 10 minutes of degradation. Finally, it is important to reiterate that the degraded films became increasingly more colored as a function of decreasing AM composition at the same degradation time. This implies that the average sequence length of conjugated cyclized runs is greater in the case of the 2.9 mole % AM copolymer and becomes progressively shorter as the concentration of AM units increases in the copolymers.

Finally it must be emphasized, that while the first 3 degradation models may confidently be discarded, one should be cautious to accept model 4 as the only alternative. A number of models are possible but the one presented in this thesis does (perhaps fortuitously) yield results in close agreement with those observed experimentally.

3.4.2 Thermal Degradation at 160°C Under Reduced Pressure.

At the onset it should be mentioned that the degradation studies performed at 160°C are considered somewhat peripheral to the major thrust of this thesis. There is no obvious rationale for performing the degradation at this temperature in the industrial manufacture of carbon fibers. There is however a good reason to study the degradation of AN/AM copolymers at 160°C. The rate of degradation is much slower at 160 than at 200°C and thus it is possible to more readily monitor the changes occurring, especially in the initial stages.

PAN homopolymer does not degrade to any measurable extent at 160°C under reduced pressure for extended periods of time up to at least 24 hours (9). In contrast, this author has previously shown that both AN/MAA and AN/AM copolymers containing approximately four weight percent of the comonomers, degrade at reasonable rates at 160°C (9).

The results obtained for the degradation of the AN/AM copolymers at 160°C are markedly different from those at 200°C. Figure 16 shows that an induction period of approximately one hour exists in the case of the 18.2, 10.6 and 5.2 mole % AM copolymers whereas for the 2.9 mole % AM copolymer it is about four hours. The mechanism suggested for the degradation of the AN/AM copolymers is rather complex (9) and the induction period could be explained on the basis of a series of first or higher order reactions (19). In any event, it is significant that one can readily observe from

the FT-IR spectra of the copolymer films at 160°C that during this induction period there is no measurable reduction in the absorbance of the band at 3460 cm^{-1}. This band is associated with unreacted AM units and suggests that initiation by AM units has not occurred to any significant extent. However, immediately after the induction period there is a marked reduction in the absorbance of the infrared bands at 3460 and 2240 cm^{-1}, as depicted in Figure 12. Concurrently, the appearance and increasing intensity of the bands at about $1580/1610$ cm^{-1} (assigned to the pyridone type degradation product) occurs. These observations are consistent with the initiation of the degradation by the AM unit. It is apparent from the curves shown in Figure 16 that after 12 hours at 160°C the rate of reaction of AN units has slowed down but has not reached a plateau. Whether or not, given sufficient time, the maximum extent of reaction of the AN units would approach that observed at 200°C is not known for certain at this time. However, for the sake of argument, if one assumes that this is correct then the "step-ladder" model suggested for the degradation at 200°C would also appear applicable at 160°C, except that the rate of reaction has been severely reduced.

3.4.3 Stereochemistry of Intramolecular Cyclization and Intermolecular Crosslinking.

Throughout this chapter the problems posed by tacticity have conveniently been avoided by assuming only isotactic units are capable of intramolecular cyclization. This may seem a rather bold assumption given that the randomly kinked

PAN chains along with the increased chain mobility at high temperatures may provide favorable conditions for any pair of monomer units to undergo cyclization regardless of tacticity. However this assumption is not without experimental justification. Several Russian authors (20,21) report that PAN synthesized in a urea canal complex is rich in isotactic sequences. These polymers were shown to exhibit enhanced rates of color formation. Unfortunately, these authors performed their degradation studies in solution where a myriad of conformations are present. Therefore it is difficult to justify an extension of their work to the thermal degradation of solid samples. In addition, these authors have suggested that intramolecular cyclization will not occur with syndiotactic AN units because of a high degree of ring strain. While these and other results indicate a greater reactivity with increasing isotactic content, such conclusions have not been universally accepted. As pointed out by Chen et al. (22), ring strain does not rule out the formation of such molecules as cyclobutane and cyclopropane and, furthermore, molecular models show that long sequences of syndiotactic AN units can be cyclized without apparent strain on the bond angles. Chen et al. also suggest a possible mechanism to explain lack of stereospecificity based on rapid imine-enamine tautomerism and the "scrambling" of propagating chiral centers. Such a reaction would eliminate the need for isotactic placements of AN units as shown below:

In spite of these latter arguments, a reconsideration of the stereochemistry of ring formation is in order. Figures 18 and 19 show the four possible stereochemical conformations of triad sequences beginning with an AM unit and the products of an initial cyclization reaction. In the case of an isotactic AN unit adjacent to the AM unit (Figure 18), a six-membered ring would be formed with both polymer chain substituents equatorial in the chair form. Conversely, for an AN unit syndiotactic to the AM unit (Figure 19), a six-membered ring would be formed with one polymer chain substituent equatorial and the other axial, again in the chair form. The chair form is energetically preferred over the boat or twist-boat conformations by about 6.5 and 5 Kcal/mole respectively (23). In addition, the equatorial/equatorial (e,e-) conformation is considered to be more stable than the equatorial/axial (e,a-) conformation, due to steric crowding in the latter structure. For example, e,e-diethylcyclohexane is favored by 1.75 Kcal/mole over the (e,a-) conformer (23) and it is reasonable to assume that if the substituents are polymeric the (e,e-) conformation would be even more favored. Therefore, it is feasible that intramolecular cyclization of the AM and an isotactic AN would be distinctly favored over that of a corresponding

59
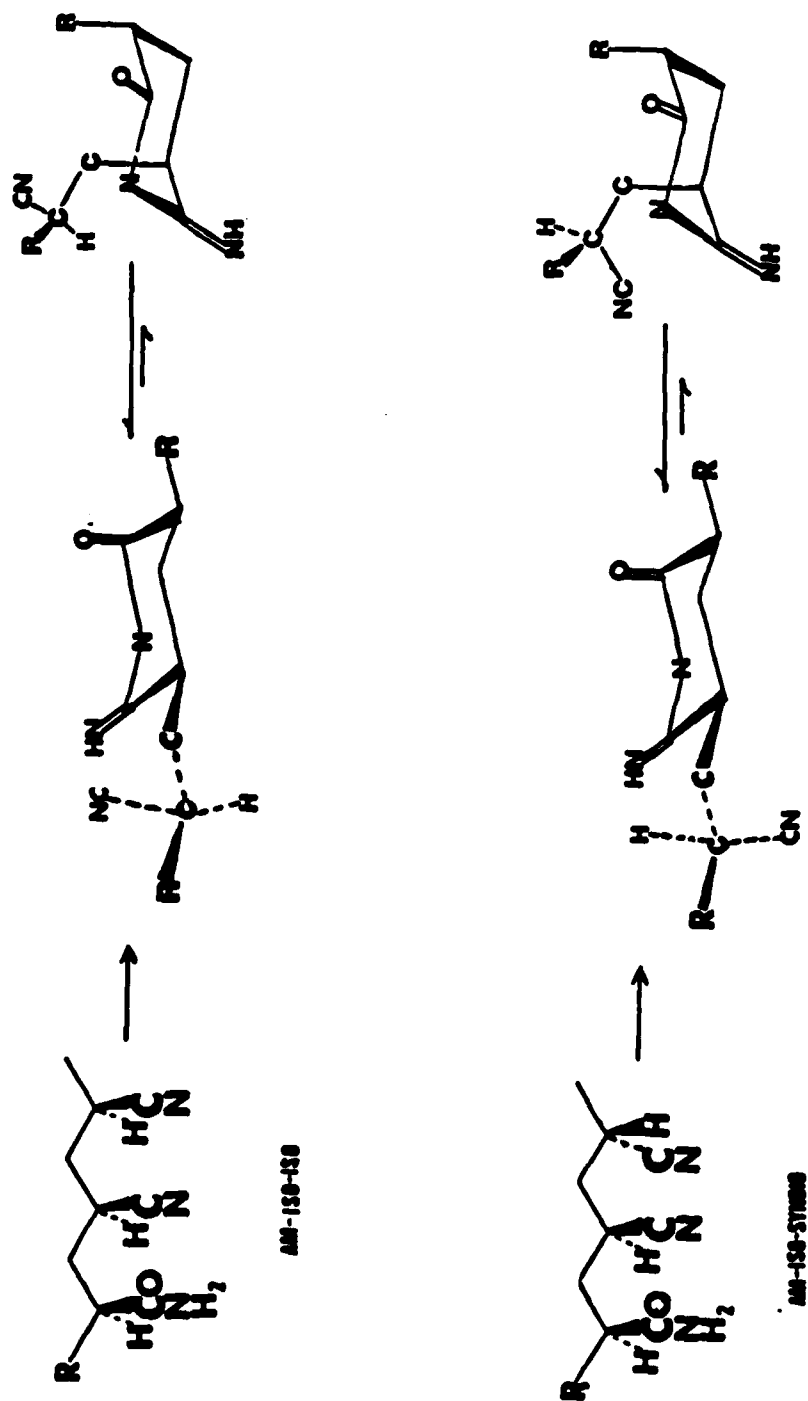
Figure 18. Possible stereochemical conformers resulting from AM initiated intramolecular cyclization of isotactic AN units.
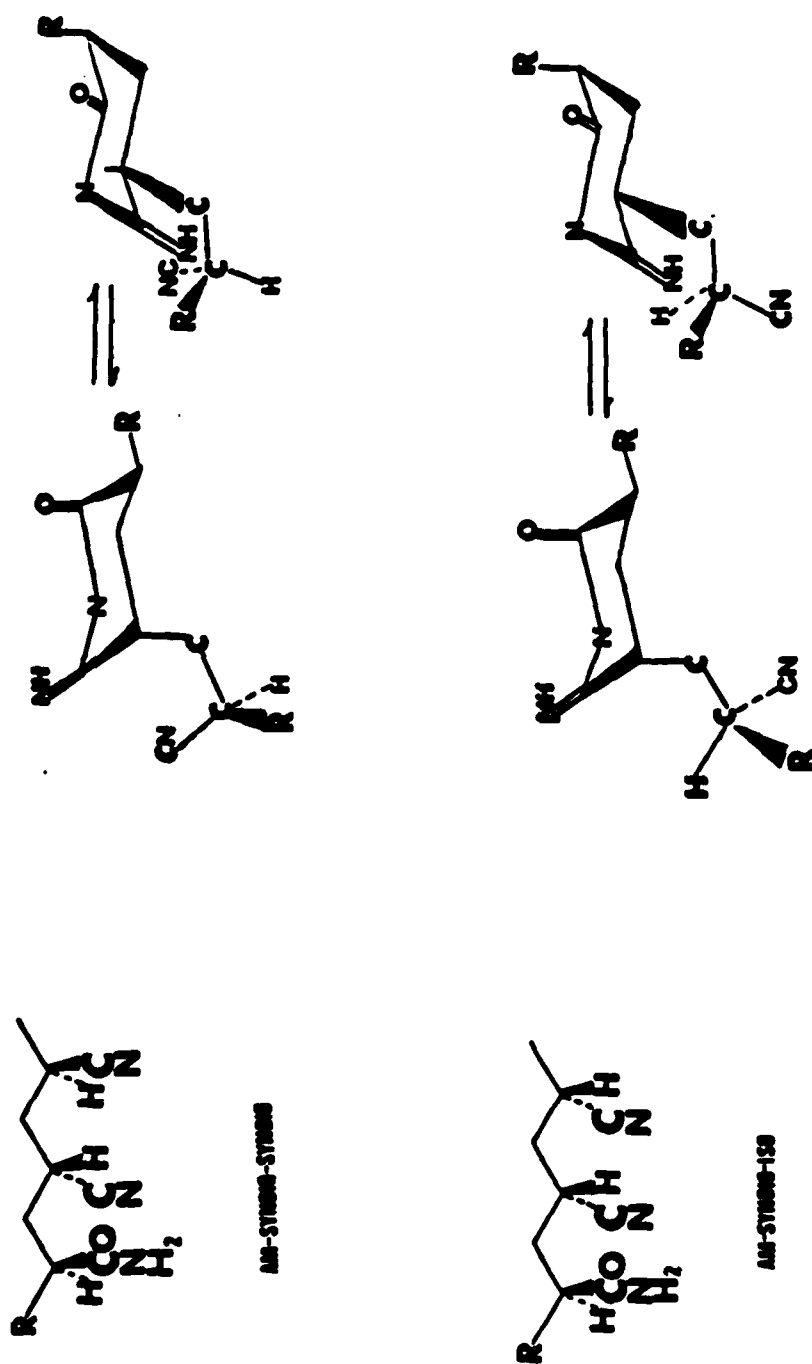
Figure 19. Possible stereochemical conformers resulting from the AM initiated intramolecular cyclization of syndiotactic AN units.

syndiotactic AN unit. Similar arguments may also be made for the subsequent intramolecular cyclization of AN units down the chain. However it is important to remember that the degradation is carried out at relatively high temperatures and that the energy barrier of forming the (e,a-) conformers may be overcome. It is therefore reasonable to assume that intermolecular crosslinking may be easier than intramolecular cyclization of a syndiotactic AN unit.

The above arguments do not take into account possible complications arising from imine-enamine tautomerism, as depicted in the mechanism for the degradation of AN/AM copolymers (Figure 6), or the "scrambling" of chiral centers suggested by Chen et al.(22). Unfortunately, the information concerning the relative rates of intramolecular cyclization; intermolecular crosslinking and imine-enamine tautomerism is lacking and any conclusions that may be drawn from the above arguments are only speculation.

As previously mentioned, upon thermal degradation PAN films or fibers become insoluble. Although insolubility does not necessarily require that the material has crosslinked to a network, (many linear polymers, especially those containing condensed rings, are insoluble in all known organic solvents), it is generally accepted that crosslinking of PAN polymers does occur upon degradation (15). In the case of the thermal degradation of the AN/AM copolymers, at temperatures in the range of 160 to 200 $^{\circ}$C and under reduced

pressure, the mechanism depicted in Figure 17 is entirely reasonable. To reiterate, intramolecular cyclization is suggested to occur sequentially along the chain if the AN units are in isotactic placements (denoted I in Figure 17). Upon meeting a syndiotactic AN unit, intramolecular cyclization is considered unfavorable relative to intermolecular crosslinking (II). Reaction of the exocyclic imine group with a nitrile group of a nearby chain then occurs to form another imine (III), which can now initiate further intramolecular cyclization with isotactic AN units of the new chain (IV). Imine - enamine tautomerism and subsequent oxidation leads to the pyridone type structures (V) as previously shown in Figure 2. Although the mechanism depicted in Figure 17 is favored, it should be mentioned that free radical mechanisms have also been suggested (and are entirely reasonable) for the degradation of PAN copolymers at temperatures of 200°C and above (15). Finally, if the model of the degradation of PAN copolymers presented in this thesis is correct, it is immediately apparent that the degree of crosslinking and the length of conjugated blocks of rings are both inversely proportional to the concentration of AM units present in the copolymer.

The color changes observed during degradation of the AN/AM copolymer films may support this theory. Recalling from Section 3.3.1, the AM copolymer containing the least AM yielded the most highly colored degradation product while the the high AM copolymer gave the least colored product. This

type of coloration is to be expected if the above arguments are correct. In the case of the high AM copolymer the average number of AN units in a sequence between AM units is about four. Therefore the maximum number of a cyclized block can only be 4 conjugated rings long. However the restrictions imposed by tacticity and the fact that cyclization is proceeding in both directions could limit the block size of conjugated rings to about 2 followed by intermolecular crosslinking. This small amount of conjugation would result in the least amount of coloration. On the other hand, for the low AM copolymer the average number of AN units between AM units is approximately 20 and by the same arguments used above the average block length of conjugated rings formed may be as high as 5 followed by intermolecular crosslinking. This increased conjugation would account for the high coloration.

3.5 Thermal Degradation at 200°C in Air.

3.5.1 Results and Discussion

Up to this point the thermal degradation studies discussed have been performed under a reduced pressure. While such conditions minimize competitive oxidative side reactions and yield relativily uncomplicated degradation spectra they do not simulate those used in the production of C/G fibers. From Chapter 1, it was mentioned that the initial step in fiber production is carried out in air and that the presence of oxygen is necessary for the production of high strength fibers. Also in that chapter it was

suggested that the oxidative side reactions could be minimized by increasing the rate of cyclization with initiating comonomers such as AM. However, as will be shown later, the reaction of oxygen with the AN/AM copolymers during degradation in air appears to occur at a much faster rate than the initiated cyclization of the nitrile groups. While these results may at first seem discouraging in that the cyclization reactions cannot be maximized in air it will be shown later that the products of the oxidation reactions may still lead to the formation of fused ring structures necessary for high strength carbon fibers.

Figures 20 and 21 show the FT-IR absorbance spectra of the AN/AM copolymer containing 5.2 mole% AM at room temperature, initially at 200°C and after 15 minutes, 30 minutes, 1 hour and 4 hours at this temperature. Note that these spectra are markedly different from those recorded for the same copolymer degraded under reduced pressure at the same temperature (Figure 13). For example, bands at 1580 and 1610 cm^{-1} which are indicative of cyclization are very intense in the spectrum of the AN/AM copolymer recorded initially at 200°C under reduced pressure. In the spectrum of the same copolymer degraded in air these bands cannot be detected initially at 200°C but do appear after approximately 15 minutes and increase steadily with degradation time. Furthermore the band at 3480 cm^{-1}, which is associated with the N-H stretching of the AM units, does not undergo the same rapid reduction in intensity as seen in degradation under

Figure 20. FT-IR absorbance spectra in the range 600-3800 cm-1 of the AN/AM copolymer containing 5.2 mole% AM recorded in air A) room temperature; B) initial at 200°C and C) after 15 minutes at 200°C.

Figure 21. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/AM copolymer containing 5.2 mole% AM recorded at 200°C in air. D) 30 minutes; E) 1 hour and F) 4 hours.

reduced pressure. This would indicate that either the AM

units are not initiating as fast or are involved in other

reactions. In fact the slow appearance of the 1580/1610 cm^{-1}

bands further verifies the initial lag in cyclization.

Contrary to this however is a reduction of the intensity of

the nitrile absorption at 2240 cm^{-1} at a rate comparable to

that seen under reduced pressure. In addition to these

spectral changes three additional bands are discernable at

1660, 960 and 810 cm^{-1}. These bands are unique to the

spectra of the air degraded AN/AM copolymers and may

therefore be attributed to oxidative effects. These bands

can best be seen in the spectra of the AN/AM copolymer

containing 2.9 mole% AM degraded in air. Figures 22 and 23

show the FT-IR absorbance spectra of this copolymer at room

temperature, initially at 200°C, and after 15 minutes, 1, 2

and 4 hours at this temperature. Once again note the lack of

bands at 1580 and 1610 cm^{-1} initially at 200°C. After 15

minutes, cyclization appears to be occuring but also at this

time the band at 810 cm^{-1} appears. Finally after 1, 2 and 4

hours the bands at 1660 and 960 cm^{-1} can easily be detected.

In order to compare the rates of the nitrile reduction of the

four AN/AM copolymers, a plot of the normalized nitrile

absorbance versus time is shown in Figure 24. From this plot

it would first appear that the rate of cyclization is very

rapid for all the copolymers with approximatly 90% of the

available nitriles reacted after 6 hours regardless of AM
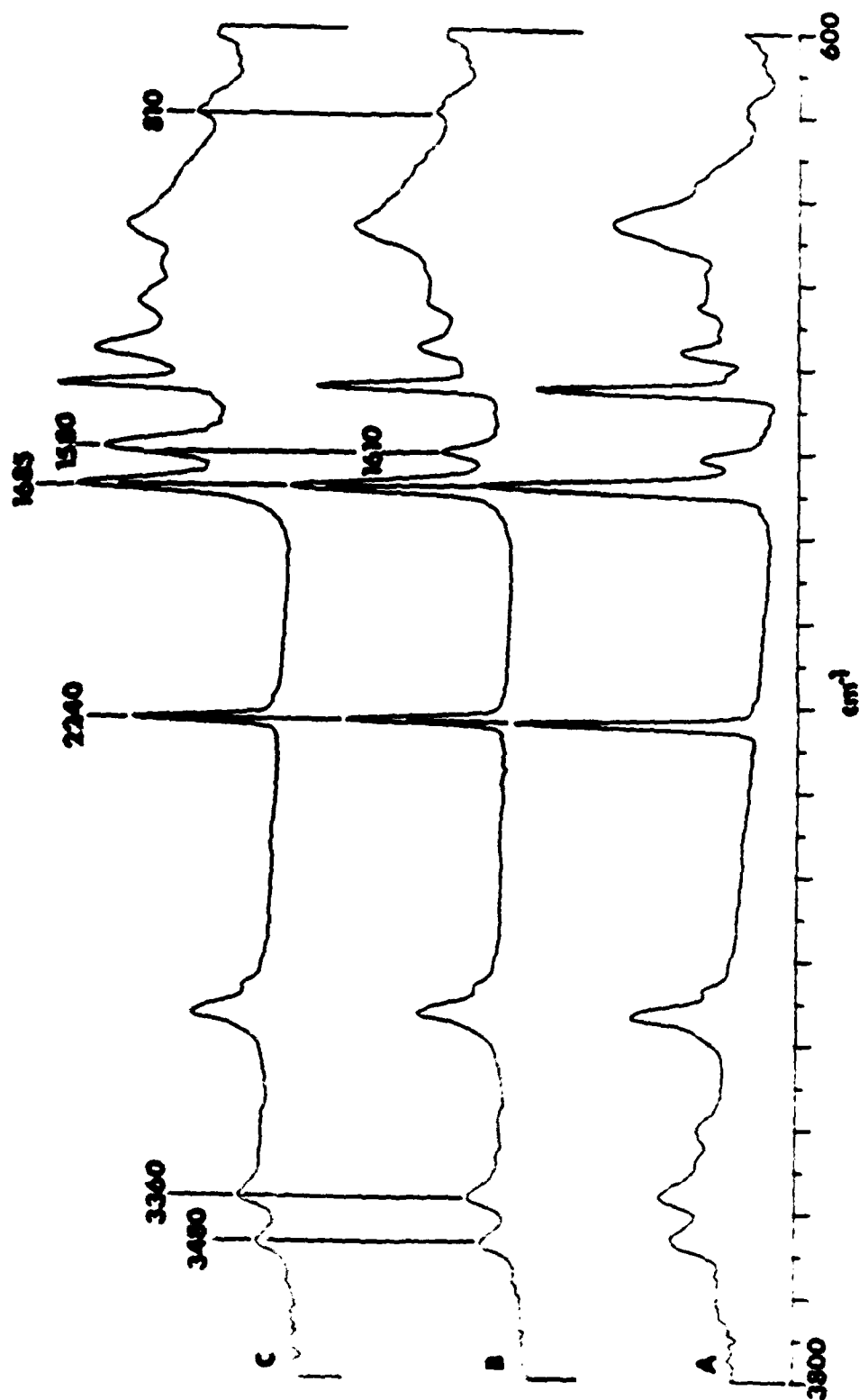
content. In fact this plot would lead one to believe that
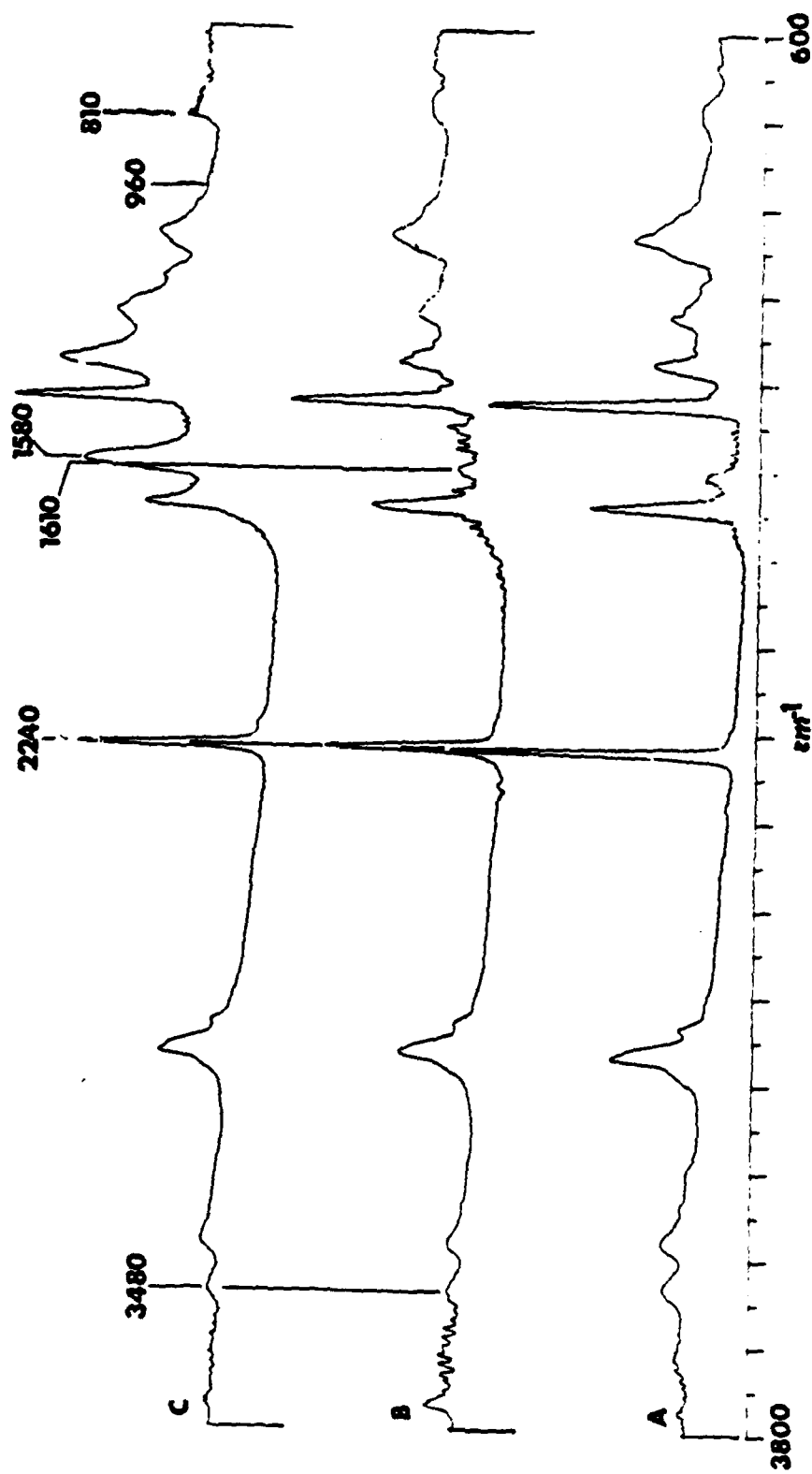
Figure 22. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/AM copolymer containing 2.9 mole% AM recorded in air. A) room temperature; B) initial at 200°C and C) after 15 minutes at 200°C.
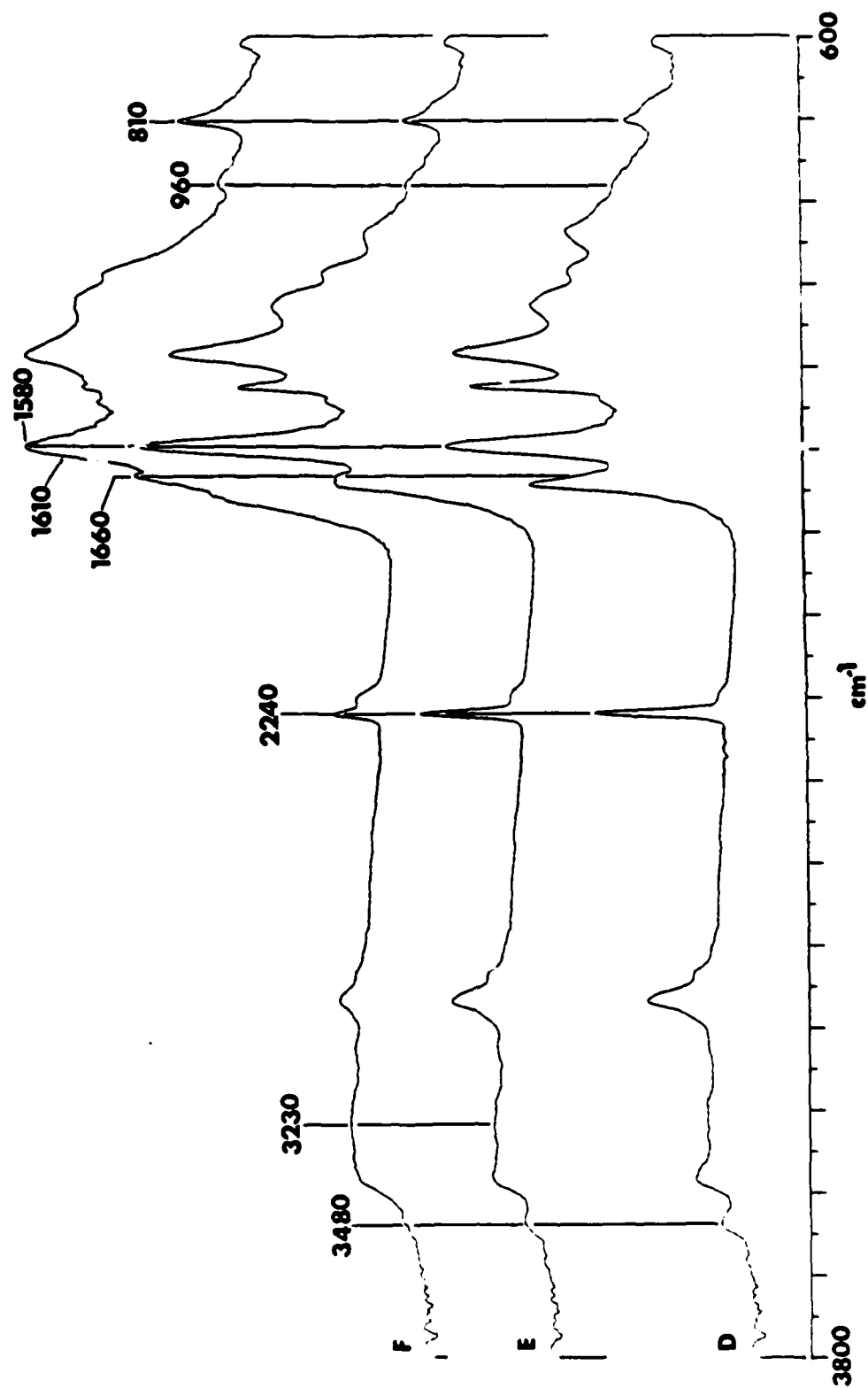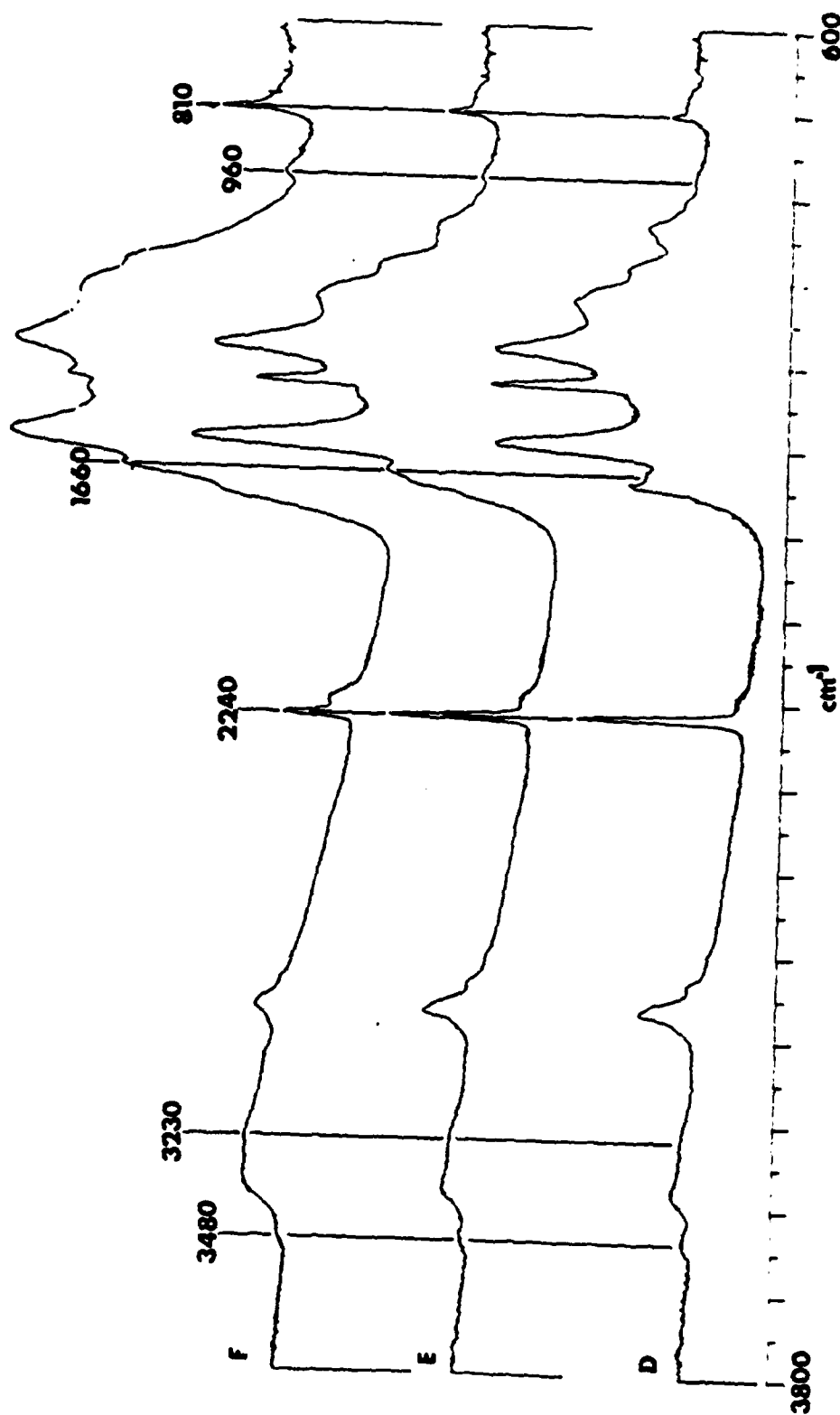
Figure 23. FT-IR absorbance spectra in the range 600-3800 cm-1 of the AN/AM copolymer containing 2.9 mole% AM recorded at 200°C in air. D) after 1 hour; E) 2 hours and F) 4hours.
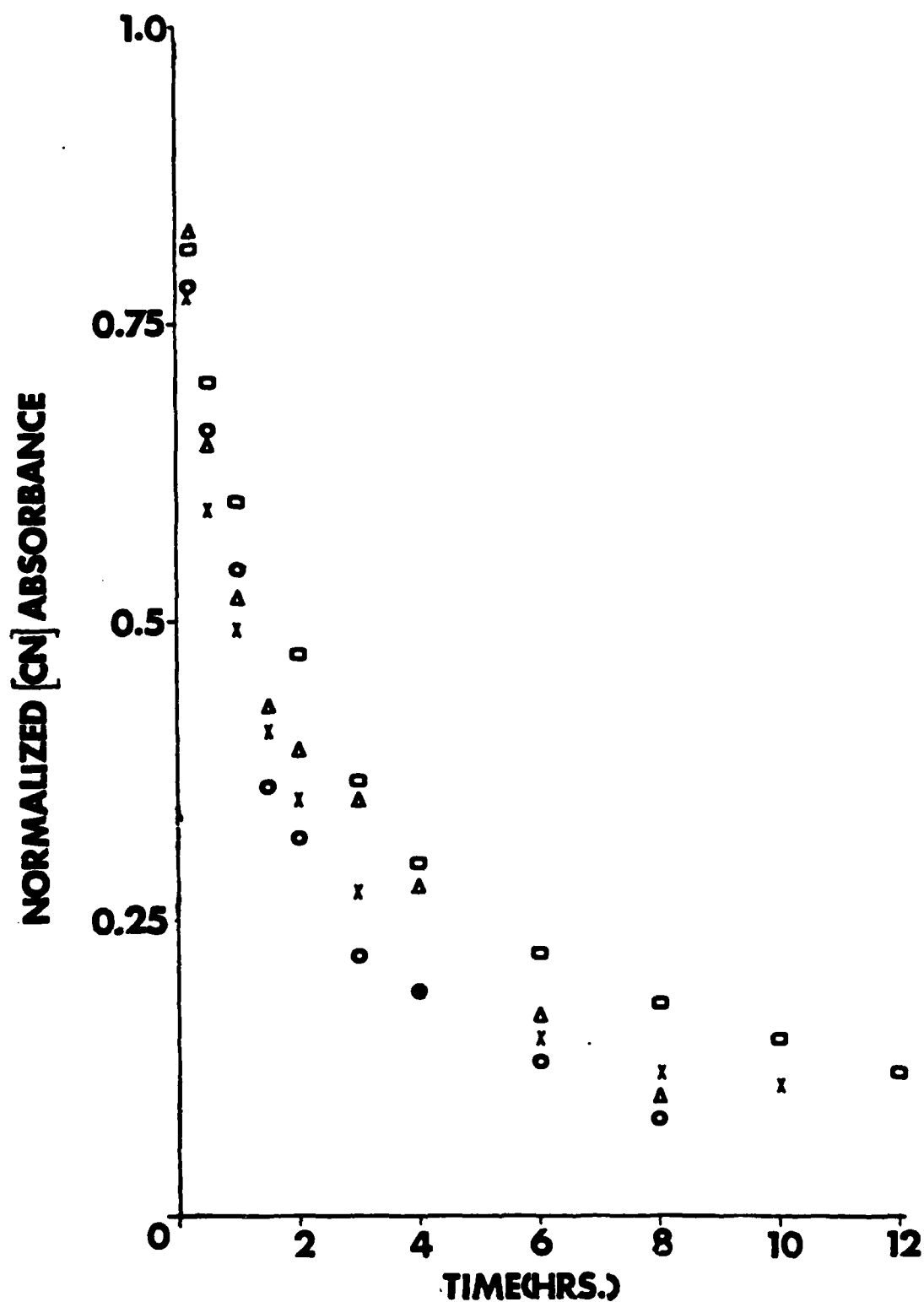
Figure 24.   Normalized C≡N absorption of the AN/AM copolymers
plotted as a function of time at 200°C in air.
(□) 2.9; (●) 5.2; (✗) 10.6 and (▲) 18.2 mole% AM.

most of the cyclization is occurring within the first 30 minutes of degradation just as in the case of degradation under reduced pressure. On the other hand, the sluggish appearance and growth of the 1580/1610 cm^{-1} bands during the first 30 minutes of degradation would suggest that cyclization is not the primary reaction in air. Given this, how can the rapid reduction of the nitrile absorption be accounted for?

In order to answer this question the reactions giving rise to the IR bands at 1660, 960 and 810 cm^{-1} must be considered. These bands may readily be assigned to vibrations of olefinic structures (24). Of particular interest is the band at 810 cm^{-1}. This band, which is the first to appear during degradation, is also seen in the spectra of PAN homopolymer and has been assigned to a C-H out of plane bending of a 1,1,2-trisubstituted olefin (25). Conely and Bieron have suggested that this type of olefin structure results from the reaction of oxygen as shown below (25):

$$\text{(structure with CN, CN)} \xrightarrow[\text{INTERMEDIATE}]{\text{PEROXIDIC}} \text{(structure with CN, CN)} + H_2O$$
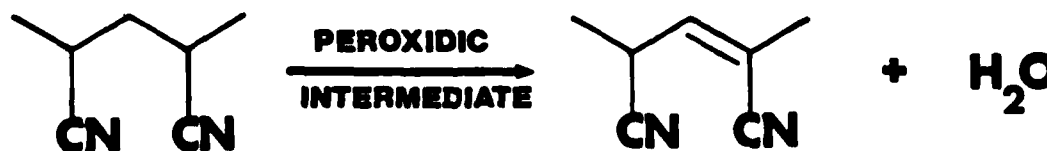
This reaction also appears to be catalysed by the presence of the AM groups in that for PAN homopolymer degraded under the same conditions, the 810 cm^{-1} band cannot be detected until after four hours. Incidentally, the appearance of the rotational bands of water in the spectra of

the copolymers recorded during heating to 200 °C further
supports this mechanism. However this is by no means
conclusive in that an improper ratio of the absorption
spectra may also give rise to these bands. This reaction is
similar to the autoxidation reactions common to most
polymers. With the introduction of this initial
unsaturation, elimination reactions are now possible due to
the activation of the allylic hydrogens and cyano groups.
Elimination of HCN in a manner similar to the "unzipping"
reaction proposed for the degradation of polyvinylchloride
(26) would not only account for the rapid reduction of the
nitrile absorbance (Figure 24) but would also yield
1,2-disubstituted olefins. This type of olefin would give
rise to the IR bands at 1660 and 960 cm^{-1} with the former
being assigned to the C=C stretching and the later to a C-H
out of plane bending. The entire reaction sequence is
summarized in Figure 25. Note that the oxidation reaction
and subsequent eliminations do not appear to be minimized by
the initiating effect of the AM units.

An important conclusion concerning the use of these
copolymers as a C/G fiber precursor may now be drawn. It is
apparent that in air the competition between cyclization and
oxidation cannot be overcome as originally anticipated. If
in fact an elimination reaction is preferred over the
intramolecular cyclization of the nitrile groups a conjugated
polyene would result. However the presence of the diene
structures may now allow for ring formation via a Diels-Alder
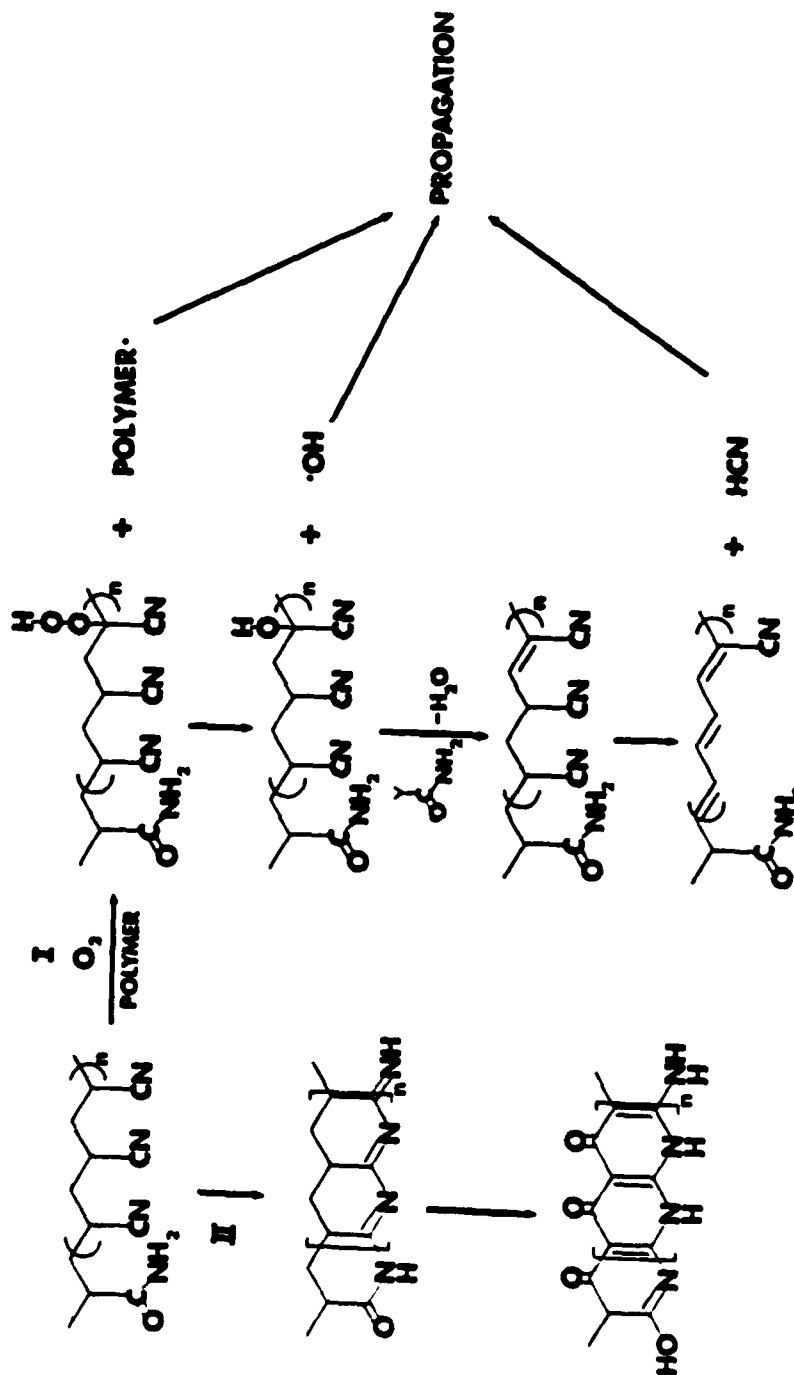
Figure 25. Scheme depicting the possible chemical reactions occuring during the thermal degradation of the AN/AM copolymers in air.

type reaction. Referring to the reaction scheme shown in Figure 25, the presence of the electron withdrawiling C≡N group makes the α,β double bond a very strong dienophile (27). These dierophiles could easily undergo the Diels-Alder addition to the diene systems of Figure 25 as shown below:
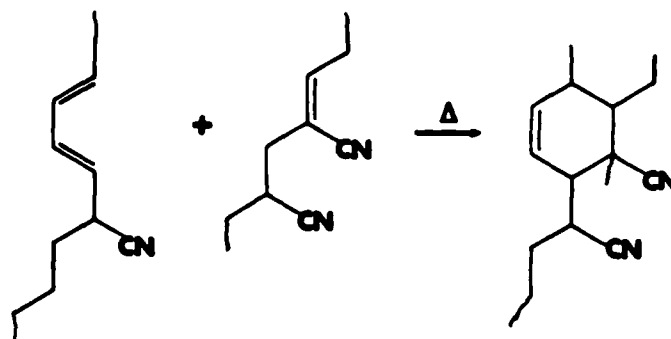
Such a reaction could proceed fairly rapidly given that at 200°C enough thermal energy exists to allow for the interaction of the π-electrons to favor the addition. At higher temperatures further elimination of HCN from the rings may occur thereby resulting in a final structure containing fused aromatic rings. It should however be mentioned that it is difficult to distinguish the double bonds of the rings from those of the polyene in the FT-IR spectra of the degraded copolymers and therefore this mechanism is only speculation. Futhermore the reaction involving the elimination of HCN to form the polyenes is tentative and may be verified with Gas Chromatography FT-IR (GC-FT-IR).

3.6 Conclusions

The degradation studies performed under reduced pressure

have demonstrated that a maximum extent of cyclization of nitrile units can be achieved by the inclusion of AM comonomer units into the PAN chain. However, contrary to the original intent of this study, the initiating effect of this comonomer has been shown to be independent of comonomer concentrations in the range of 6 to 20 mole% AM. From the experimental observations a "step-ladder" type model consisting of blocks of cyclized AN units, interrupted occasionally by "jumps" or crosslinks to other cyclized blocks may be envisioned. Finally it is suggested that the stereochemical distribution of monomer units in the copolymer chain as well as the stereochemistry of intramolecular ring formation play a key role in limiting the length of cyclized blocks, the degree of intermolecular crosslinking and ultimately the overall extent of reaction.

From the degradation studies performed in air it was shown that while intramolecular cyclization is initiated by the AM units, elimination reactions due to the presence of oxygen predominate. Furthermore these reactions lead to the formation of conjugated polyenes which may be capable of ring formation via a Diels-Alder reaction. Such ring formation may be desired for the production of high strength C/G fibers.

CHAPTER 4

THERMAL DEGRADATION OF ACRYLONITRILE/ACRYLIC ACID COPOLYMERS

4.1 Original Objectives

This author has previously reported the results of the thermal degradation of a PAN/MAA copolymer (9). A mechanism by which this copolymer degrades was suggested and is shown in Figure 6 of Chapter 1. At that time it was believed that two-way initiation was restricted due to the presence of the α-methyl group. This group will not tautomerise and effectivily blocks further reaction along one direction of the chain. However, since this copolymer exhibits a very fast rate of degradation it could not be overlooked as a potential precursor material. The problem posed by the presence of the α-methyl group could easily be overcome by simply substituting an acrylic acid (AA) comonomer for the methacrylic acid. The AA unit possesses an α-hydrogen which may potentially tautomerise and it was hoped that two-way initiation could take place and, as with the AN/AM copolymers, the cyclization of the AN groups could be maximized by increasing the AA concentration.

4.2 Analysis of Copolymers.

In contrast to the AN/AM copolymers, the composition of the AN/AA copolymers can be readily calculated from elemental analysis data. The results of these analyses and the calculated copolymer compositions are shown in Table 1.

In Chapter 3, the determination of the reactivity ratios

from the feed and polymer composition ratios was described. Fineman-Ross plots for the AN/AA copolymers are shown in Figure 26. From a least squares fit the values of the reactivity ratios for AN and AA were estimated to be 0.96 and 2.0, respectively. It must be emphasized that these results can only be considered approximate. The product of the two reactivity ratios, $r_a r_b$, is 1.92 which implies a tendency toward "blocking". This is in contrast to the AN/AM copolymerization which was shown to be essentially random. Table 5 shows the calculated copolymer compositions and sequence information for the AN/AA copolymers using the experimentally determined reactivity ratios. The Chi values, which are all less than unity, further indicate a tendency toward "blocking". In addition, the number and weight fractions of sequences of AA units are skewed towards higher amounts of sequences greater than one compared to the totally random case. (For example, compare the AN/AM copolymer II in Table 2, which is essentially random, with AN/AA copolymer IIA in Table 5. Both polymers contain the same concentration of B units.)

4.3. Results

4.3.1 Thermal Degradation at 160 and 200°C Under Reduced Pressure.

Figure 27 shows the FT-IR absorbance spectra of the three AN/AA copolymers containing 2.3, 6 and 9 mole% acrylic acid (denoted IA thru IIIA) recorded at room temperature. Two bands, one at 2240cm^{-1} associated with the C≡N stretching
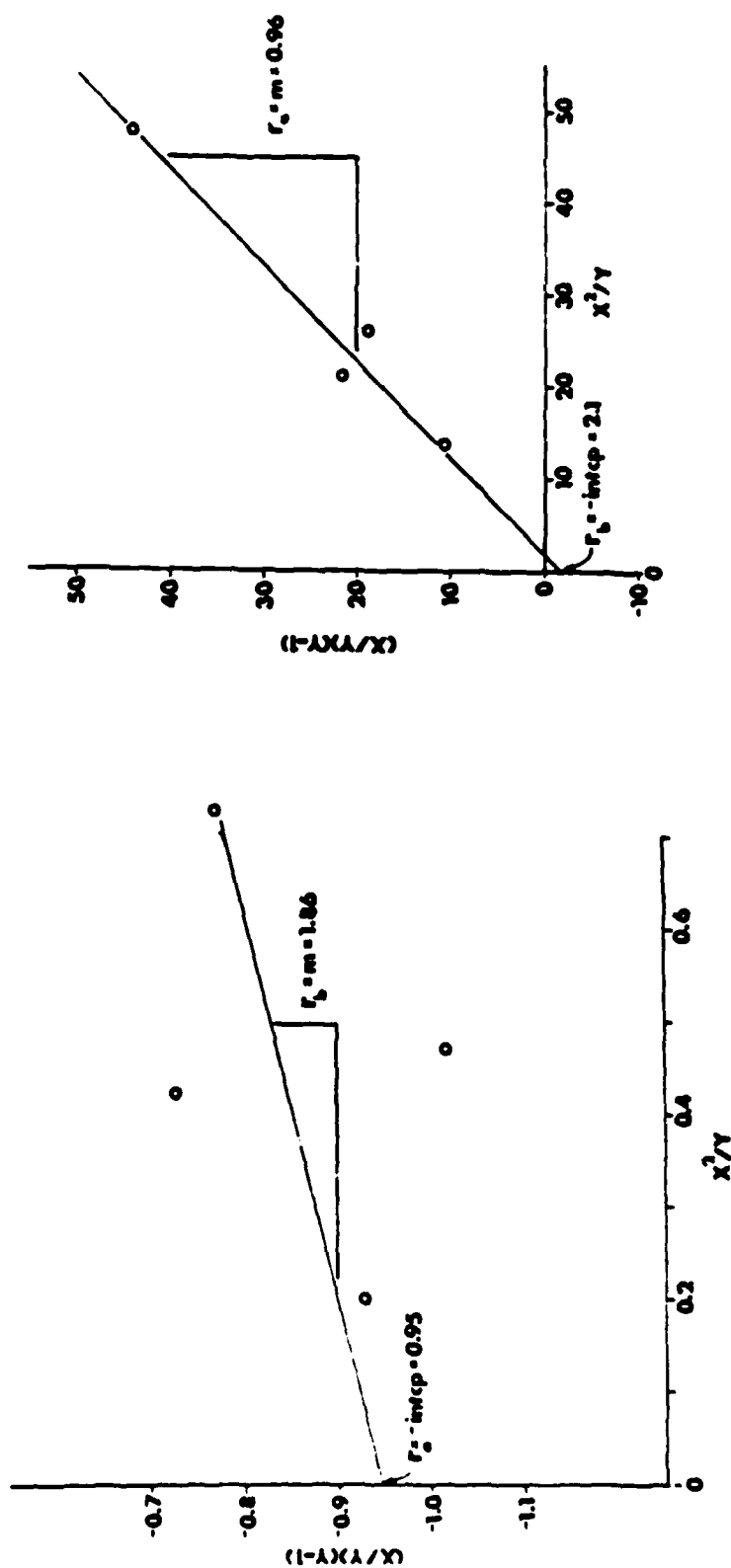
Figure 26. Fineman-Ross plots for the determination of reactivity ratios for the AN/AA copolymers. The plot on the left results from defining AN to r_a and AA to r_b. Plot on right results from switching the definitions.

TABLE 5

AN/AA COPOLYMERS

COPOLYMER COMPOSITION AND SEQUENCE INFORMATION

Number	Composition Monomer		Polymer		Chi	La	Lb
	AN	AA	AN	AA			
IA	.98	.03	.976	.023	.983	43.4	1.04
IIA	.95	.05	.950	.050	.965	20.3	1.10
IIIA	.92	.08	.913	.087	.945	12.2	1.15
IVA	.96	.04	.960	.040	.971	25.5	1.07

COPOLYMER IA

NA(1)=.02	WA(1)=0.0	NB(1)=.95	WB(1)=.92
(2)=.02	(2)=0.0	(2)=.03	(2)=.07
(3)=.02	(3)=0.0	(3)=0.0	(3)=0.0
(4)=.02	(4)=0.0	(4)=0.0	(4)=0.0
(5)=.02	(5)=0.0	(4)=0.0	(4)=0.0

COPOLYMER IIA

NA(1)=.04	WA(1)=0.0	NB(1)=.91	WB(1)=.83
(2)=.04	(2)=0.0	(2)=.07	(2)=.14
(3)=.04	(3)=0.0	(3)=0.0	(3)=.01
(4)=.04	(4)=0.0	(4)=0.0	(4)=0.0
(5)=.04	(5)=0.0	(5)=0.0	(5)=0.0

COPOLYMER IIIA

NA(1)=.08	WA(1)=0.0	NB(1)=.86	WB(1)=.74
(2)=.07	(2)=.01	(2)=.11	(2)=.20
(3)=.06	(3)=.01	(3)=.01	(3)=.04
(4)=.06	(4)=.02	(4)=0.0	(4)=0.0
(5)=.05	(5)=.02	(5)=0.0	(5)=0.0

COPOLYMER IVA

NA(1)=.03	WA(1)=0.0	NB(1)=.93	WB(1)=.87
(2)=.03	(2)=0.0	(2)=.06	(2)=.11
(3)=.03	(3)=0.0	(3)=0.0	(3)=.01
(4)=.03	(4)=0.0	(4)=0.0	(4)=0.0
(5)=.03	(5)=0.0	(5)=0.0	(5)=0.0

END

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MICROCOPY RESOLUTION TEST CHART
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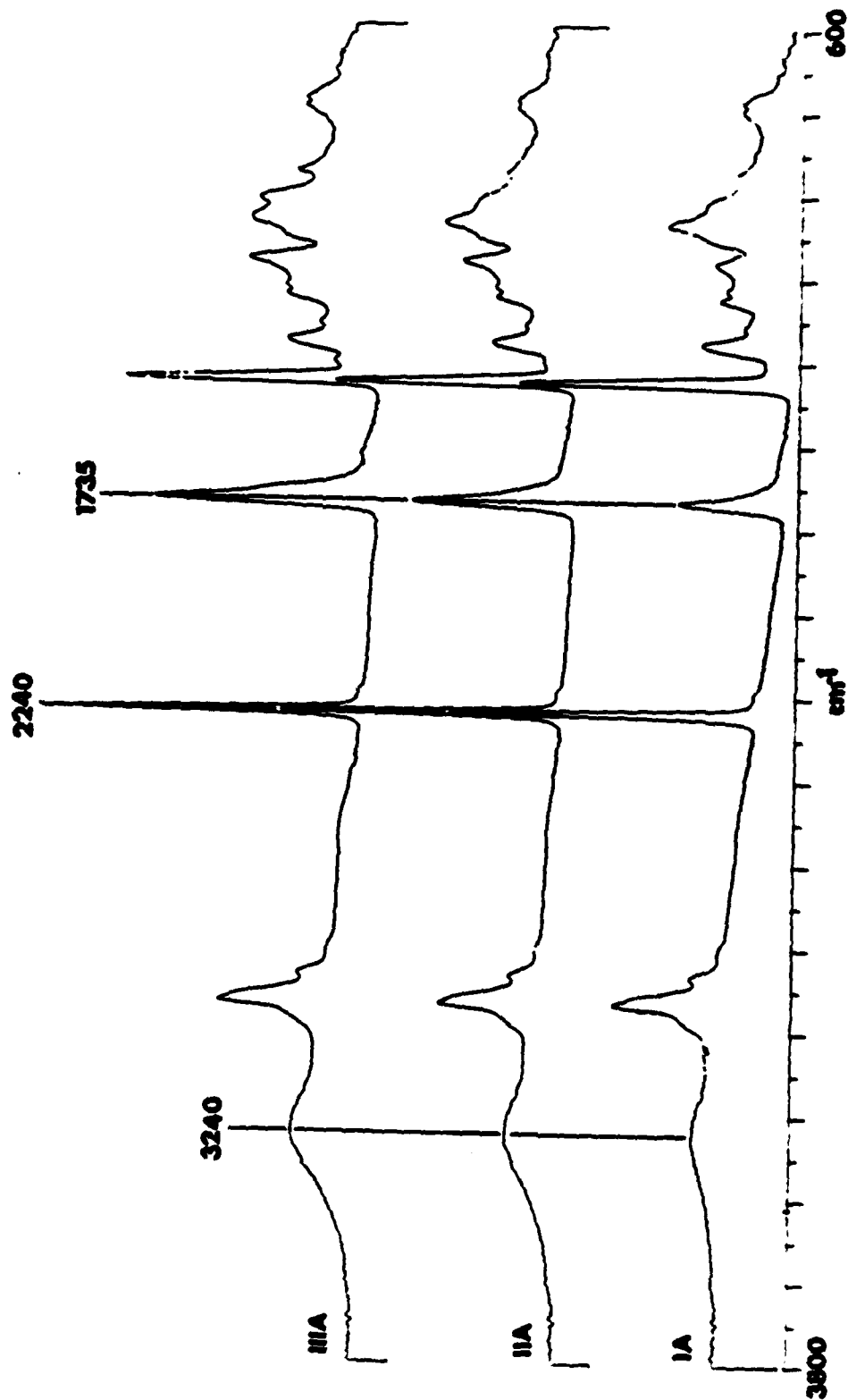Figure 27. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/AA copolymers recorded at room temperature. (IA) 2.3; (IIA) 6 and (IIIA) 9 mole% AA.

of the AN units and another at 1735cm^{-1} associated with the C=O stretching of the AA units, are of particular interest. As anticipated, the ratio of the 1735 to 2240 cm^{-1} bands varies in a systematic fashion with copolymer composition. A very broad band centered at 3400 cm^{-1} which is due to O-H stretching is also observed but will not be quantitatively useful.

These copolymers also undergo significant degradation at 160°C and 5 X 10^{-2} torr, but the reaction is sufficiently slow to allow for the observation of subtle spectral changes. Figure 28 shows the infrared absorbance spectra of the 6 mole% AN/AA copolymer recorded at 160°C as soon as the film attained this temperature and after 30 minutes, 1 and 4hours at 160°C. The spectral occurrences observed upon degradation are similar to those previously reported by this author for a PAN/MAA copolymer (9). As the degradation reaction proceeds there is the expected reduction in the absolute intensity of the nitrile absorbance at 2240 cm^{-1} and the appearance and growth of bands at 1580 and 1610 cm^{-1} attributable to pyridones. In common with this author's previously reported work, the band associated with the C=O stretching of the acid group (1735 cm^{-1}) steadily decreases in intensity. Concurrently, a new band at 1700cm^{-1} appears and becomes increasingly more intense. This new band is assigned to the carbonyl group formed by the acid initiation of the AN units as shown in Figure 29 (The reader is referred to Reference 9 and Figure 6 of this thesis for further details). The band
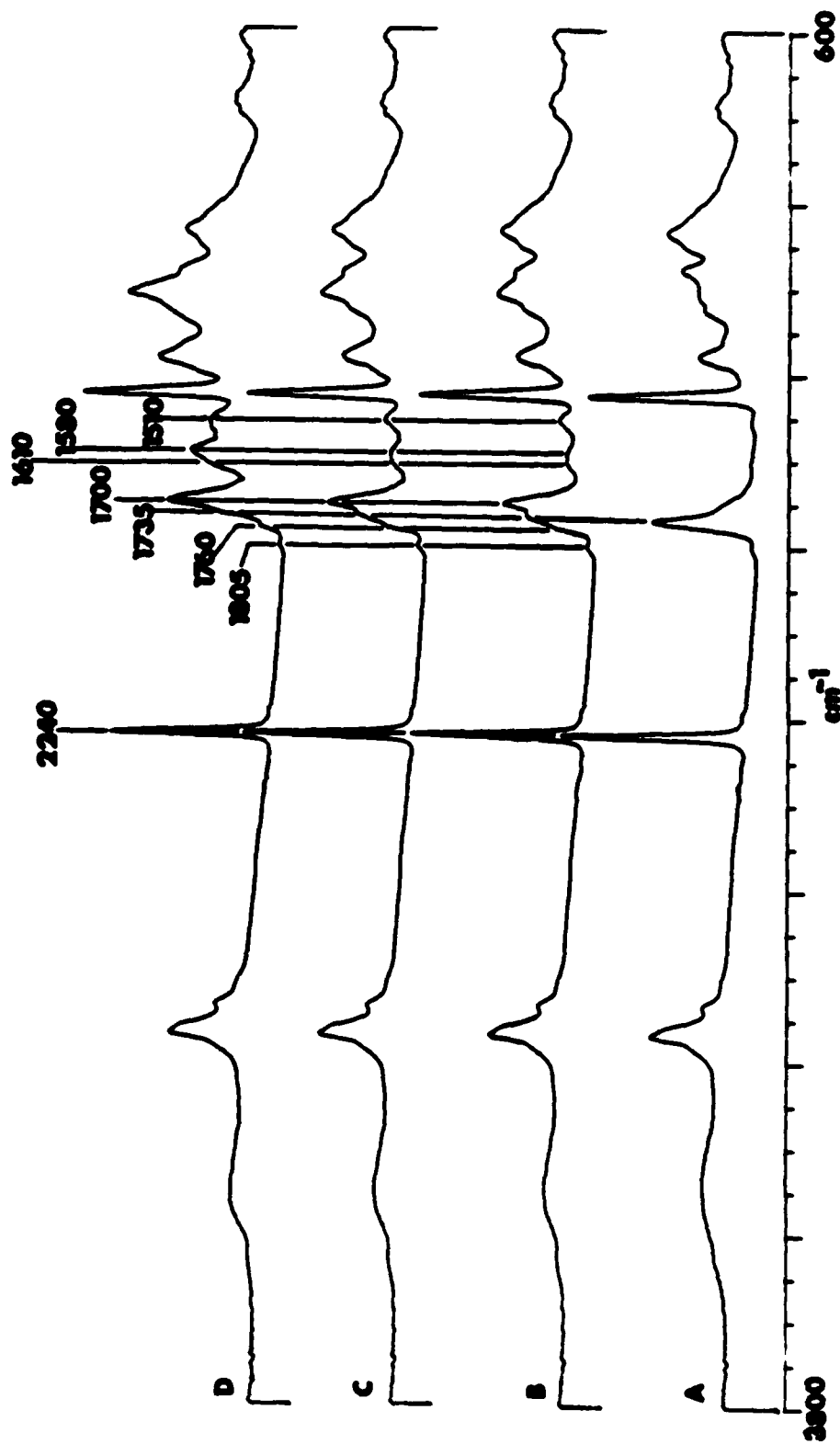
Figure 28. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/AA copolymer containing 6 mole% AA recorded at 160°C under reduced pressure. A) initial at 160°C; B) 30 minutes; C) 1 hour and D) 3hours.
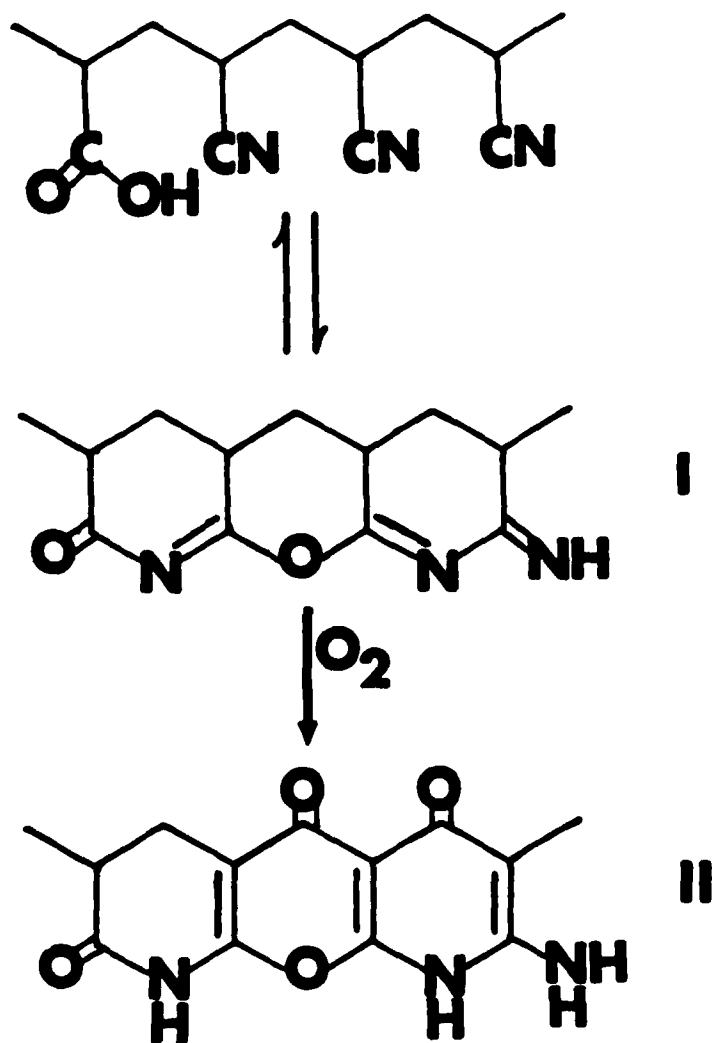
Figure 29. Scheme depicting the proposed acid initiated cyclization during the degradation of the AN/AA copolymers.

occurring at 1510 cm^{-1} in the spectra of the degrading
copolymer has previously been assigned to the N-H bending
vibration associated with structure II of Figure 29.
Finally, the band at 1805 cm^{-1} and the shoulder at 1760 cm^{-1}
indicate that some cyclic anhydride is formed by the
condensation of neighboring groups.

The spectral changes that occur during the degradation
at 200°C are much more rapid than at 160°C. Figure 30 shows
the FT-IR absorbance spectra of the AN/AA copolymer
containing 6 mole% AA recorded at room temperature, initially
at 200°C, after 30 minutes and 1 hour at this temperature.
When compared to the spectra recorded at 160°C, there is a
very rapid reduction of the nitrile absorption at 2240 cm^{-1}
and an immediate appearance of the 1700 cm^{-1} band in the
spectrum recorded initially at 200°C. In addition, the bands
indicative of cyclization at 1580 and 1610 cm^{-1} are very
intense in the initial 200°C spectrum and grow steadily
throughout the degradation. The two IR bands assigned to
cyclic anhydrides at 1805 and 1760 cm^{-1} are not detected at
this temperature.

Degradation studies were also performed for the other
AN/AA copolymers at 160 and 200°C under reduced pressure, and
the spectral occurrences observed are similar to those
described above.

4.4 Discussion

4.4.1 Thermal Degradation at 200°C Under Reduced Pressure.

Figure 31 shows a plot of the normalized nitrile
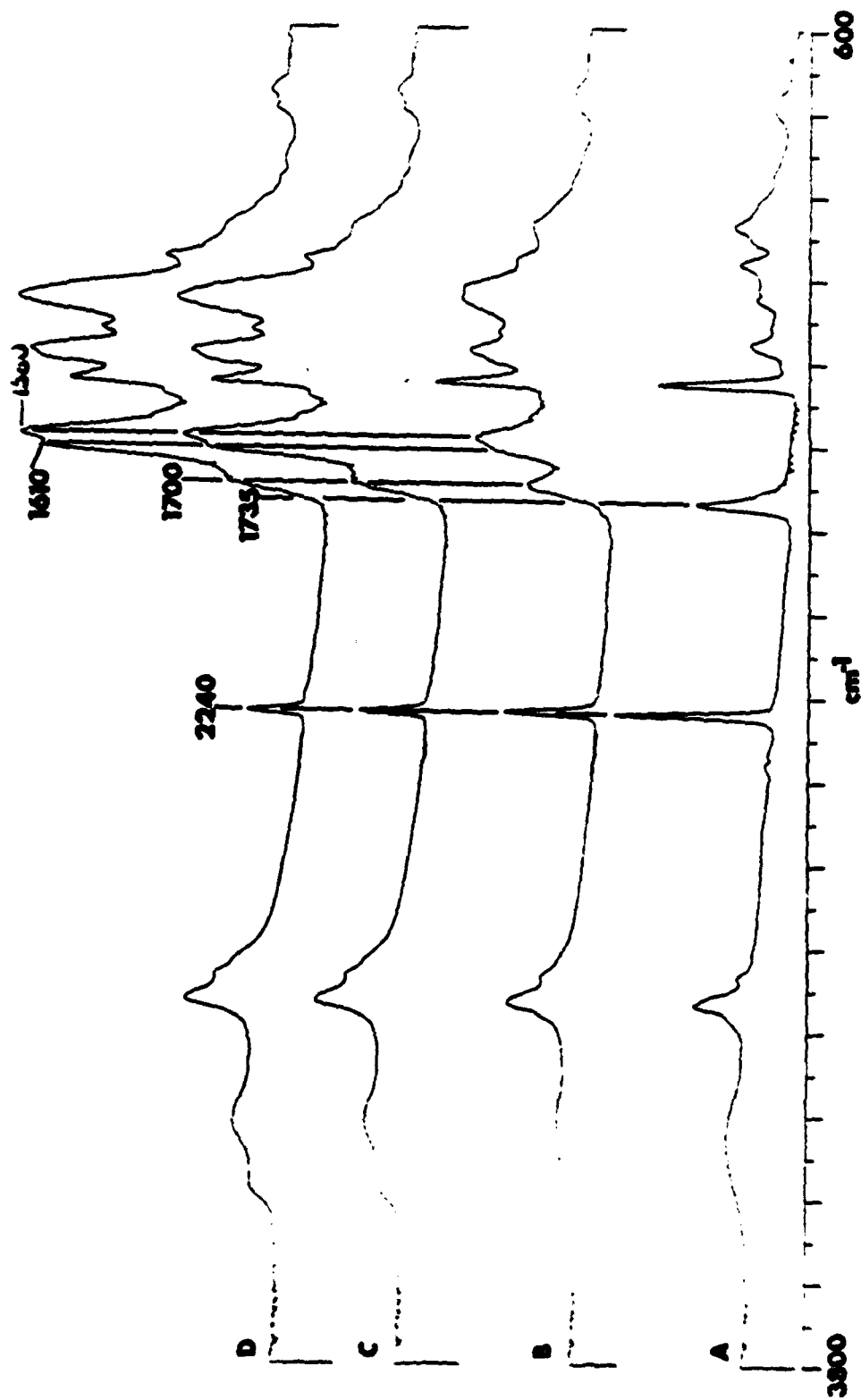
Figure 30. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/AA copolymer containing 6 mole% AA recorded under reduced pressure. A) room temperature B) initial at 200°C; C) after 30 minutes and D) after 1 hour at 200°C.

absorbance of the three AN/AA copolymers as a function of time at 200°C under reduced pressure. Note that like the AN/AM copolymers under these conditions, these data may also be represented by a single rate curve. Interestingly enough, all three copolymers appear to be reaching a plateau with approximately 75% of the AN groups reacted after 4 hours. This trend is very similar to that seen in the case of the AN/AM copolymers and within experimental error it may be said that both AA and AM appear to have the same effect on the rate of cyclization. Because of this analogous behavior with the AM copolymers it would appear that the tautomerism mentioned earlier in this chapter is occurring, thereby allowing for two-way initiation. Therefore, the degradation model 4 used for the AN/AM copolymer may be applicable here. However the computer program used for calculations of extents of reaction based on the assumptions of this model cannot be justifiably employed. Recall that this program is based on a random placement of initiating units. With the complications introduced by the blocking tendency of the AA units, calculated extents of reaction from the computer program would be misleading.

Nevertheless it may be said that these AN/AA copolymers follow the same trends of degradation as the AN/AM copolymers at 200°C.

4.4.2 Thermal Degradation at 160°C Under Reduced Pressure.

The results obtained at 160°C markedly differ from those of the AN/AM copolymers at the same temperature. The spectra
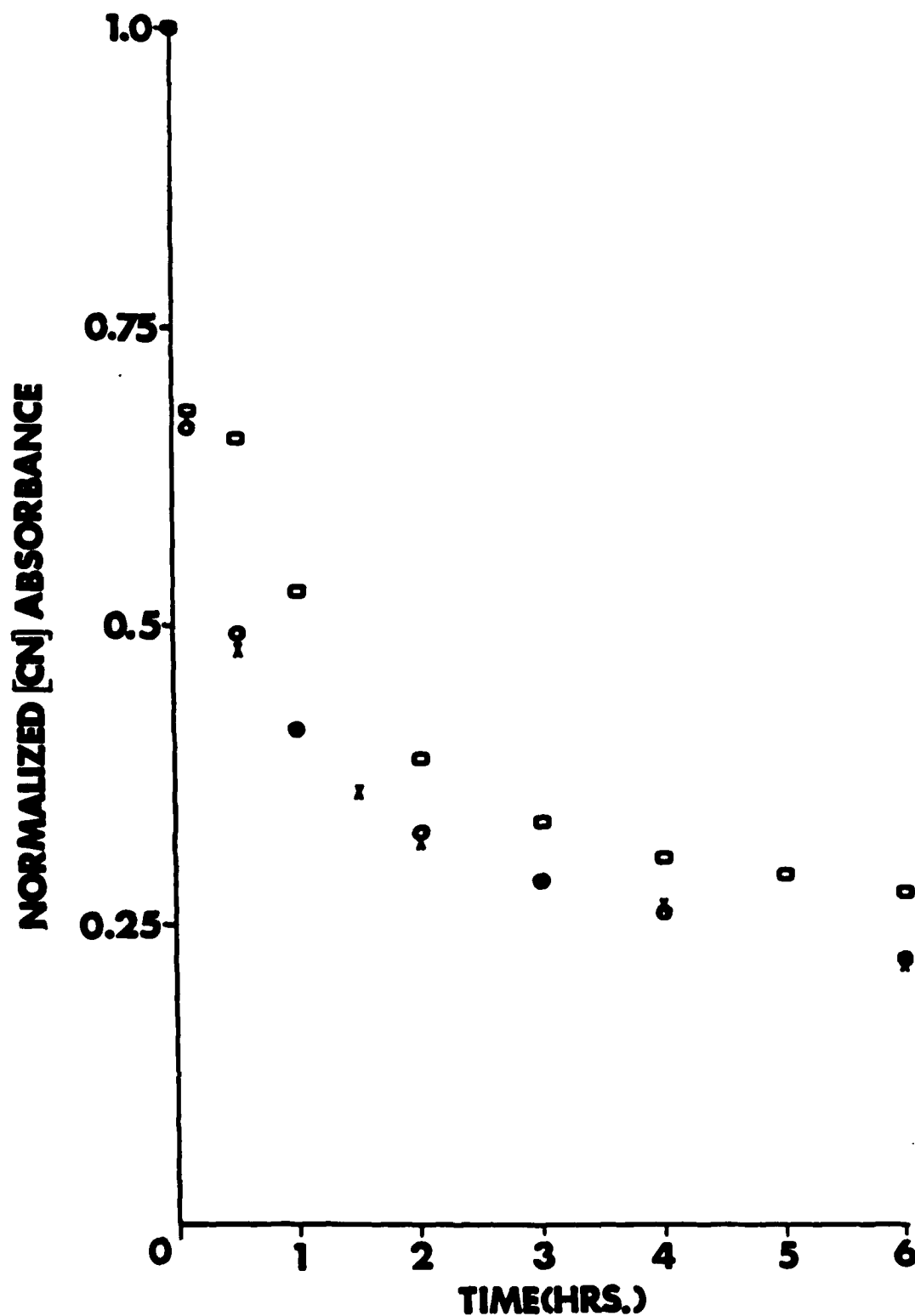
Figure 31. Normalized C≡N absorption of the AN/AA
as a function of time at 200°C under reduced
pressure. (□) 2.3; (⊙) 6 and (✗) 9 mole% AA.

recorded for the 6 mole% AA copolymer degraded at 160°C under
reduced pressure have been shown in Figure 28 along with an
interpretation of spectral occurrences during degradation.
Of paramount concern to this study is the plot of the
normalized nitrile absorbance versus time at 160°C. Such a
plot is shown in Figure 32. In contrast to the AN/AM
copolymers there is no apparent induction period. Within
experimental error, however, the curves for the 6 and 9 mole%
copolymers are also superimposable.

From a comparison of the rate curves for the AN/AM
copolymers at 160°C (Figure 16) and the curves shown in
Figure 32, the reaction in the latter appears to level off
with approximately 70% AN remaining while in the former the
reaction seems to level off with approximatly 45-50% AN
remaining. This behavior is consistent with this author's
previous comparison of the degradation rates of PAN/AM and
PAN/MAA copolymers. For an explanation of this behavior one
is referred to the mechanisms shown in Figure 6 and the
accompanying discussion in Section 1.3.1. From this
mechanism it was hoped that the presence of an α-hydrogen
atom in the AA comonomer unit would allow for tautomerism of
the carbonyl group and thus allow for two-sided initiation as
in the case of the AN/AM copolymers. Unfortunately this does
not seem to be the case in that the amount of AN units
cyclized for the AN/AA copolymers appears to be roughly 1/2
that cyclized by the AM comonomers after the same period of
time. In addition to the absence of the tautomerism
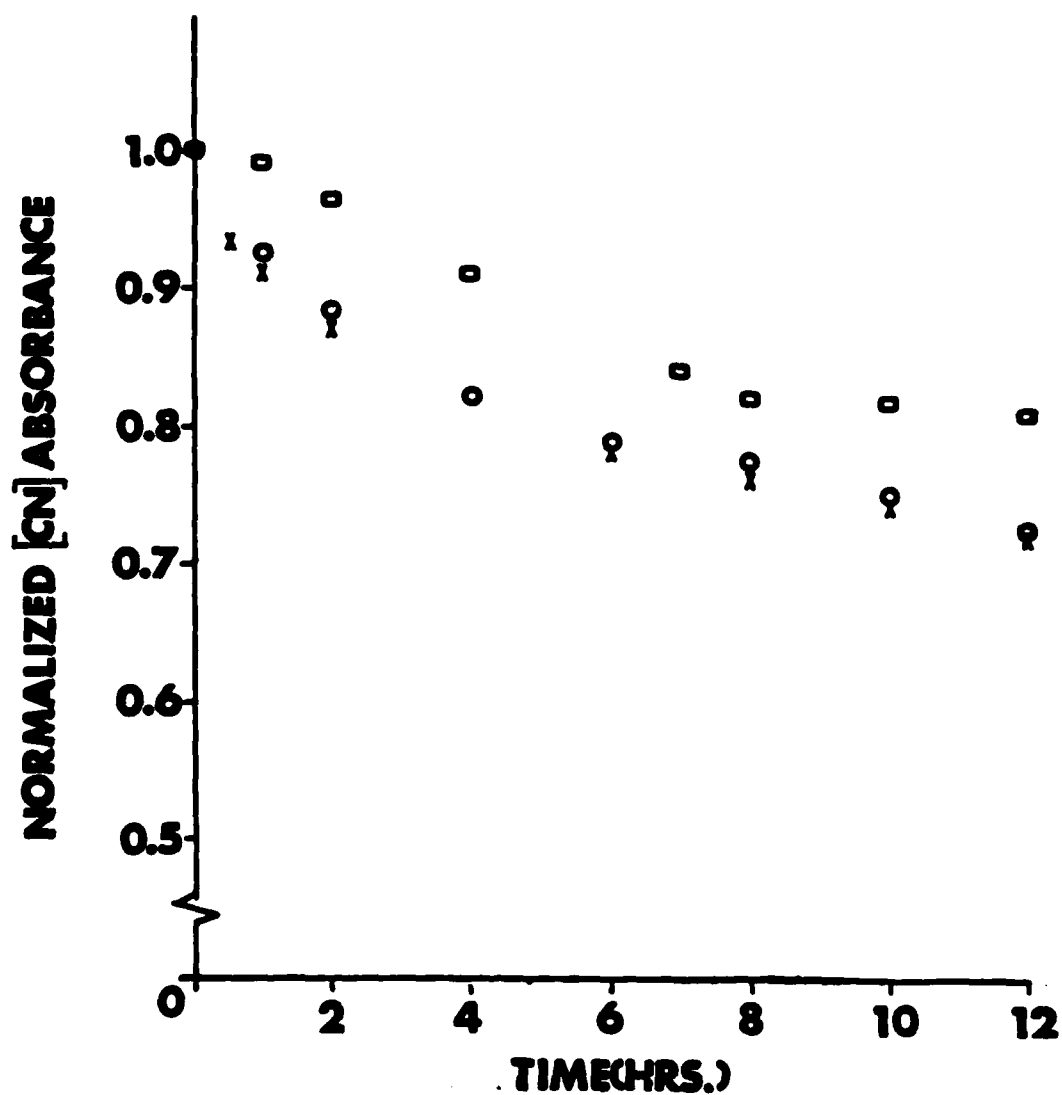
Figure 32. Normalized C≡N absorption of the AN/AA
copolymers as a function of time at 160°C under
reduced pressure. (□) 2.3; (⊙) 6 and (✗) 9 mole%

mentioned above, three other factors may contribute to the slower degradation rate of the AN/AA copolymers at 160°C. First, the fact that the anhydride bands remain visible for a rather long period of time as degradation proceeds demonstrates the stability of the glutaric anhydride structure at this temperature and thereby reduces the amount of acid groups capable of initiation. Second, the lower temperature may not provide sufficient thermal energy to provide enough chain mobility for intermolecular cross-linking. And finally, Davidson and Skovronek (28) have shown that below 200°C very little reaction between acid and nitrile is observed. Furthermore when reaction is achieved equilibrium is quickly reached with very little imide present. A consequence of this equilibrium is that it permits nitrile-acid interchange. In the case of these AN/AA copolymers it is likely that once an acid group reacts with a nitrile the imide will quickly revert back to the starting moieties if the imide cannot propagate due to tacticity of the next nitrile group.

4.4.3 Effect of Anhydride Formation During Degradation.

As stated in the previous section, the IR bands at 1805 and 1760 cm^{-1} indicate that some intramolecular condensation of neighboring AA units is occuring thereby resulting in the fomation of 6-membered cyclic anhydrides during degradation. McGaugh and Kottle have shown that the formation of glutaric anhydride type structures is the major reaction during the thermal degradation of poly(acrylic acid) homopolymer at 150

to 200°C (29). Grassie et al. (30) have also reported the formation of glutaric anhydride during the degradation of poly(methacrylic acid) (PMA) at 200°C. These authors also reported a small amount of isobutyric anhydride which results from the intermolecular condensation of acid groups of neighboring chains.

One would expect that the formation of anhydride groups would effectively reduce the amount of acid groups available for initiation, particularly at high acid concentrations. This appears to be the case for degradation at 160°C where the anhydride bands appear and remain as degradation proceeds. However after extended periods of time these bands do begin to decrease. At 200°C the bands are only observed during heating to this temperature and are difficult to distinguish in the initial spectra at 200°C. This suggests that the anhydrides are being destroyed at the higher temperatures. However it is well known that glutaric anhydrides are stable at very high temperatures (>200°C) (30). This high temperature stability of the .nhydrides prepared "in-situ" is possible only when the condensed water is removed. If water is allowed to remain the equilibrium between acid and anhydride is driven to the left with the acid predominating. This may be the case for these AN/AA copolymers. Slow difussion of water through the degrading film may allow for a majority of the acid groups to initiate AN units rather than condense to anhydride. Furthermore, remaining anhydrides may by broken down by reaction with a

propagating species as shown in Figure 33a. Finally Peebles et al. (31) have suggested that any acid units that have not reacted may be involved in the degradation scheme as shown in Figure 33b.

The main conclusion that may be drawn from the above discussion and schemes is that the concentration of the initiating species is uncertain.

4.4 Conclusions

The degradation results obtained for the AN/AA copolymers at 200°C under reduced pressure suggest that the rate of degradation is very similar to that of the AN/AM copolymers under the same conditions. However the data obtained at 160°C is markedly different from that for the AN/AM copolymers and suggests that the kinetics of acid-nitrile reactions is a limiting factor retarding the acid initiated cyclization of AN units. Furthermore, the results tend to indicate that two-way initiation via tautomerism of the α- hydrogen of the AA unit does not occur at 160°C.
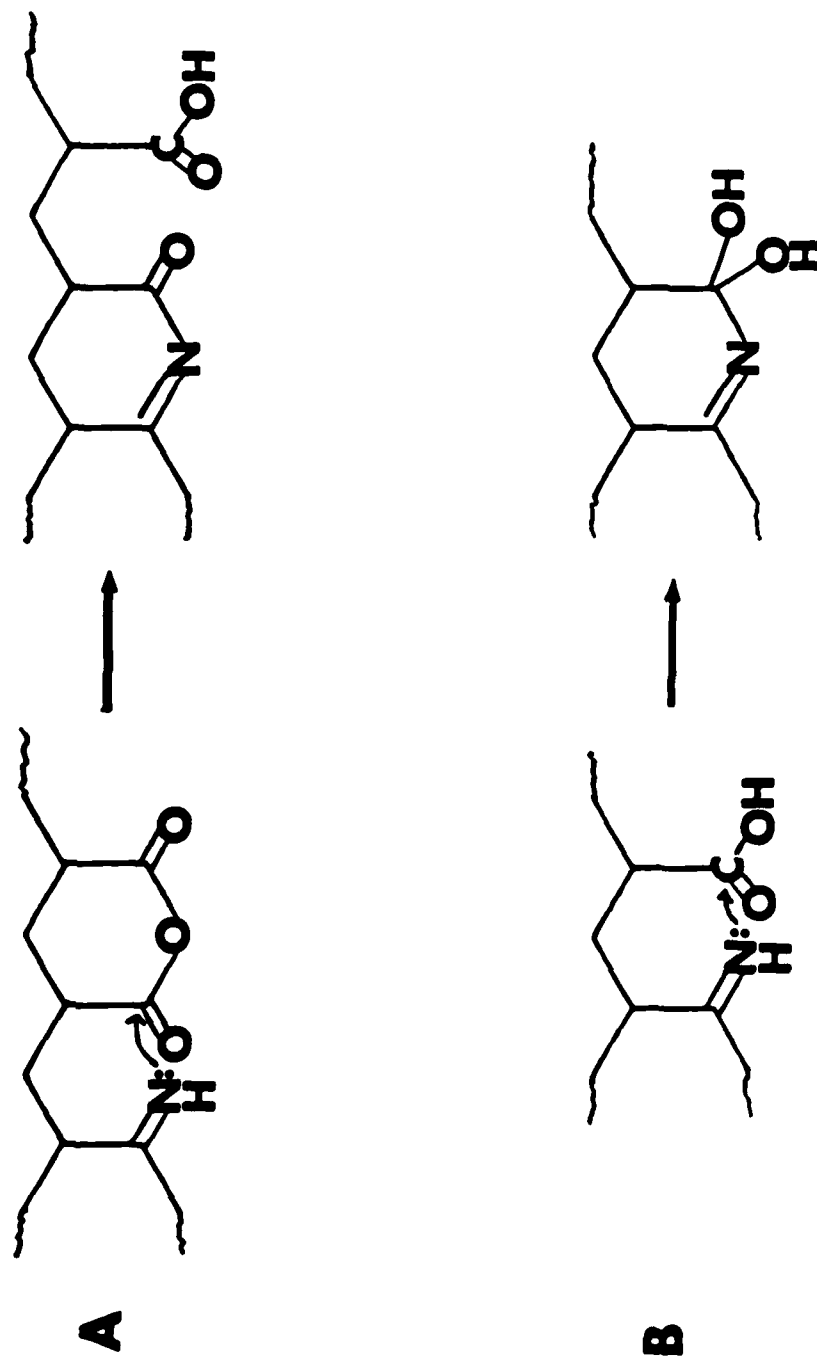
Figure 33. Schemes suggested for alternative reactions of the AA groups during thermal degradation of AN/AA copolymers. A) Reaction of anhydrides and B) non-initiation reaction of AA units.

CHAPTER 5

PRELIMINARY STUDIES OF ACRYLONITRILE/ITACONIC ACID COPOLYMERS

5.1 Introduction

It must be at first emphasized that the work presented in this chapter is preliminary and may be considered as a "scouting" study.

In the preceding chapter, studies of the degradation of AN/AM and AN/AA copolymers have been reported. For both these copolymers, initiation of the cyclization reaction was considered to be dependent upon the stereochemical sequence distribution. It was postulated that if an initiation site containing reactive groups on both sides of the polymer chain could be incorporated into the PAN polymer, then initiation of the cyclization reaction should not be dependent upon stereochemistry. Itaconic acid (IA), which may be considered a vinylidene dicarboxylic acid, is one such monomer and has the structure shown below:

Whereas the free-radical copolymerization of AN with AM or AA is relativily straightforward, the copolymerization of AN with IA is rather complex. Ideally, a copolymer containing IA units incorporated in the following manner is desired:
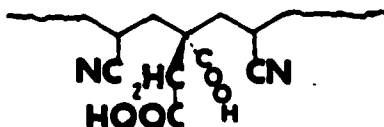
Unfortunately, depending upon such factors as the pH of the polymerization solution and the presence of chain transfer reagents (e.g. methanol), other structural units may be incorporated into the polymer chain. In addition to the incorporation of IA units, amides and methyl esters are most likely to be present. Amides may be formed by acid catalysed hydration of nitrile groups (27):

$$\text{(nitrile)} + H_2O \xrightarrow{H^+} \text{(amide, } C(=O)NH_2\text{)} + H^+$$
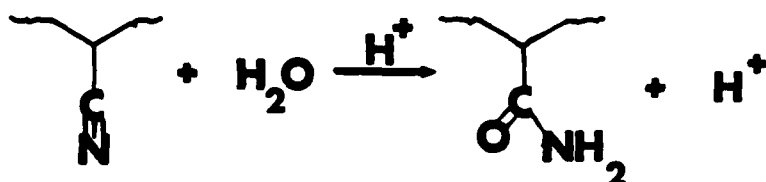
Similarly, methyl esters may be formed by the acid catalysed esterification of acid groups with the methanol used in the polymerization as a chain transfer agent:

$$\text{(}C(=O)OH\text{)} + MeOH \xrightleftharpoons{H^+} \text{(}C(=O)OMe\text{)} + H^+ + H_2O$$
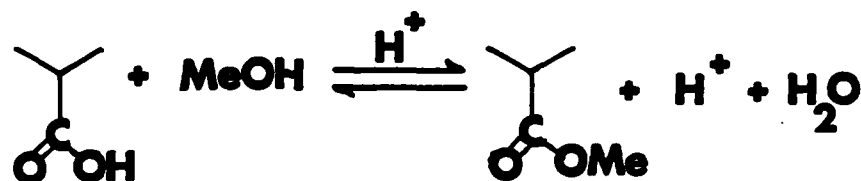
Acid-nitrile interchange is also feasible in this system. Frankly, these factors were not fully appreciated at the time the copolymers were synthesized. Therefore, two copolymers were prepared which are markedly different in their chemical structure and composition. These differences are readily apparent if one considers the room temperature FT-IR spectra of the two copolymers (designated 1b and 2b) shown in Figure 34. These spectra are complex and there are spectral features present in both copolymers which suggest that other chemical entities exist in addition to AN and IA units. Infrared bands at 1180, 1735 and 3250 cm^{-1} may be assigned to

Figure 34. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/IA copolymers recorded at room temperature.
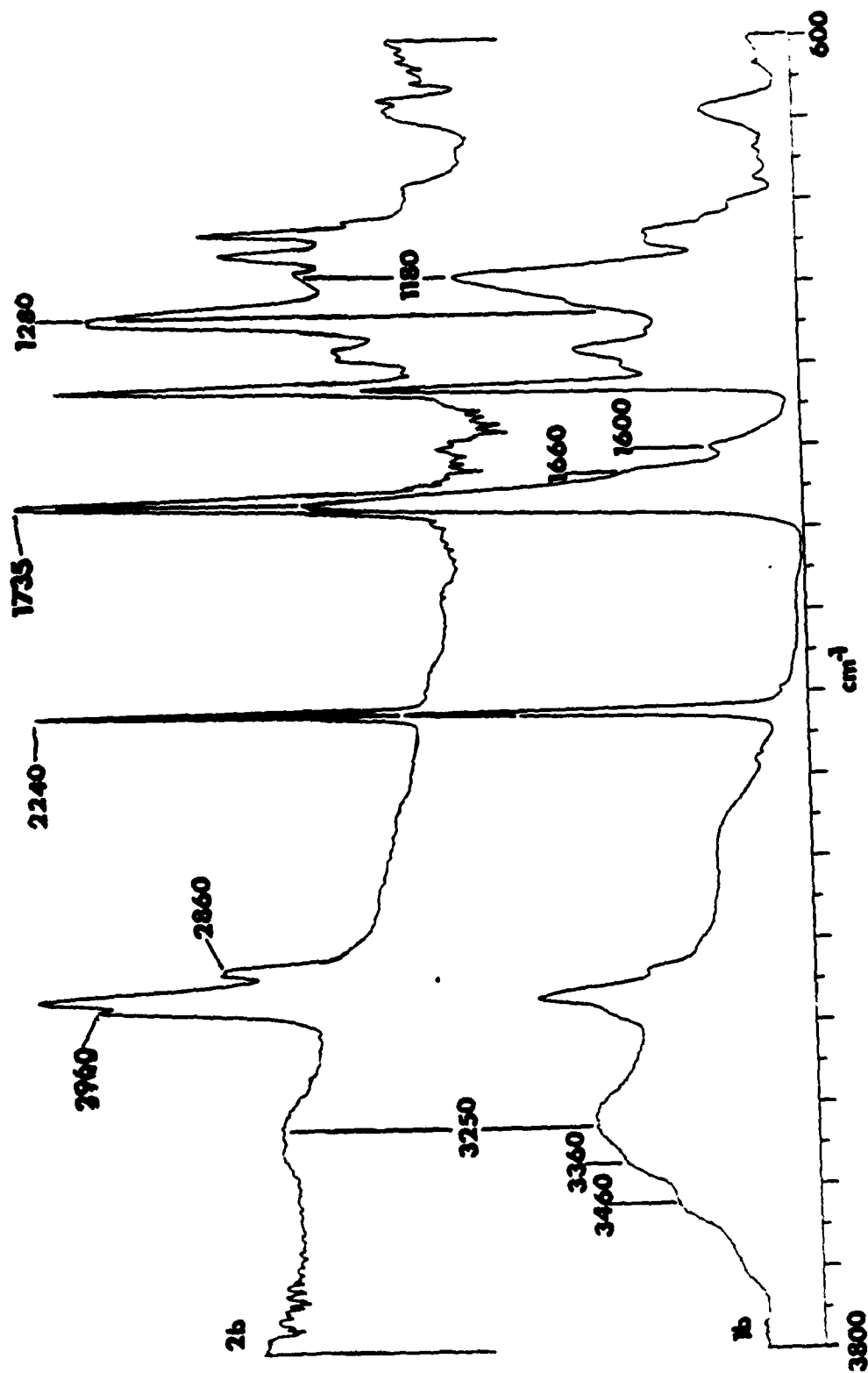
the C-O, C=O and O-H stretching vibrations of the IA units
(32). Other bands in the spectrum of copolymer 1b may be
assigned to amide groups (III). Specifically the 3460/3360
cm^{-1} doublet which is typical of the NH_2 stretching
vibrations and the bands appeareing near 1600 and 1660 cm^{-1}
which could possibly be due to a N-H bending vibration (9).
In contrast, the spectrum of copolymer 2b, suggests the
presence of a considerable concentration of methyl esters.
The presence of IR bands at 2960 and 2860 cm^{-1} may be
reasonably assigned to vibrations associated with methyl
groups (32,33). Futhermore the band at 1280 may tentatively
be assigned to the C-O-C stretching vibration of alkyl
esters.

In summary, copolymer 1b appears to be an AN/IA with
some amide groups present. On the other hand, copolymer 2b
appears to be an AN/IA copolymer containing a significant
amount of methyl esters. Given the complexity of these two
copolymers, it is not practical to obtain a quantitative
measure of the structural units present. Elemental analyses
data of the two copolymers are given in Table 1. It is
perhaps significant that the relative concentration of carbon
is greater in the AN/IA copolymer 2b which would be
consistent with the presence of methyl esters. If it is
assumed that all the nitogen is attributable to AN units (a
dubious assumption given that amide groups have been detected
in copolymer 1b) then the amount of AN units in the two
copolymers is roughly 87-90 mole%.

5.2 Thermal Degradation Studies of the AN/IA Copolymers Under Reduced Pressure.

5.2.1 AN/IA Copolymer 1b.

Figure 35 shows the FT-IR absorbance spectra of the AN/IA copolymer 1b recorded at room temperature, 130, 150, and 185°C. The most striking difference between the spectra recorded at room and elevated temperatures is the presence of the infrared bands occurring at 1780 and 1855 cm^{-1}. These two bands are confidently assigned to a 5-membered cyclic anhydrides (29,32) which may be formed as follows:
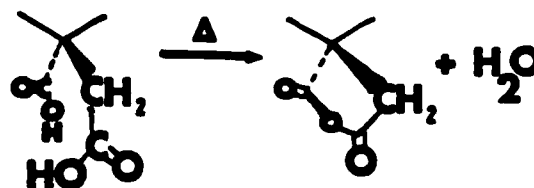
The relative concentration of these cyclic anhydrides appears to be a maximum at about 150°C. Similar bands at 1760 and 1805 cm^{-1} were seen in the spectra of the degrading AN/AA copolymers and were shown to arise from the formation of 6-membered anhydrides by the condensation of neighboring acid units. In the spectra of the degrading AN/IA copolymer, 1b (and 2b), the bands attributable to a 5-memberd anhydride suggest that a succinic anhydride type structure is formed more easily by the condensation of geminal acid groups rather than the formation of glutaric anhydrides via the condensation of nieghboring acid repeat units. Furthermore this indicates very little blocking of the IA units.

Concurrent with the formation of these cyclic anhydrides

Figure 35. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/IA copolymer 1b recorded under reduced pressure. A) room temperature; B) 130°C and D) 185°C.
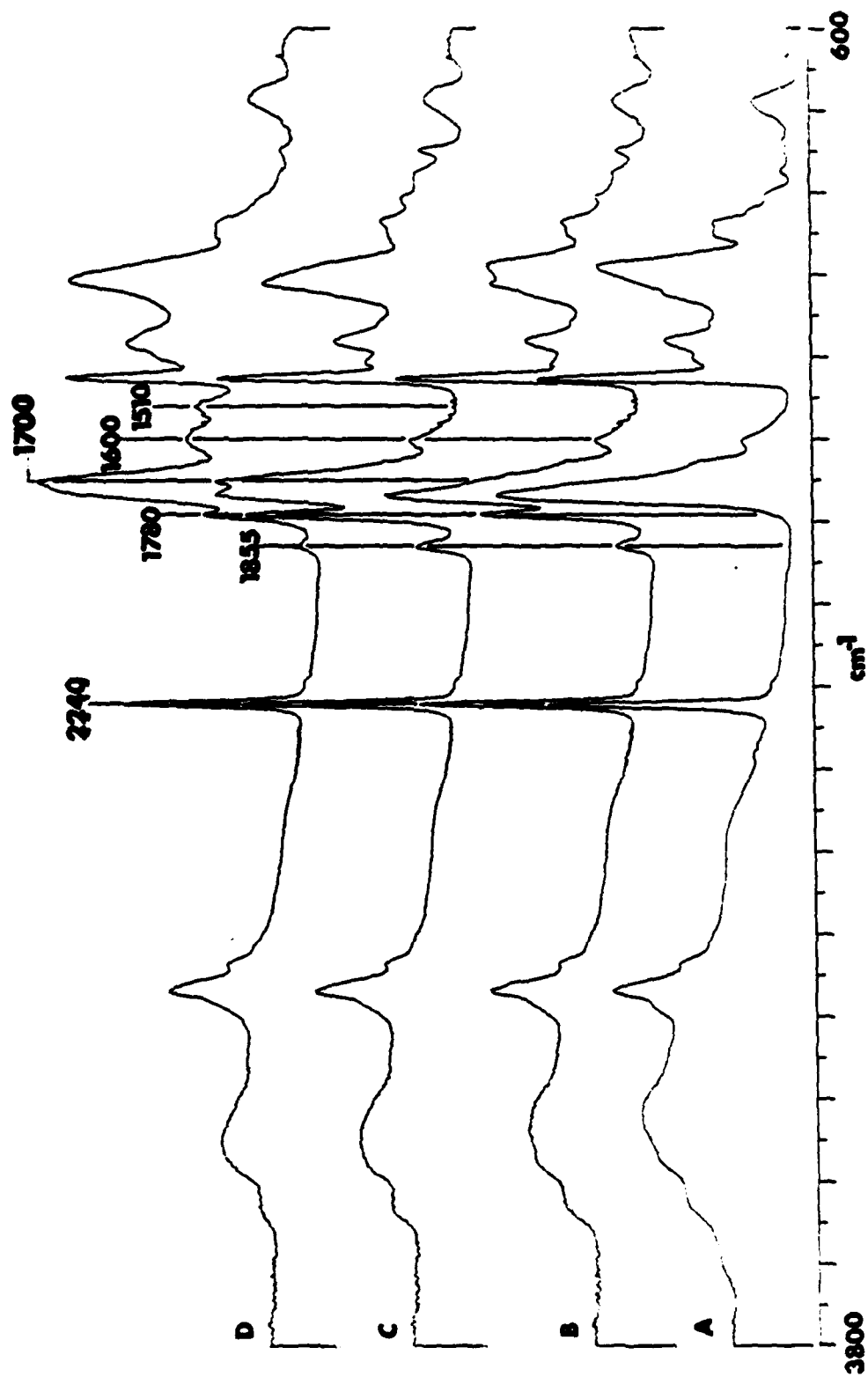
new infrared bands at 1700, 1600 and 1510 cm^{-1} are observed
which increase in intensity as the temperature is raised.
These spectral features are very similar to those seen in the
analogous AN/AA copolymers and indicates that initiation of
intramolecular cyclization has occured. Assignment of these
bands was given previously in Chapter 4.

Figure 36 shows the spectra of the same copolymer
recorded initially at 200°C and after 15 minutes, 1 and 4
hours at 200°C. A comparison of Figures 35 and 36 shows that
the relative concentration of the cyclic anhydrides is
greatly reduced at 200°C. This is somewhat surprising as
succinic anhydride type structures are known to be stable at
temperatures as high as 260°C (30). As was suggested for the
AN/AA copolymers, it appears that in the complex degradation
reactions occuring at 200°C, these anhydrides are opened and
the acids formed can initiate intramolecular cyclization.
This is supported by the concurrent large increase in the
relative intensity of the 1580/1610 cm^{-1} bands, assigned to
the pyridone structures, during heating from 185 to 200°C.
In addition, the relative intensity of the 2240 cm^{-1} band,
assigned to the nitrile group, decreases markedly during this
period. Upon heating for periods of up to four hours, little
additional information is gained with the obvious exception
that the relative concentration of nitrile groups is
decreasing.

5.2.2 AN/IA Copolymer 2b.

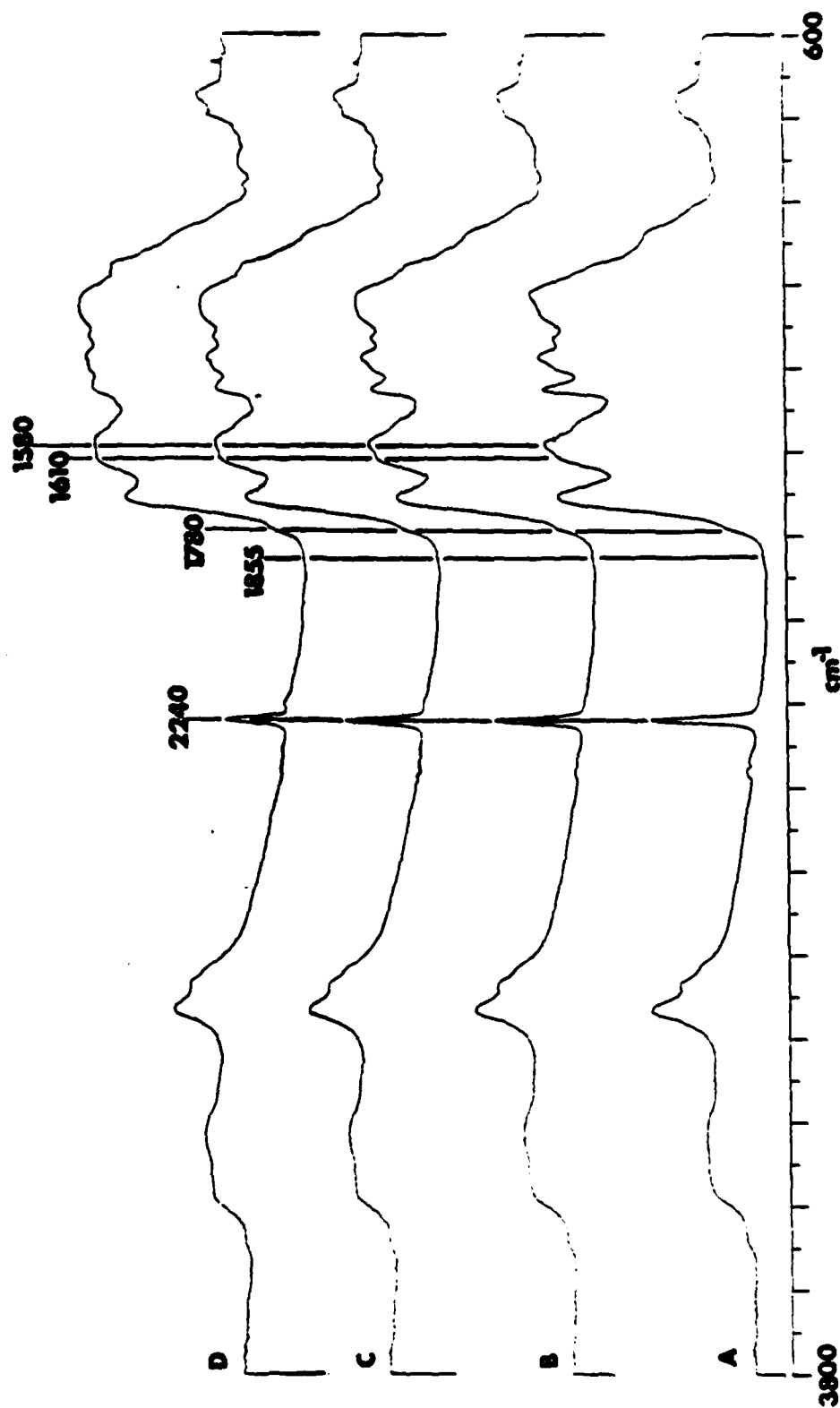It should be recalled that this copolymer is thought to

Figure 36. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/IA copolymer 1b recorded at 200°C under reduced pressure. A) initial spectrum; B) 15 minutes; C) 1 hour and D) 4 hours.

contain a significant concentration of methyl esters in addition to the AN and IA units. Figure 37 shows the FT-IR absorbance spectra of AN/IA copolymer 2b recorded at room temperature, 130, 150 and 175°C. For this copolymer the same anhydride bands at 1780 and 1855 cm^{-1} appear and decrease as seen in copolymer 1b. However, for copolymer 2b, these bands are less intense which indicates a lesser amount of anhydride formation. Another interesting difference between the spectra of this copolymer and those of copolymer 1b, is that there is no definitive evidence for the presence of the 1700, 1600 or 1510 cm^{-1} bands. This indicates that no significant initiation of intermolecular cyclization has occurred at temperatures up to 175°C.

Figure 38 shows the spectra of the AN/IA copolymer 2b recorded initially at 200°C and after 15 minutes, 1 and 4 hours. At 200°C, the presence of the 1610/1580 cm^{-1} bands is obvious, which, together with a decrease in the relative intensity of the 2240 cm^{-1} nitrile band, indicates that significant intramolecular cyclization has occurred. This trend continues as a function of time at 200°C. Significantly, the 1735 cm^{-1} band remains rather intense throughout the degradation time at 200°C which is in contrast to copolymer 1b at the same temperature. In order to explain the persistence of this band as well as the smaller amount of anhydride formation and slower initiation it must be recalled that this copolymer is rich in methyl esters. Such esters give rise to carbonyl stretching absorptions at 1735 cm^{-1}.
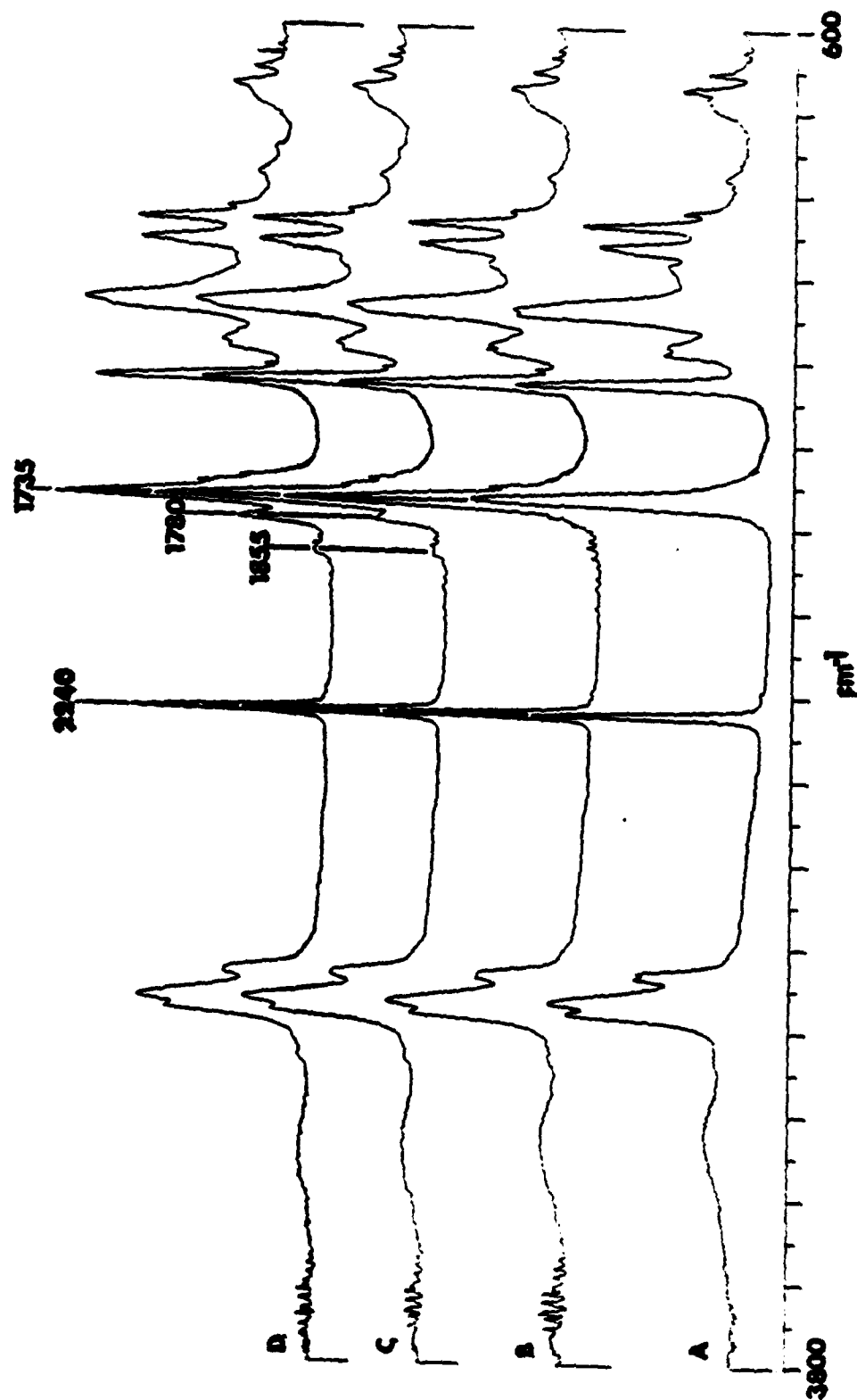
Figure 37. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/IA copolymer 2b recorded under reduced pressure. A) room temperature; B) 130°C; C) 150°C and D) 175°C.
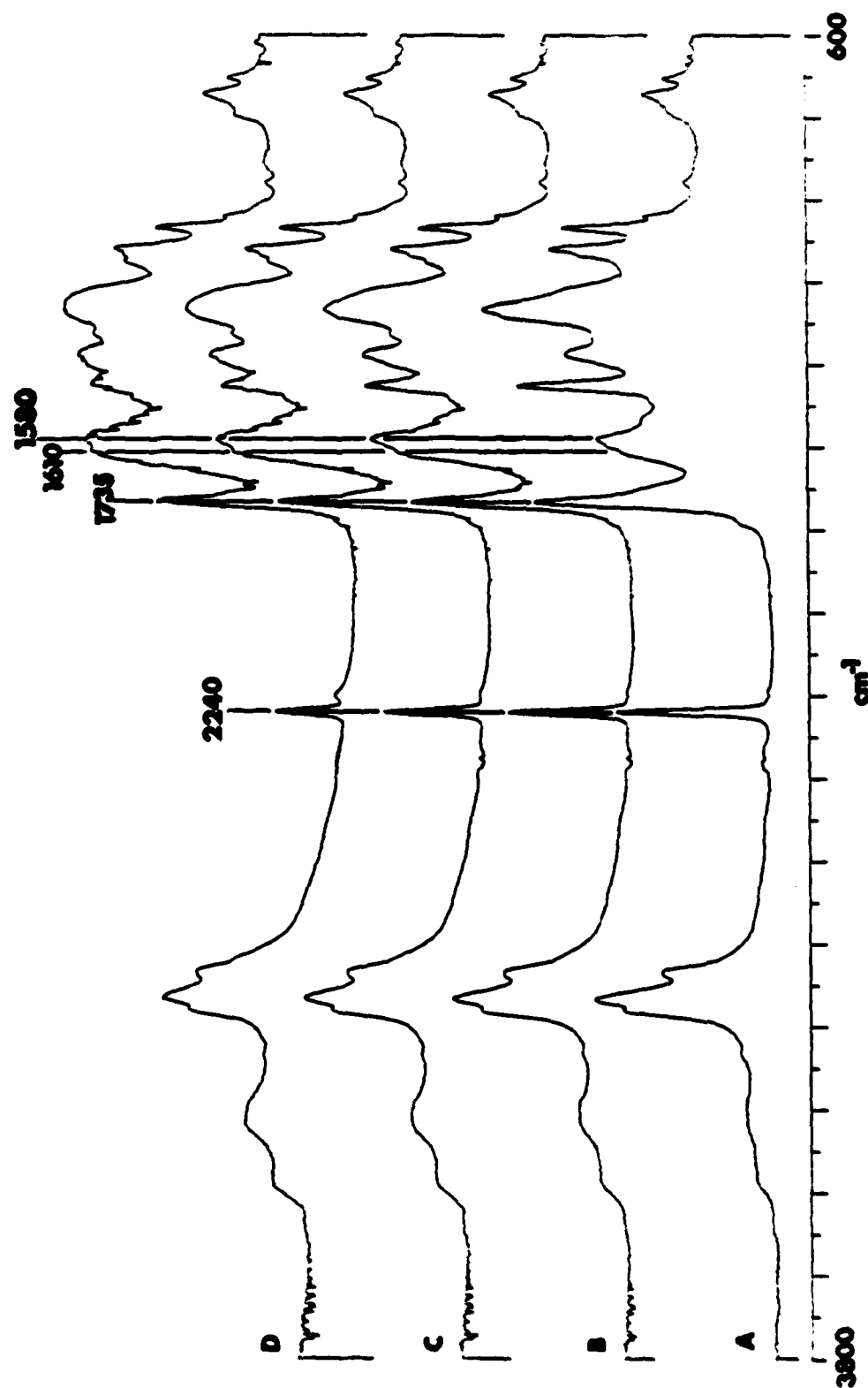
Figure 38. FT-IR absorbance spectra in the range 600-3800 cm^{-1} of the AN/IA copolymer 2b recorded at 200^{0}C under reduced pressure. A) initial spectrum; B) 15 minutes; C) 1 hour and D) 4 hours.

Apparently what is happening as degradation proceeds is that the available acid units are initiating and propagation is proceeding. The methyl esters are not capable of initiation and remain as esters. Grassie (30) has suggested that while methyl esters cannot initiate cyclization, propagation may pass through these units as shown below:
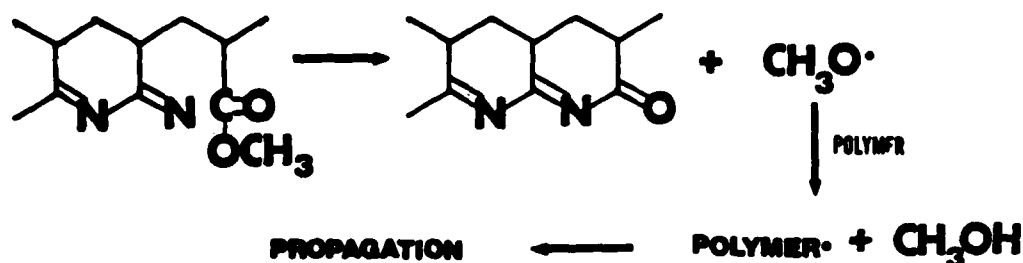
It should be mentioned that Grassie performed his experiments at temperatures well above $200^{\circ}C$ where such a reaction is possible. However, this does not seem to be the case here. The intensity of the 1735 cm^{-1} band remains reasonably constant even after 6 hours at $200^{\circ}C$. This suggests that the esters are not undergoing the reaction suggested by Grassie but serve as blocking points where intermolecular cross-linking could occur.

5.3 Rate of Degradation at $200^{\circ}C$ Under Reduced Pressure.

In common with the results given in the two previous chapters, the rate of disappearance of the nitrile groups has been plotted against time at $200^{\circ}C$. The data are shown in Figure 39. Note that, the rate curves for the two AN/IA copolymers are indeed very similar to those shown for both the AN/AM and AN/AA copolymers. Presumably, there is a sufficient concentration of either acid or amide initiation
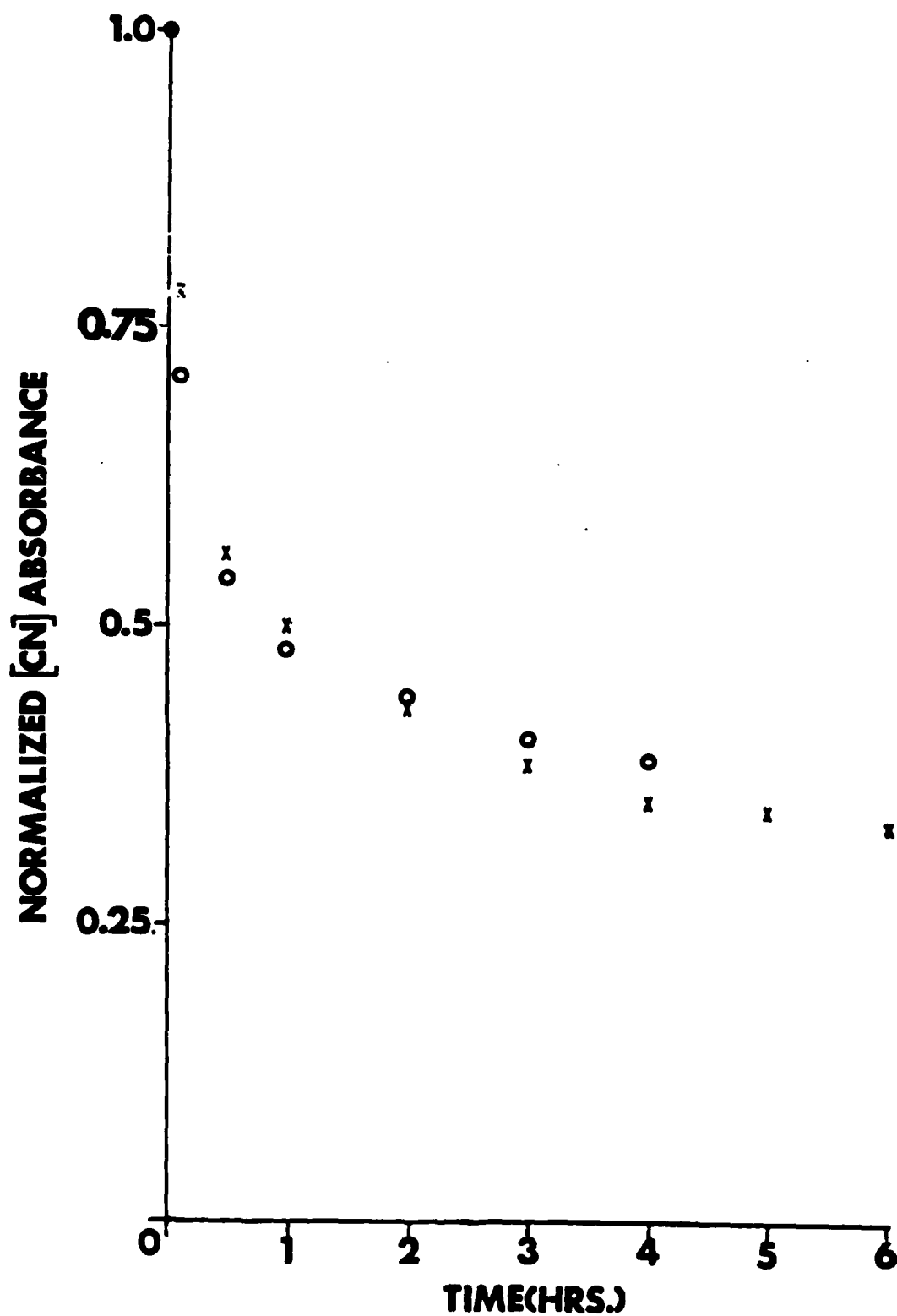
Figure 39. Normalized C≡N absorption of the AN/IA copolymer copolymers as a function of time at 200°C under reduced pressure. (○) 1b and (✗) 2b.

sites in both AN/IA copolymers to ensure rapid degradation.

5.4 Conclusions

The results obtained from this preliminary study of the AN/IA copolymers do not suggest that there are any unique features attributable to IA that would warrant futher work in this area. The premise that a vinylidene comonomer containing two reactive initiation sites would enhance the cyclization reaction appears to be unfounded.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

At the onset of this study it was originally thought that by varying the concentration of initiating comonomers in the PAN chain, a maximum amount of AN units could be cyclized, thereby leading to a superior C/G fiber. Furthermore, it was anticipated that the initiating effect of these comonomers would promote rapid cyclization of the AN units and thus minimize any detramental oxidative side reactions that occur during the preoxidation step in the production of C/G fibers.

The work presented in this thesis has demonstrated that inclusion of the comonomers AN, AA and IA into the PAN chain does increase the rate of reaction of the AN units. However, contrary to the original intent of this study, it appears that above a certain concentration of comonomers there is a limited amount of AN units that will react.

The oxidation studies of the AN/AM copolymers indicate that while cyclization is hastened, there are also a significant amount of oxidative side reactions occurring during degradation. However it is possible for the products of these side reactions to form ring systems which have the potential to yield the graphitic structure of C/G fibers. Plans for future work should include:

1) Briefly examine the air oxidation of the AN/AA copolymers. These copolymers exhibit similar degradation rates when

compared to the AN/AM copolymers. However, they may behave differently when degraded in air.

2) Examine more closely the air oxidation of all the copolymers. It has been suggested that in air, the cyclization and crosslinking of AN units are competing with elimination of HCN. Such elimination reactions may result in the formation of olefins and polyenes. GC-FT-IR could be used to detect the elimination of HCN as well as any other off-products. Resonance Raman and UV spectroscopy would be particularly useful to detect the presence of the olefins and polyenes.

3) Examine the effects of dienophiles and polyenes on the formation of C/G fibers. Perhaps the cyclization of the AN units does not lead to the formation of high strength C/G fibers. The presence of dienophiles and polyenes in the air degraded copolymers does offer the potential for ring systems which could more easily lead to a graphitic structure. These initial rings are formed by a Diels-Alder reaction. Materials capable of polyene and dienophile formation such as polyvinylchloride should by examined under reduced pressure and in air.

4) Preparation of C/G fibers. Should any of the work suggested above appear promising, plans for the actual preparation and testing of resulting fibers should be made.

APPENDIX

DESCRIPTION OF COMPUTER PROGRAM

The computer program used to calculate the extent of reaction of the AN units upon thermal degradation of the AN/AM copolymers was written by Dr. R.W. Snyder for the Apple II Plus minicomputer containing 48K of memory. The assumptions described previously in Model IV, the so-called step-ladder model, were incorporated into the program. The program is designed to consider a hexagonal array consisting of a primary chain surrounded by six secondary chains. These secondary chains are, in turn, each surrounded by six further chains. This is depicted in Figure 1. In essence, the computer program calculates the fraction of AN units reacted in the primary chain after initial intramolecular cyclization followed by intermolecular crosslinking and subsequent intramolecular cyclization generated from the secondary chains.

(1) Generation of Polymer Chains.

From the comonomer composition (i.e. molar % AM) and assuming probabilities for isotactic (I) and syndiotactic (S) AN placements of 0.48 and 0.52 respectively, the computer randomly generates a primary and six secondary chains each containing 450 units (the limit of the computer memory) and these are stored in a matrix. Thus chains of 450 units (equivalent to a molecular weight of approximately 22,500) resembling -ISIIIAISSIISISASIS- are generated.

(2) Initial Intramolecular Cyclization.

For each chain, the computer searches for the position of the AM (A) units. If the A units are adjacent to an I unit in either direction of the chain the I's are changed to R's (denoting ring formation) and the A's to X's (denoting reaction of the AM units). Similarly, any I units adjacent to the propagating ring structure are also changed to R's. If the A units or the propagating ring structure (R) are adjacent to a S unit the sequence is stopped. This information is stored in the matrix. The extent of reaction of the AN units, which represents the initial intramolecular cyclization step, is calculated for the primary chain (i.e. the number of I's changed to R's over the total number of original I and S units).

(3) Intermolecular Crosslinking From The Six Secondary Chains.

The computer now searches the six secondary chains for AM units that have not reacted (those which have not been changed to X's; e.g. in sequences such as -SAS- etc.). These units are assumed to have the potential of reacting (crosslinking) to the primary chain. In addition, the computer also searches for blocks of cyclized units in the secondary chains of the type -S(R) X(R) S- . The R units immediately adjacent to the S units in either direction of the chain have reactive sites and can potentially crosslink to the primary chain.

The position of the A units or reactive R units in the

secondary chains are designated (n,m) in the matrix, where n =(1 to 450) is the number of units in the chain, and m= (2 to 7) is the number of secondary chains. If the corresponding position in the primary chain, (n,1), is an I or S unit then crosslinking is assumed to be feasible. however, the restriction that crosslinking cannot occur to an I or S unit that is immediately adjacent to a block of initially cyclized sequences (i.e. at positions n-1,1 or n+1,1) has been included. The rationale for this restriction is based on the belief that these positions will be severely sterically hindered. Frankly, this restriction does not make a significant difference to the overall result.

Once it has been determined that crosslinking to an I or S unit can occur, a non-stereospecific reaction, the I or S unit of the primary chain is changed to C (denoting a crosslinked unit). This is repeated for all six secondary chains.

(4) Intramolecular Cyclization Of The Primary Chain Resulting From Intermolecular Crosslinking.

The crosslinked unit C is reactive and can now initiate intramolecular cyclization in one direction down the chain if it is adjacent to an I unit. Using a random number generator, the computer randomly selects a direction (right or left) and determines whether or not the adjacent unit is an I unit. If it is, this unit is changed to an R. Similarily, if the next unit in the same direction is an I this is also changed to a R. This procedure is continued

until a S unit is encountered. If upon selecting the direction, the computer encounters an S unit immediately adjacent to the C unit, the other direction is considered in a similar manner. The computer now once again calculates the fraction of AN units that have reacted.

(5) Effects Of Tertiary Chains.

Especially in the case of chains containing a low concentration of AM units (i.e. < 10%) it is necessary to consider crosslinking occurring from tertiary chains to secondary chains. This will lead to further reactive sites on the secondary chains that have the potential to crosslink to the primary chain. In turn these crosslinked sites may then initiate further intramolecular cyclization of the primary chain.

In order to simplify the problem, the computer considers each secondary chain in turn and operates steps (3) and (4) with six new generated chains. In effect this means the computer generates a total of 43 random chains. Once this procedure has been completed, the secondary chains, which may now be considered pseuo-primary chains, now operate on the primary chain in a manner similar to that described in steps (3) and (4). The final fraction of AN units that have reacted in the primary chain is now calculated.

The computer time taken for each run is approximately 40 mins. A total of ten runs was performed for each copolymer composition and the results were averaqed.

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