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PENNSYLVANIA STATE UNIV UNIVERSITY PARK APPLIED RESE--ETC F/G 11/9
FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDIES ON THE THERMAL--ETC(U)
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FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDIES
ON THE THERMAL DEGRADATION OF POLYACRYLONITRILE
COPOLYMERS

George T. Sivy

Technical Memorandum
File No. TM 80-227
November 21, 1980
Contract No. N00024-79-C-6043

Copy No. 5

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TM 80-227	2. GOVT ACCESSION NO. AD-A093270	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDIES ON THE THERMAL DEGRADATION OF POLYACRYLONITRILE COPOLYMERS.		5. TYPE OF REPORT & PERIOD COVERED MS Thesis, March 1981
7. AUTHOR(s) George T. Sivy		6. PERFORMING ORG. REPORT NUMBER TM 80-227
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Pennsylvania State University Applied Research Laboratory P. O. Box 30, State College, PA 16801		8. CONTRACT OR GRANT NUMBER(s) N00024-79-C-6043
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Sea Systems Command Department of the Navy Washington, DC 20362		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1122 NOV 80
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 1122 AB / PSC/TM-80-227		12. REPORT DATE November 21, 1980
		13. NUMBER OF PAGES 81 pages & figures
		15. SECURITY CLASS. (of this report) Unclassified, Unlimited
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited, per NSSC (Naval Sea Systems Command), 1/12/81		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) thesis, polymer, degradation, fourier, transform, infrared, spectroscopy		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Poly(acrylonitrile) (PAN) and copolymers of PAN containing comonomers of vinyl acetate (VAc), methacrylic acid (MAA), acrylamide (AM) and other acrylics are important precursors to the formation of carbon fibers. Fourier transform infrared spectroscopy has proved to be an excellent technique with which to study the degradation of these polymers in the initial stages where cyclization of the polymer chain takes place. A comparison of the rates of degradation of each of these copolymers at various temperatures and under		

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S/N 0102-LF-014-6601

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT (continued)

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ABSTRACT

Poly(acrylonitrile) (PAN) and copolymers of PAN containing comonomers of vinyl acetate (VAc), methacrylic acid (MAA), acrylamide (AM) and other acrylics are important precursors to the formation of carbon fibers. Fourier transform infrared spectroscopy has proved to be an excellent technique with which to study the degradation of these polymers in the initial stages where cyclization of the polymer chain takes place. A comparison of the rates of degradation of each of these copolymers at various temperatures and under reduced pressure is presented. This comparison indicates that each comonomer initiates cyclization of the nitrile groups, with the MAA and AM comonomers actually lowering the temperature at which the cyclization reaction occurs. Degradation mechanisms for each copolymer, consistent with the infrared results obtained under reduced pressure, are advanced.



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ACKNOWLEDGEMENTS

The author would like to express his sincere appreciation to Dr. Michael M. Coleman for his valuable advice, encouragement and patience throughout this investigation. In addition the author would like to thank Dr. Paul C. Painter for his stimulating discussions and suggestions.

The acrylonitrile copolymers provided by Dr. S. Olive of the Monsanto Company are gratefully acknowledged. Finally, the financial support by the Applied Research Laboratory of The Pennsylvania State University under contract with the Naval Sea Systems Command is gratefully acknowledged.

INTRODUCTION

A. Importance and Production of Carbon Fibers

Carbon fibers, commercially important because of their very high strength to weight ratio, are used extensively as reinforcing fibers in epoxy and other resins. Since the fibers were first introduced in the mid 1960's, the price has dropped from \$300 per pound to \$20 per pound (1). This dramatic price reduction is attributed to the ease of production from poly(acrylonitrile) (PAN) precursors. The transition of white PAN fibers to black carbon fibers involves three processes (2). In the first process, PAN fibers are heated at 220°C in air or under N₂ for several hours. It is believed that at these temperatures cyclization of the pendant nitrile groups occurs yielding a stabilized ladder type polymer. The following two processes involve the elimination of non-carbon atoms at 1500°C and then at 3000°C to yield the final graphite crystal structure of carbon fibers. Since the first process involves the initial ring formation, and therefore a more continuous network for carbonization, it would be most advantageous to understand the mechanism of formation and structure of the product obtained.

Commercially, PAN fibers often contain low concentrations of a comonomer as a consequence of impurities during polymerization or reaction of nitrile groups with oxygen. However, comonomers are often purposely copolymerized into the PAN chain to aid in the

dye-ability or solubility of the textile fibers (3). The possibility of using such copolymers as precursor material has received considerable attention over the past decade. Thermal studies performed on copolymers of Methacrylic acid (MAA), Acrylamide (AM), Methylmethacrylate (MMA), and Amideoxime demonstrate that the rate of cyclization is influenced by the type of comonomer present.

B. Use of FTIR for Degradation Studies

Several analytical methods have been employed to study the thermal degradation of PAN. Techniques such as Thermal Volatilization Analysis (TVA), and Differential Thermal Analysis (DTA), have provided some data concerning the rate of degradation of PAN and PAN copolymers. However, the temperatures used in these techniques are usually well above the 220°C temperature used in fiber production. Furthermore, neither of these techniques can give direct information concerning the structure of the degraded product.

Infrared spectroscopy has also been used to examine the thermal degradation of PAN and copolymers. The spectra obtained on conventional dispersive infrared spectrometers tend to be very broad and poorly resolved due to the color change from white to black as pyrolysis time is increased. However, taking advantage of the high-energy throughput of Fourier transform systems, coupled with signal averaging capabilities, excellent quality spectra of the optically dense degraded product may be obtained (4). With such spectra the structure of degraded PAN

and PAN copolymers may be ascertained and some information concerning the cyclization kinetics can be obtained.

C. Review of the Thermal Degradation of PAN Homopolymer

Many mechanisms have been suggested in order to explain the reactions occurring during the thermal degradation of PAN homopolymer. A majority of these mechanisms include the following reaction sequence (3): (1) cyclization of pendant nitrile groups yielding a ladder type polymer, (2) dehydrogenation reactions occurring along the polymer backbone and in the condensed rings, and (3) oxygen uptake leading to a variety of functional groups.

Recently Coleman and Petcavich (5) using FTIR spectroscopy have shown that at temperatures of 200°C and under reduced pressure PAN homopolymer degrades to yield pyridone type structures via the mechanism depicted in Figure (1). This type of structure [5] results from the imine-enamine tautomerism and subsequent O₂ stabilization of the conjugated azadiene structure [3] proposed by Grassie, et al. (8). Major FTIR bands at 1610 and 1580 cm⁻¹, being assigned to C = O and C = C stretching frequencies, are consistent with the pyridone structure. Furthermore, hydrogen bonding between the amino hydrogen and the C = O group would impart rigidity along the polymer chain and thus conserve a uniform structure throughout the high temperature carbonization processes.

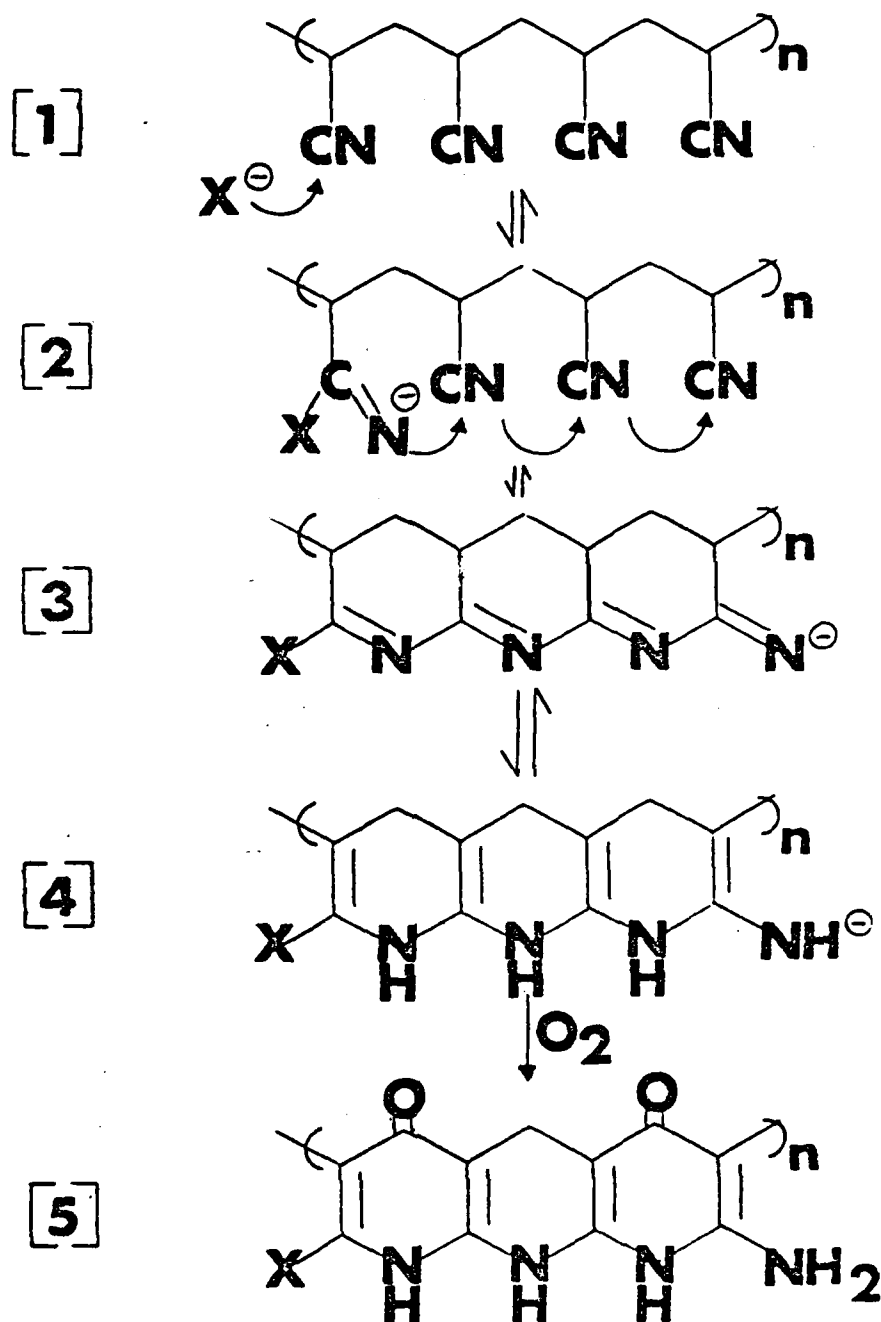


Figure 1. Scheme depicting the chemical reactions occurring during the degradation of PAN at 200°C under a reduced pressure of 5×10^{-2} torr.

From U.V. data (9) it has been suggested that a maximum of four nitrile units are cyclized for each initiation site. The exact nature of the initiation step is not well understood. However, as previously mentioned, inclusion of certain comonomers into the PAN chain has been shown to enhance the rate of degradation.

D. Degradation of Some Representative PAN Copolymers

Degradation mechanisms have been proposed for a variety of PAN copolymers. These mechanisms can be classed into three categories:

- (1) Those in which the comonomers initiate cyclization and are themselves incorporated in the final stabilized product;
- (2) The comonomer slows cyclization by permitting the propagating species to pass through it, and
- (3) The comonomer completely blocks cyclization.

Category 1

1. Carboxylic Acid Comonomers

Grassie and McGuchan (10) have shown that carboxylic acid comonomers are not eliminated during degradation but are incorporated in the stabilized product. Furthermore a lowering of the initial temperature at which cyclization occurs indicates an initiating effect.

The chemistry involved in this initiating effect is believed to follow classic acid-nitrile reactions (10) which are known to result in the formation of imidic structures (11). Therefore the first product formed in the case of acrylic acid copolymers would be a glutarimide type structure [6].

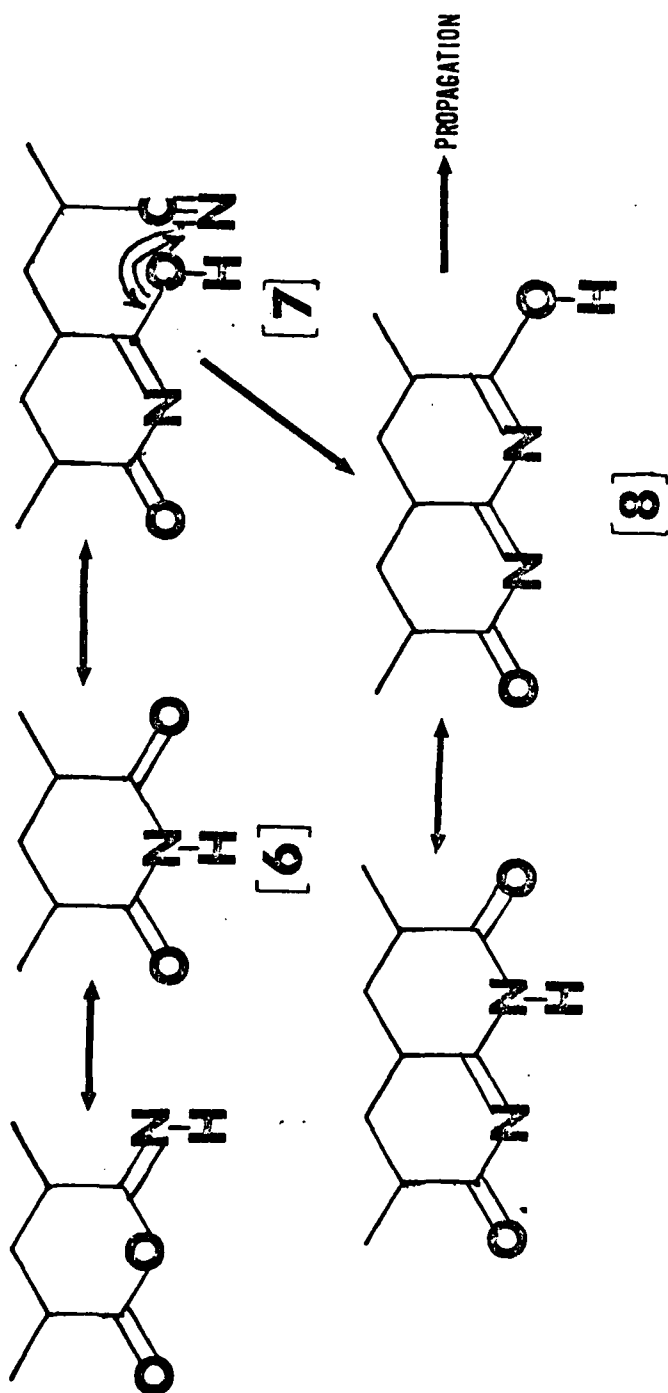
Propagation may then proceed via tautomeric forms of the imide as shown in Scheme 1. An alternative mechanism, based on FTIR data will be suggested later.

2. Acrolein Comonomers

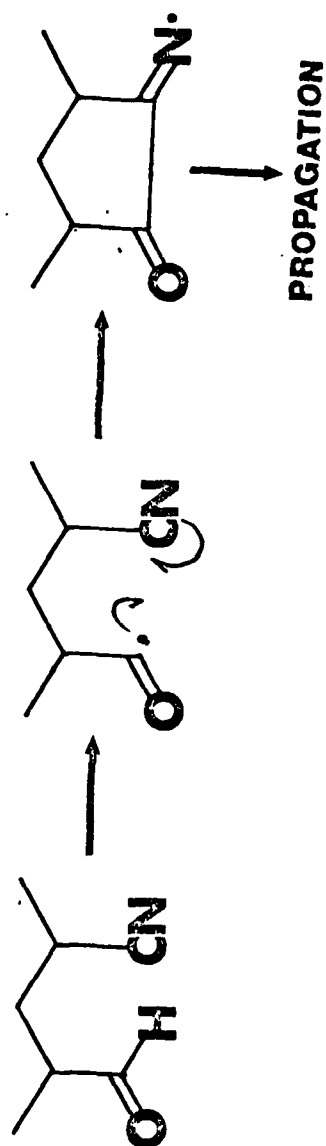
The nature of this comonomer suggests the elimination of formaldehyde followed by immediate decomposition to CO and H₂ (12). However, this does not seem to be the case since no large amount of noncondensable material (CO + H₂) is detected (13). Furthermore the elimination of the carbonyl stretching frequency in the IR spectrum of this copolymer suggests the acrolein units are incorporated in the stabilized product. Grassie and McGuchan (13) have suggested homolytic cleavage of the C - H bond yields initiating radicals as shown in Scheme 2.

While this mechanism explains the TVA data, it is not satisfactorily consistent with IR data. The presence of a shoulder at 2750 cm⁻¹ suggests that an aldehydic type structure is still present. This type of structure would result from an elimination and subsequent reaction of formaldehyde as shown in Scheme 3.

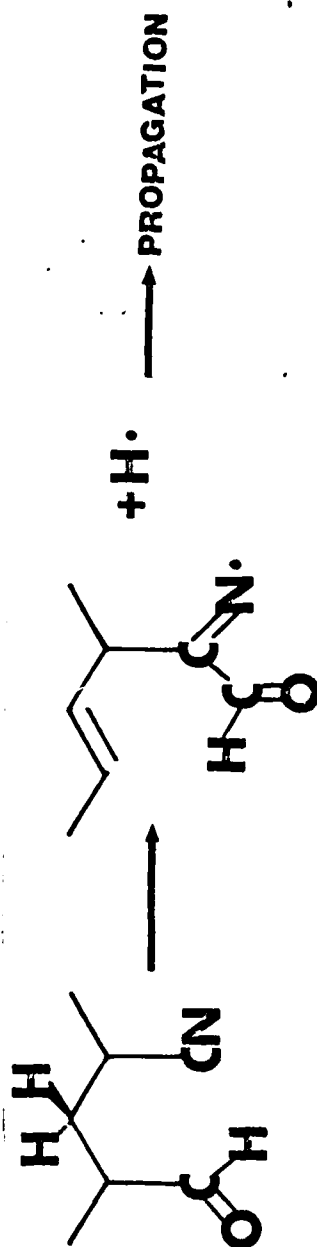
Furthermore an IR band at 810 cm⁻¹, indicative of a 1,1,2-trisubstituted olefinic structure (14) suggests that some



Scheme 1



Scheme 2



Scheme 3

oxidative-dehydrogenation has occurred. This dehydrogenation is more likely to occur if the β -hydrogen of a nitrile group is in an allylic position. This would be the case if formaldehyde elimination had occurred (Scheme 4). This type of mechanism is similar to that proposed by Conley and Bieron (15) for PAN homopolymer

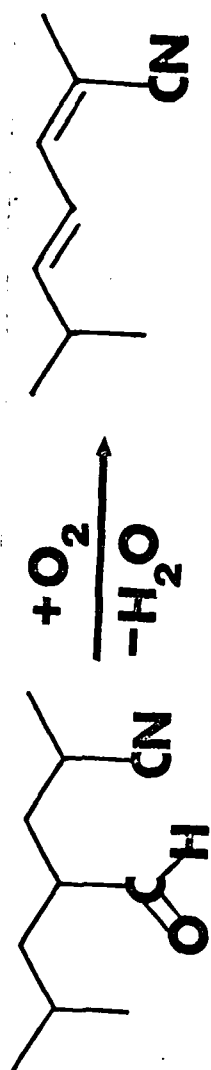
3. Amideoxime Comonomers

The most interesting feature of this comonomer is its very low weight loss. The low weight loss is attributed to the increased amount of cyclization over the heating range due to the very low initiation temperature. It is believed that a concerted mechanism involving stepwise migration of the hydroxyl group is responsible for initiation (Scheme 5) (10).

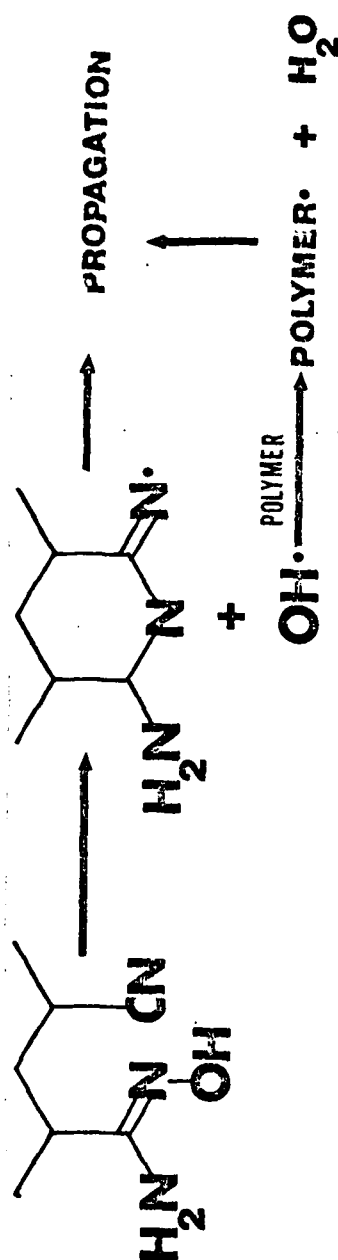
This mechanism also accounts for the elimination of H_2O . While the hydroxyl radical may migrate it is still free to abstract a hydrogen from a polymer chain.

4. Acrylamide Comonomers

PAN copolymers containing acrylamide exhibit DTA behavior similar to pure PAN. Grassie (10) has shown that only a small amount of the AM units have reacted with each other to produce NH_3 . However, IR changes show that the AM units are completely eliminated during the exotherm. Therefore, it is believed that the comonomer is incorporated in the final stabilized product. A free radical mechanism has been suggested (10) in which homolytic cleavage of the C - N bond of the AM unit yields initiating radicals as shown in Scheme 6.



Scheme 4



Scheme 5



[9]

Scheme 6

It will later be shown that the initiation reaction involved for this copolymer requires an induction period. A mechanism to account for this reaction will also be suggested.

5. Benzyl Acrylate Comonomers

The normal degradation product of pure poly(benzyacrylate), benzyl alcohol (16), is not detected during the copolymer degradation. Instead toluene is eliminated. This suggests the elimination of benzyl radical followed by hydrogen transfer (17) as shown in Scheme 7.

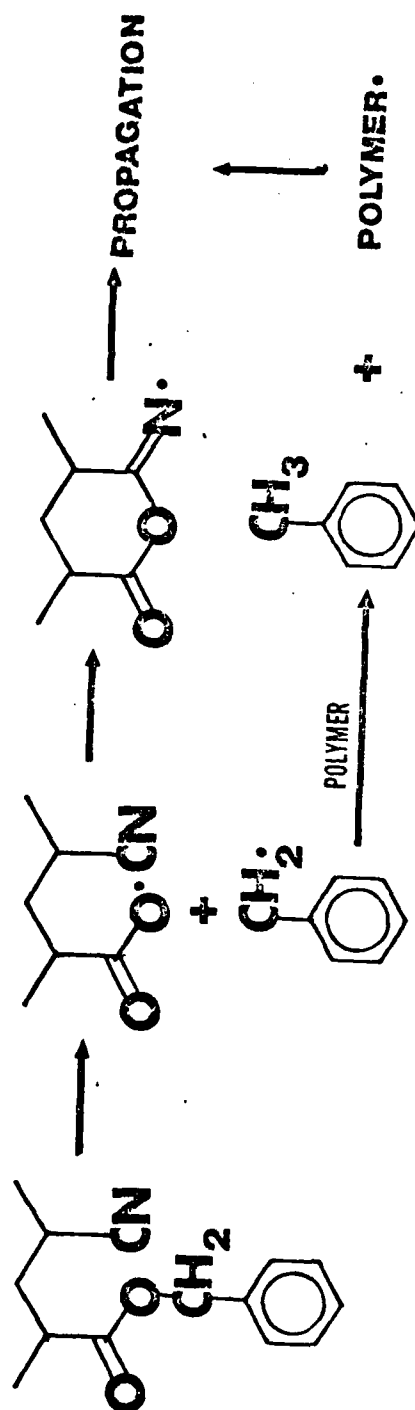
The splitting out of the benzyl radical is believed to be due to steric crowding from the nitrile groups thus causing a weaker C - O bond. Furthermore, the presence of benzyl radicals accounts for observed lowering of the initiation temperature.

Category 2

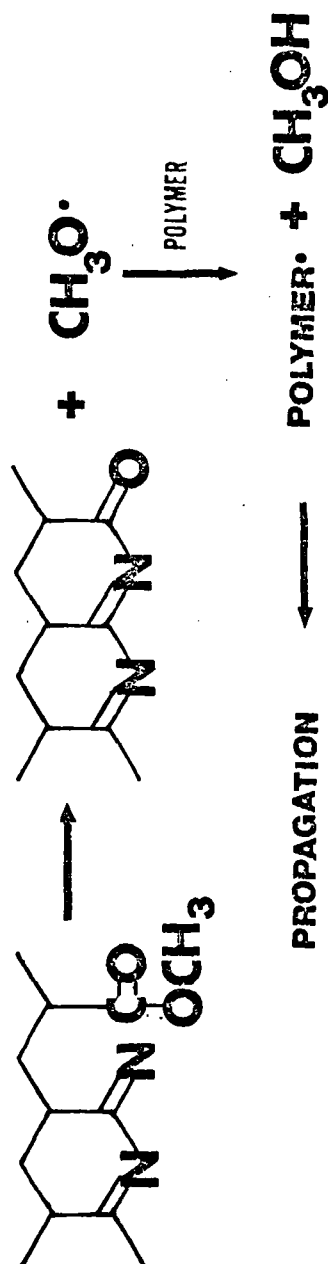
1. Alkyl Acrylate Comonomers

While low alkylacrylates (methyl, ethyl, etc.) have less of an initiating effect than benzyl acrylate, the presence of a DTA exotherm coupled with the evolution of methanol, indicates that a propagating species can pass through acrylate units. Grassie (17), has suggested that the process of passing through acrylate units introduces a slow step shown in Scheme 8.

Unlike benzyl acrylate, there is very little steric strain on the ester linkage. Therefore initiation via elimination of alkyl radical seems unlikely.



Scheme 7



Scheme 8

The evolution of monomer, CO, and CH₄ from alkyl acrylates (especially alkyl methacrylates) suggests that the comonomer can react in another way shown in Scheme 9.

Category 3

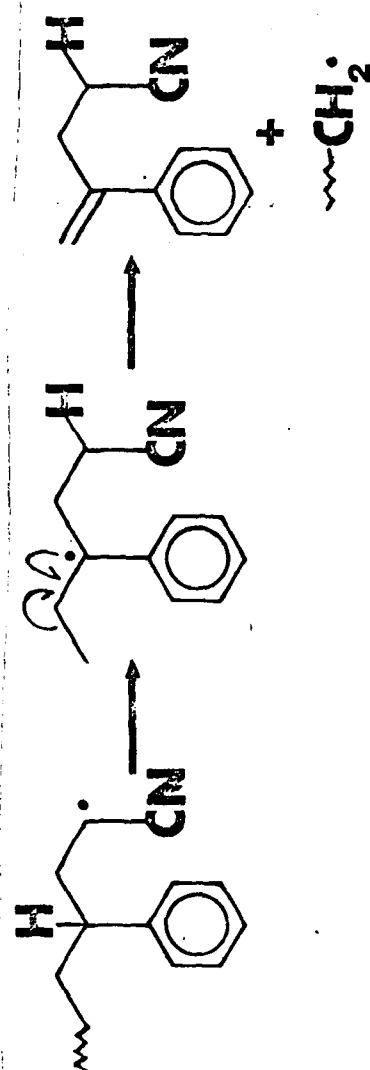
1. Styrene Comonomers

While the previous copolymer systems (with the exception of high acrylate concentrations) have an initiating effect on cyclization, styrene monomer has been found to block cyclization. Increased chain fragmentation also results from the relatively weak ST - AN bond (18). The chain fragments present, particularly at high styrene concentrations, consist mainly of short sequences of styrene-acrylonitrile terminated oligomers. This is due to the fact that an AN terminated radical is very likely to undergo intramolecular transfer to the nearest styrene unit (18) as shown in Scheme 10.

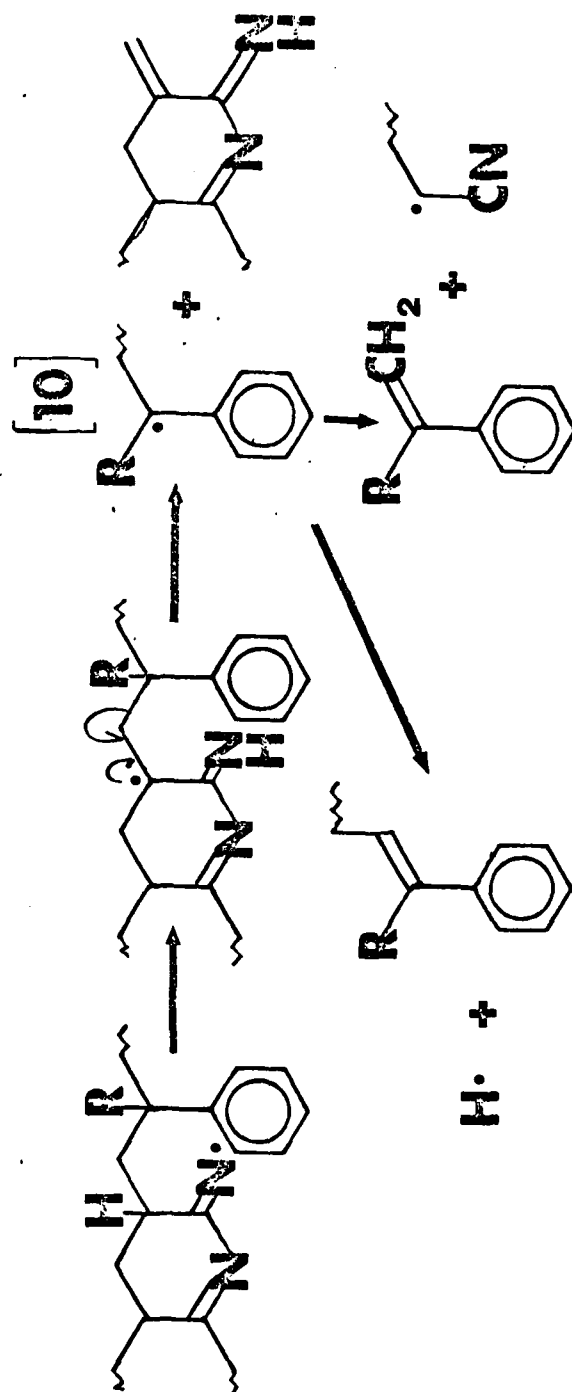
The blocking effect displayed by styrene is believed to result from deactivation of a propagating nitrile radical by transfer to a relatively stable comonomer radical (10) as shown in Scheme 11.

The radical stability of structure [10] would then inhibit further cyclization.

The above mechanisms have been based on data obtained from various thermal analysis techniques (DTA, TVA, GC-MS, etc.) and conventional dispersive IR. By employing the advantages of FTIR previously mentioned it is possible to monitor subtle spectral changes during the degradation of PAN copolymers. The remainder



Scheme 10



Scheme 11

of this thesis will deal with FTIR data obtained for PAN copolymers of Methacrylic Acid (MAA), Acrylamide (AM), and Vinyl Acetate (VAc), each at a concentration of 4% by weight.

EXPERIMENTAL

A. Sample Preparation

The polymers used in this study were kindly supplied by Dr. S. Olive of the Monsanto Company. The PAN homopolymer has been described previously (5). Copolymers of acrylonitrile containing approximately four weight percent of MAA, AM and VAc were synthesized by a continuous free radical polymerization technique and have reported weight-average molecular weights in the range of $100,000 \pm 20,000$ (Monsanto Company).

Thin films (<0.5 mil) employed for the FTIR degradation studies were prepared by evaporation of a 3% dimethylsulfoxide solution. Excess solvent was removed by stirring in water for several days and subsequently dried under high vacuum. The films were then transferred to KBr discs and placed in a specially designed cell contained in the spectrometer which allows continuous monitoring while under reduced pressure at elevated temperatures. Temperature control ($\pm 2^\circ\text{C}$) was attained using a Specac automatic temperature controller.

For deuteration studies of PAN/MAA samples the following procedure was adopted. A film of the PAN/MAA copolymer was degraded for six hours at 130°C under a reduced pressure of 5×10^{-2} torr in the special infrared cell contained in the FTIR spectrometer. This film was then quenched to room temperature, removed from the cell and placed in D_2O at 80°C for 20 hours.

After drying in vacuum in the infrared cell the spectrum of the exchanged sample was recorded at room temperature.

B. Instrumentation

The infrared spectra were recorded on a Digilab model FTS-15/B FTIR spectrometer. Each spectrum was recorded at a resolution of 2 cm^{-1} utilizing 128 scans. The frequency scale is accurate to 0.02 cm^{-1} . Particular care was made to ensure that the films were sufficiently thin to be in a range where the Beer-Lambert Law is obeyed (4).

RESULTS AND DISCUSSION

A. Comparison of Degradation Rates

Room temperature absorbance infrared spectra of undegraded PAN, PAN/VAc, PAN/AM and PAN/MAA are presented in Figure 2. Of particular interest are the major infrared bands characteristic of the acrylonitrile unit in the polymer chain at approximately 2240 ($\text{C} \equiv \text{N}$ stretching frequency), 1451 (CH_2 bending frequency), 1360, 1250 and 1070 cm^{-1} (mixed modes). Major infrared bands characteristic of the comonomers present in each of the three copolymers studied are as follows:

PAN/VAc - 1735 cm^{-1} C = O stretching mode of the acetate group.

PAN/AM - 1740 cm^{-1} Mixed modes containing contributions of the C = O, C - N stretching and
 1685 cm^{-1} N - H bending modes of the acrylamide group.
 1605 cm^{-1}

PAN/MAA - 1730 cm^{-1} C = O stretching mode of the acrylic group.

Figure 3 shows the initial absorbance infrared spectra of the four polymers obtained as soon as the samples had attained a temperature of 200°C under a reduced pressure of 5×10^{-2} torr (approximately 10 minutes). It is immediately apparent from a comparison of the room temperature spectra and these initial spectra that the PAN and PAN/VAc polymers show no significant degradation as indicated by the absence of bands at 1610 and 1580 cm^{-1} which are characteristic of degraded PAN. The spectrum

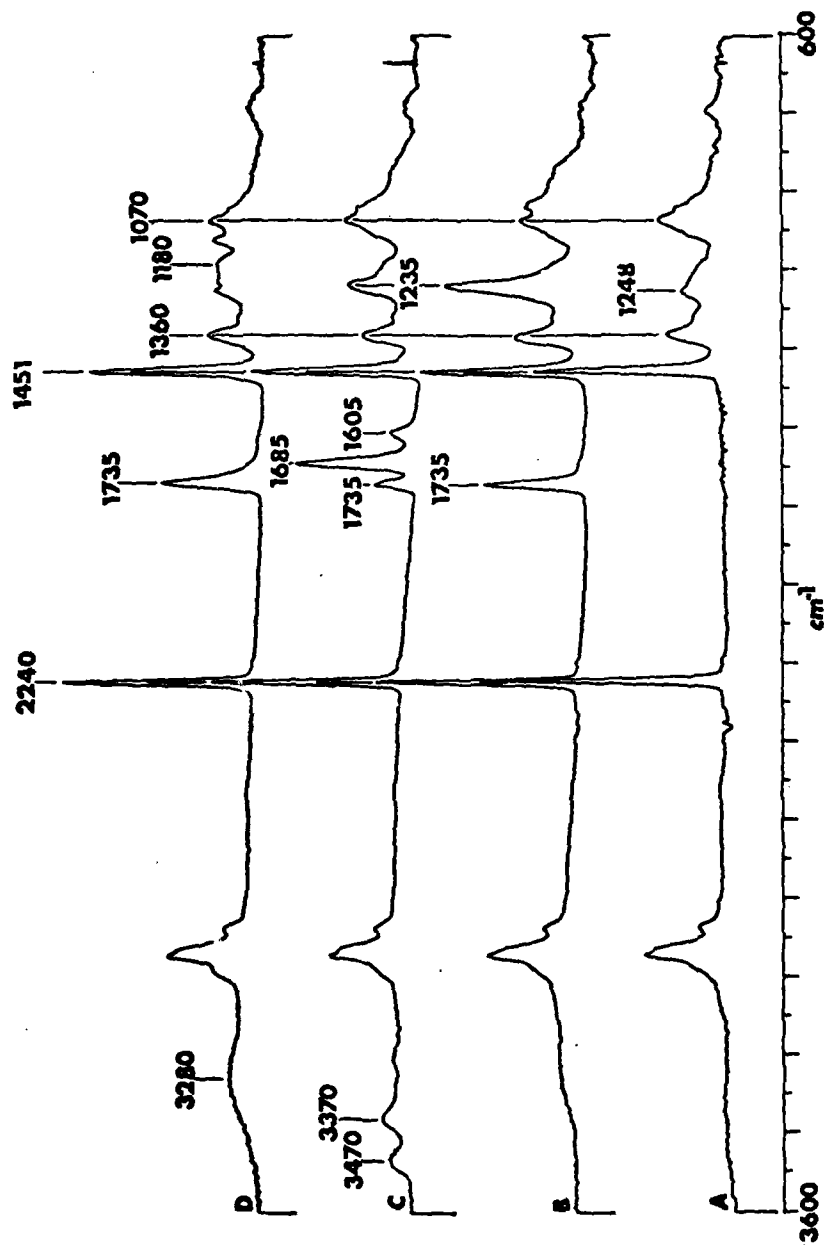


Figure 2. FTIR absorbance spectra in the range 600 - 3600 cm^{-1} recorded at room temperature. A) PAN homopolymer; B) PAN/VAc copolymer; C) PAN/AM copolymer and D) PAN/MAA copolymer. Each of the copolymers contains approximately four weight percent of the comonomer VAc, AM and MAA respectively.

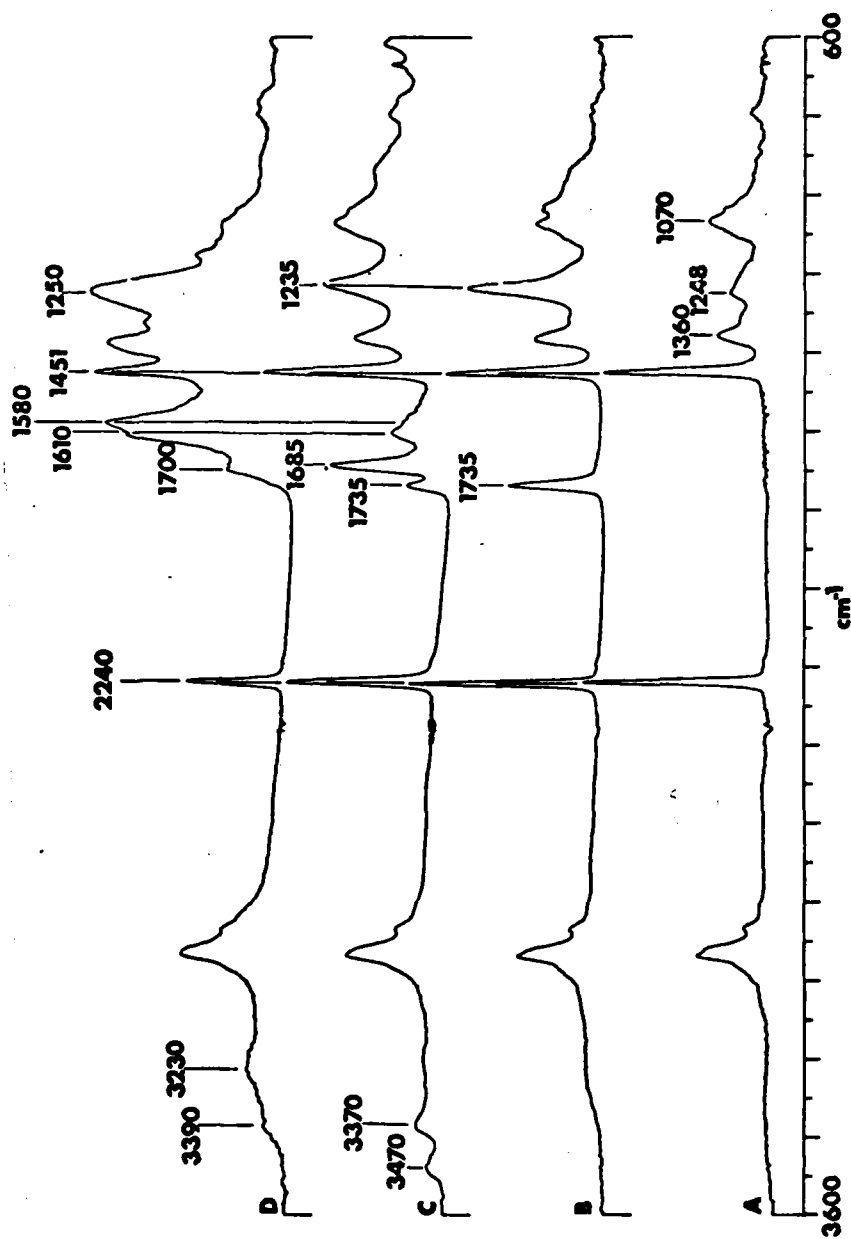


Figure 3. Initial FTIR absorbance spectra in the range 600 - 3600 cm^{-1} recorded as soon as the sample attained 200°C under a reduced pressure of 5×10^{-2} torr. A) PAN; B) PAN/Vac; C) PAN/AM and D) PAN/MAA.

of the PAN/AM copolymer does indicate that minor degradation has occurred. In contrast, the PAN/MAA copolymer has obviously degraded quite extensively (note the presence of the relatively strong 1610 and 1580 cm^{-1} bands which are not present in the room temperature spectrum; the shifting of the C = O stretching band to 1700 cm^{-1} and the reduction in intensity of the C $\equiv$ N stretching frequency at 2240 cm^{-1}).

After four hours at 200°C (Figure 4) the presence of the cyclized pyridone structure in the PAN homopolymer is indicated by the appearance of the 1610/1580 cm^{-1} bands. However, the degradation is not extensive as indicated by the relatively strong C $\equiv$ N stretching frequency at 2240 cm^{-1} . The PAN/VAc copolymer has definitely degraded to a greater extent than pure PAN but there is still evidence of a significant amount of undegraded material present. Conversely, both the PAN/MAA and PAN/AM copolymers have almost completely degraded as evidenced by the very weak contribution of the C $\equiv$ N stretching frequency.

In order to compare the relative rates of degradation of PAN and the three copolymers at 200°C under a reduced pressure of 5×10^{-2} torr a graph of the normalized absorbances of the C $\equiv$ N band at 2240 cm^{-1} as a function of time was prepared and is presented in Figure 5. The assumptions made in the preparation of this figure deserve further comment. Normalized absorbances for the C $\equiv$ N stretching frequency band at 2240 cm^{-1} are readily obtained for the PAN and PAN/VAc polymers from measurement of the peak height or area of this band as a function of degradation time

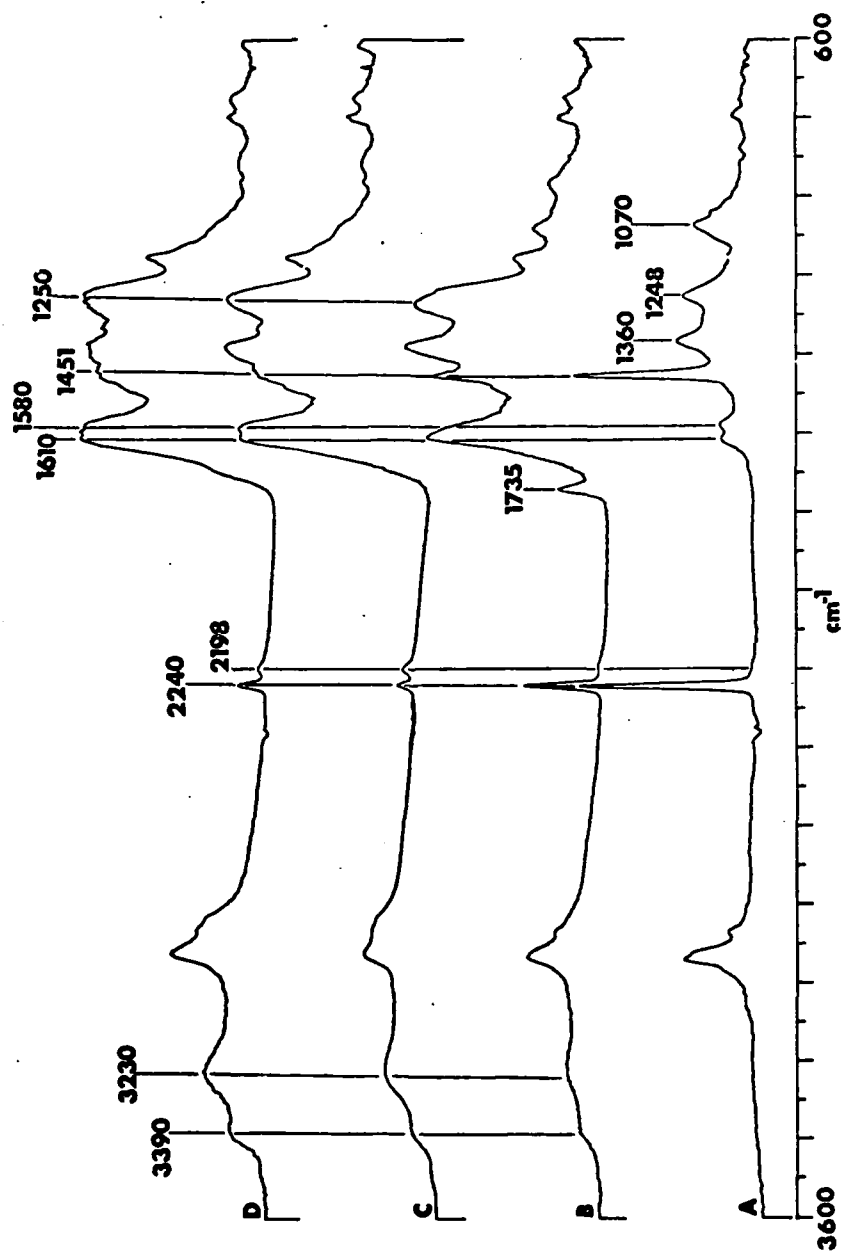


Figure 4. FTIR absorbance spectra in the range 600 - 3600 cm⁻¹ recorded after four hours at 200°C under a reduced pressure of 5 x 10⁻² torr. A) PAN; B) PAN/Vac; C) PAN/AM and D) PAN/MAA.

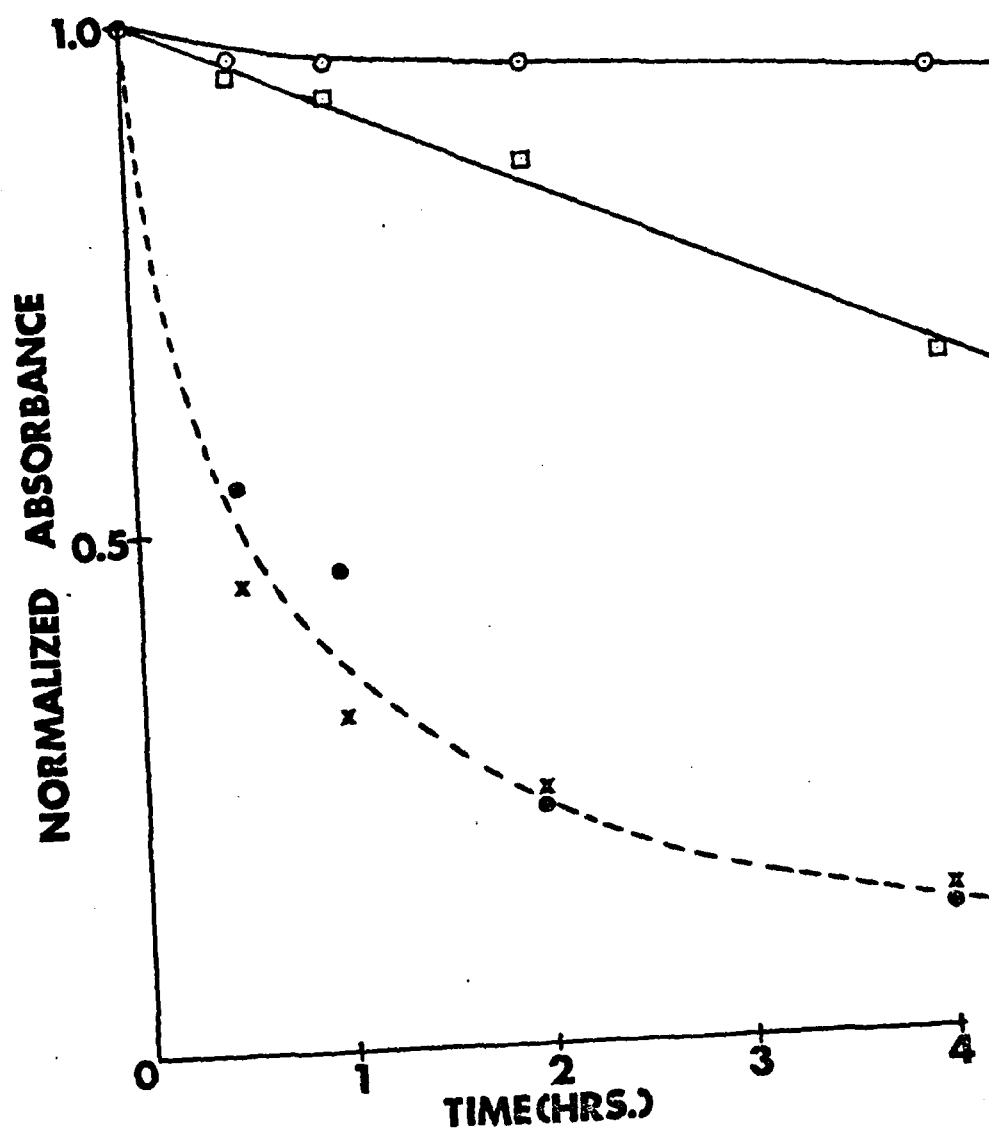


Figure 5. Normalized absorbance measurements of the C≡N stretching frequency at 2240 cm^{-1} plotted against time at 200°C under a reduced pressure of 5×10^{-2} torr. ○ PAN homopolymer, ◻ PAN/VAc, × PAN/AM and ● PAN/MAA.

at 200°C. However, in the case of the PAN/MAA and PAN/AM samples, a reduction of the absorbance of the $C \equiv N$ band has occurred by the time the sample has attained 200°C due to significant degradation. In this case normalization was achieved using the following approximation. The absorbance of the $C \equiv N$ band of the PAN and PAN/VAc polymers was determined on the same film at room temperature (Figure 2) and on immediately attaining a temperature of 200°C (Figure 3). It is well known that band broadening and a reduction of intensity occurs at elevated temperatures and it was determined that a decrease in peak intensity by a factor of 0.85 occurs at 200°C. It should be recalled that no evidence of degradation was observed in the initial 200°C spectra of the PAN or PAN/VAc polymers (see Figure 2). For the PAN/AM and PAN/MAA films the absorbance of the $C \equiv N$ band was measured at room temperature and multiplied by 0.85 to yield an estimation of the undegraded absorbance at 200°C. Normalized intensities were then calculated and plotted as shown in Figure 5. It is realized that accurate absolute rates of degradation at 200°C cannot be obtained for the PAN/AM and PAN/MAA polymers but this approximate procedure at least demonstrates the relative rate differences in the degradation of the four polymers.

As mentioned previously, significant degradation of the PAN/MAA and PAN/AM copolymers was detected in the initial spectra recorded as soon as the sample attained 200°C. Accordingly, similar rate experiments were performed at temperatures of 130°C and 160°C under reduced pressure. Spectral details are presented in parts B and C of this section. Figure 6 shows a graph of normalized intensities of the $C \equiv N$ stretching frequency as a function of time for the

PAN/MAA and PAN/AM copolymers at temperatures of 130°C and 160°C under reduced pressure. A comparison of the data obtained at 160°C is informative. It is apparent that in the case of the PAN/MAA copolymer the initiation of the degradation reaction occurs almost immediately. Conversely, the degradation reaction for the PAN/AM copolymer appears to require an induction period of approximately one hour after which the degradation reaction propagates at a faster rate and is more extensive at times exceeding two hours than the PAN/MAA copolymer. This is also consistent, although not so readily detectible, from the results obtained at 200°C. On examination of the initial spectra obtained at 200°C (Figure 3) it can be seen that the PAN/MAA copolymer has degraded to a greater extent than the PAN/AM copolymer. However, after 4 hours there is little difference in the extent of degradation of either polymer. This implies that initiation of the degradation of the PAN/MAA occurs more rapidly but this is offset by a more rapid degradation of the PAN/AM copolymer upon initiation. Further support for this hypothesis is found from a consideration of the data obtained at 130°C. The PAN/MAA copolymer still degrades at a reasonable rate at this temperature (see Figure 6). However, in the case of the PAN/AM copolymer it is impossible to detect any significant degradation for time periods up to four hours.

In summary, it is obvious that the inclusion of MAA or AM comonomers into the PAN chain has the greatest effect on the rate of degradation.

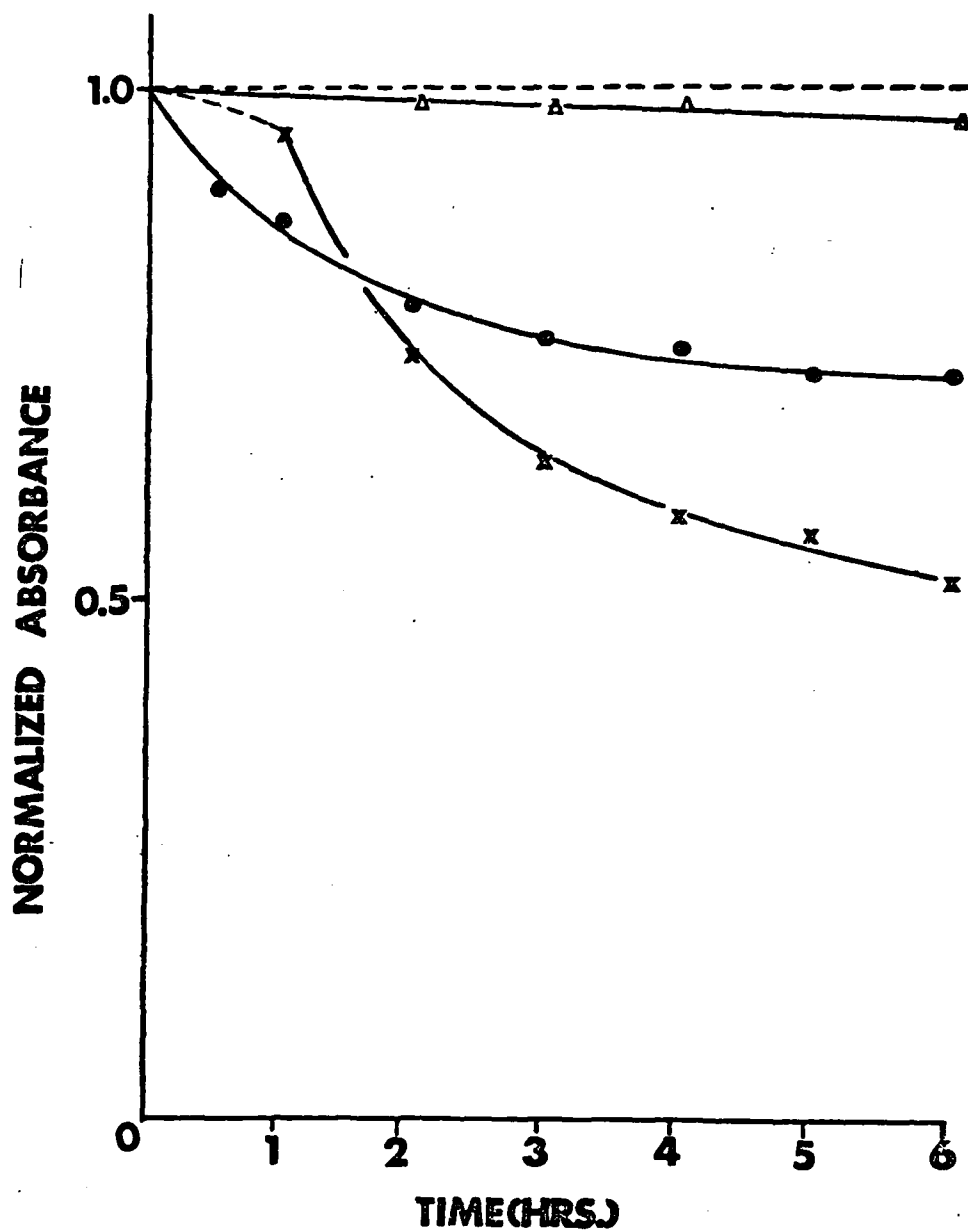


Figure 6. Normalized absorbance measurements of the $\text{C}\equiv\text{N}$ stretching frequency at 2240 cm^{-1} as a function of time and temperature under reduced pressure of 5×10^{-2} torr. (---) AN/AM copolymer at 130°C , Δ AN/MAA copolymer at 130°C , $\bullet$ AN/MAA copolymer at 160°C , $\times$ AN/AM copolymer at 160°C .

B. Thermal Degradation of PAN/MAA Copolymer Under Reduced Pressure

Given the relatively rapid rate of degradation of the PAN/MAA copolymer at 200°C it was decided to lower the degradation temperature to a level at which the spectral changes could be readily followed. A temperature of 130°C was found to be optimum. Incidentally, at this temperature the rate of degradation of PAN homopolymer is insignificant, if it occurs at all. Figures 7 and 8 show the absorbance infrared spectra of the PAN/MAA copolymer recorded as a function of time at a temperature of 130°C under a reduced pressure of 5×10^{-2} torr. Of immediate interest are the infrared bands occurring at 2236, 1735, 1700, 1610, 1580, 1510 and 1214 cm^{-1} . The former band at 2236 cm^{-1} is characteristic of unreacted $\text{C} \equiv \text{N}$ groups and, by measuring the absorbance of this band as a function of time, the number of AN units involved in the degradation process can be estimated. The 1735 and 1700 cm^{-1} bands are assigned to $\text{C} = \text{O}$ stretching modes. The former is associated with the unreacted MAA comonomer while the latter is due to the reacted material. Bands characteristic of the pyridone structure, similar to those observed in degraded PAN homopolymer (15), are observed at 1610 and 1580 cm^{-1} . The 1510 and 1214 cm^{-1} bands are associated with the reaction of MAA and their assignment will be discussed later. All of the absorbances of the above bands can be measured and related to the mechanism of degradation.

In order to accentuate the changes that occur upon degradation, especially at the initial stages when the major component is still the unreacted material, the application of spectral digital

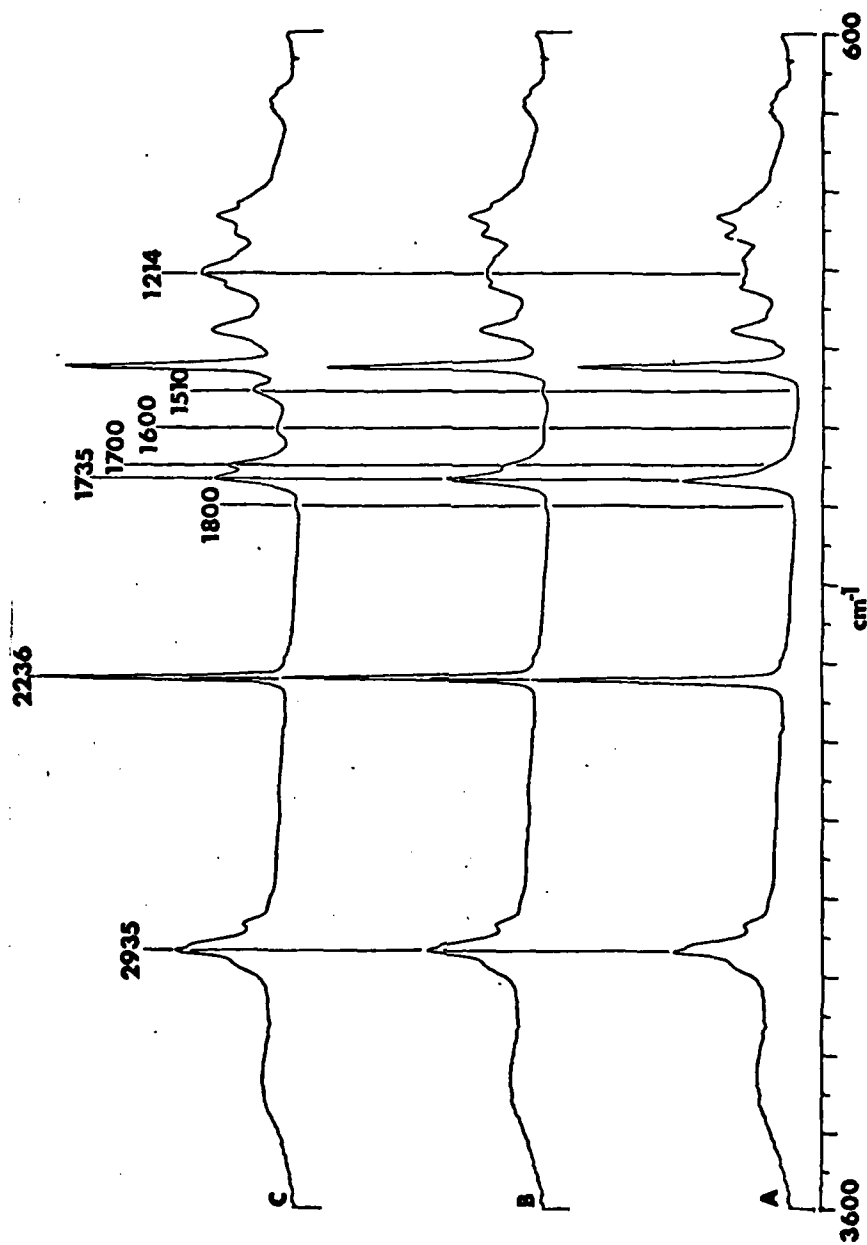


Figure 7. FTIR absorbance spectra of the PAN/MAA copolymer in the range 600 - 3600 cm^{-1} recorded at 130°C under a reduced pressure of 5×10^2 torr.
A) Initial spectrum taken as soon as the sample attained 130°C,
B) degraded 1 hour, and C) degraded 4 hours.

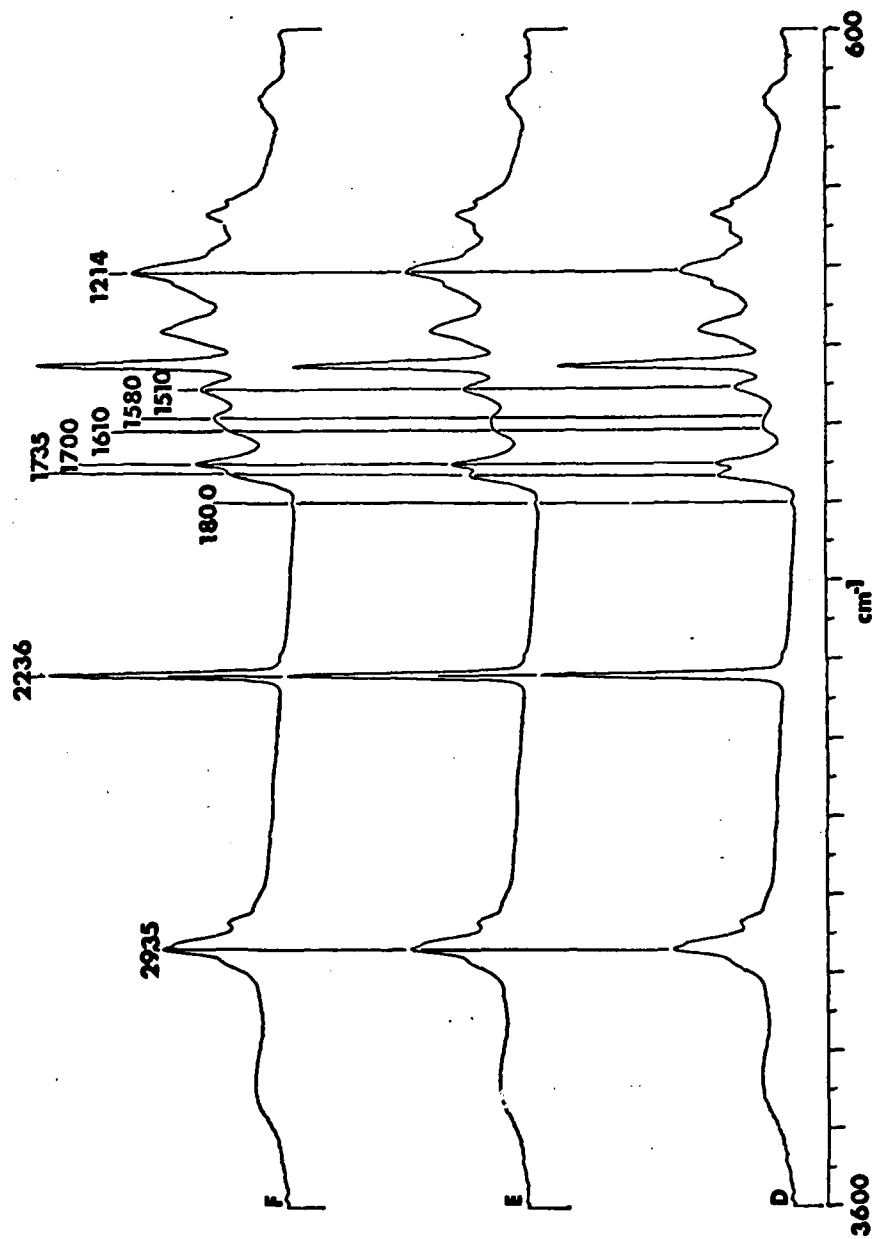


Figure 8. FTIR absorbance spectra of the PAN/MAA copolymer in the range 600 - 3600 cm^{-1} . A) Initial spectrum taken as soon as the sample attained 130°C, B) degraded 1 hour, C) degraded 6 hours, D) degraded 8 hours and E) degraded 20 hours.

subtraction techniques can be most revealing. Figure 9 illustrates difference spectra obtained by subtraction of the initial spectrum from that of the degraded spectra after 1/2, 2 and 4 hours. The criterion used for digital subtraction was to eliminate the 1735 cm^{-1} band associated with unreacted MAA comonomer. Note that all the difference spectra have been scale expanded so that the strongest infrared band is set to full scale. It is immediately apparent that the bands due to the degraded material have been accentuated. Even at a degradation time of 1/2 hr the changes associated with the degraded material are easily identified and measured. Note also the two new bands at 1805 and 1760 cm^{-1} which are now revealed by difference spectroscopy. These bands are highly characteristic of cyclic anhydrides. They are formed at the earliest stages of the degradation and do not appear to increase significantly in concentration as the degradation reaction proceeds. These cyclic anhydrides are rapidly formed from adjacent MMA units incorporated in the chain as shown in Scheme 12. Although the concentration of MAA units is relatively small (3 mole %) and it would be anticipated that the probability of two adjacent MAA units in a random copolymer is correspondingly insignificant, the disparity in the reactivity ratios of the two monomers suggest that there would be a tendency towards "blocking" of the MAA units.

Returning to the major degradation process, measurements of the relative absorbances of the important infrared bands at 1735 , 1700 , 1510 , and 1214 cm^{-1} as a function of degradation time are revealing.

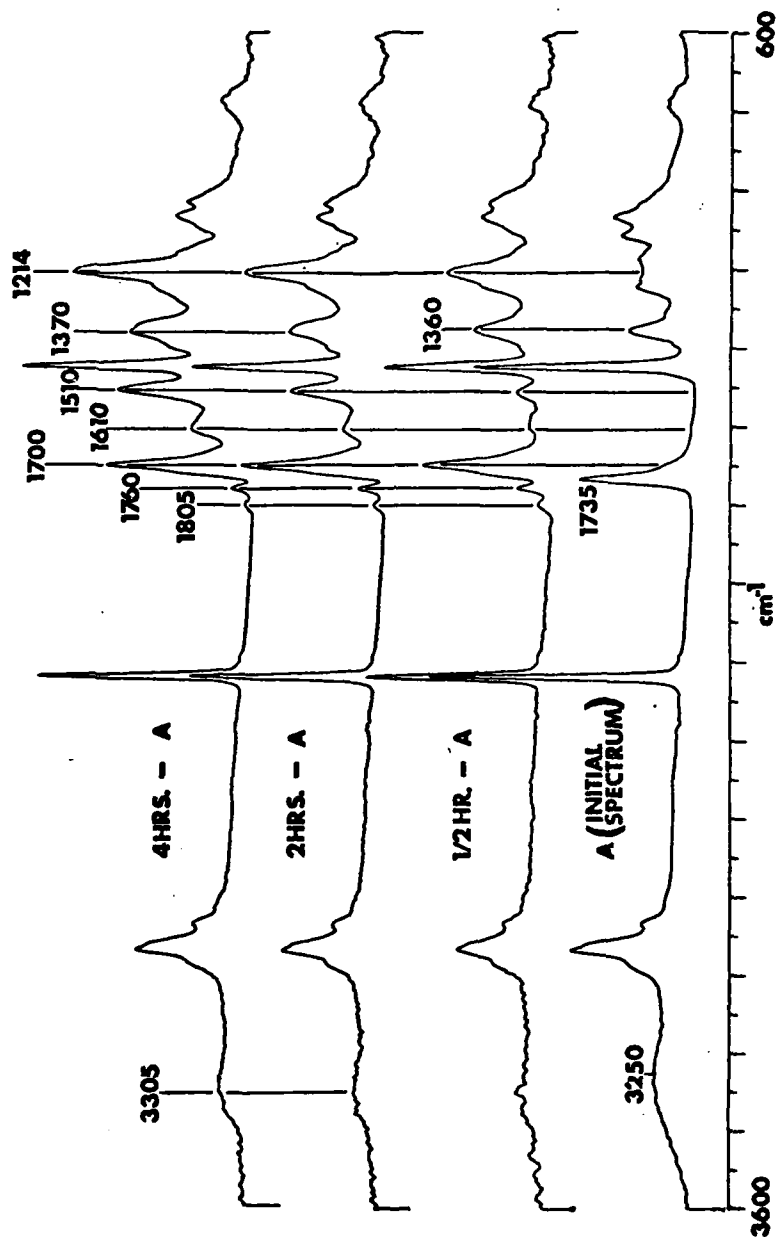
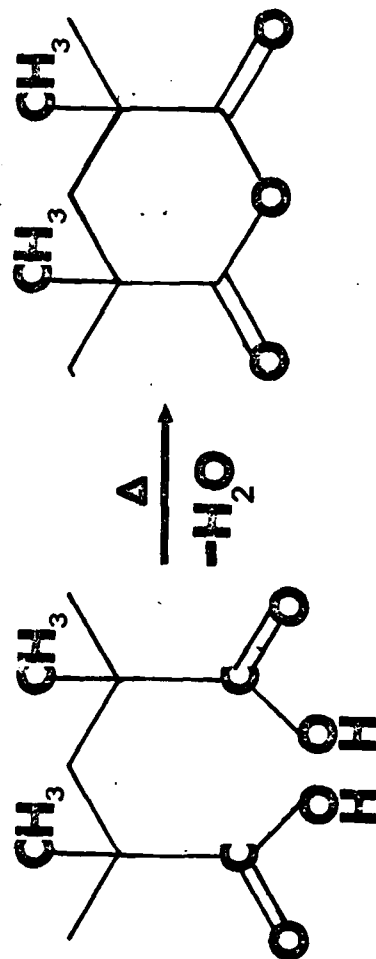


Figure 9. FTIR absorbance spectra of the PAN/MAA copolymer in the range 600 - 3600 cm^{-1} . Initial spectrum recorded as soon as the sample attained 130°C. The top three difference spectra were obtained by subtracting A) from the spectra recorded after 1/2, 2 and 4 hours.



Scheme 12

These measurements are displayed in Figure 10. These results can only be considered approximate due to the assumptions inherent in assuming a reasonable baseline but they nevertheless do indicate trends. Note particularly the decrease in the relative absorbance of the 1735 cm^{-1} band and the parallel increase in the absorbance of the 1700 cm^{-1} band. The absorbances of the 1510 and 1214 cm^{-1} bands also increase in a similar fashion to the 1700 cm^{-1} band. From these observations it is reasonable to assume that the original MAA comonomer unit as represented by the band at 1735 cm^{-1} is being converted into a degraded product characterized by the major infrared bands at 1700 , 1510 and 1214 cm^{-1} . A graph of the normalized absorbances of the $\text{C} \equiv \text{N}$ stretching frequency at 2236 cm^{-1} and the $\text{C} = \text{O}$ stretching frequency of the unreacted methacrylic acid at 1735 cm^{-1} is given in Figure 11. From this graph and a knowledge of the copolymer composition it is possible to estimate the relative number of acrylonitrile units involved in the degradation process for each acrylic acid unit that undergoes reaction. On average, it has been determined that an approximate ratio of three to four nitrile groups to one acrylic acid group are involved in this initial stage of degradation.

Figure 12 shows the infrared spectral results of a deuterium exchange experiment on a PAN/MAA sample that had previously been degraded for 6 hours at 130°C under a reduced pressure of 5×10^{-2} torr. The lower spectrum is that of a degraded protonated sample which was quenched to room temperature. This spectrum is entirely consistent with that shown in Figure 2A and represents an intermediate stage of the degradation. After exposure to D_2O (details

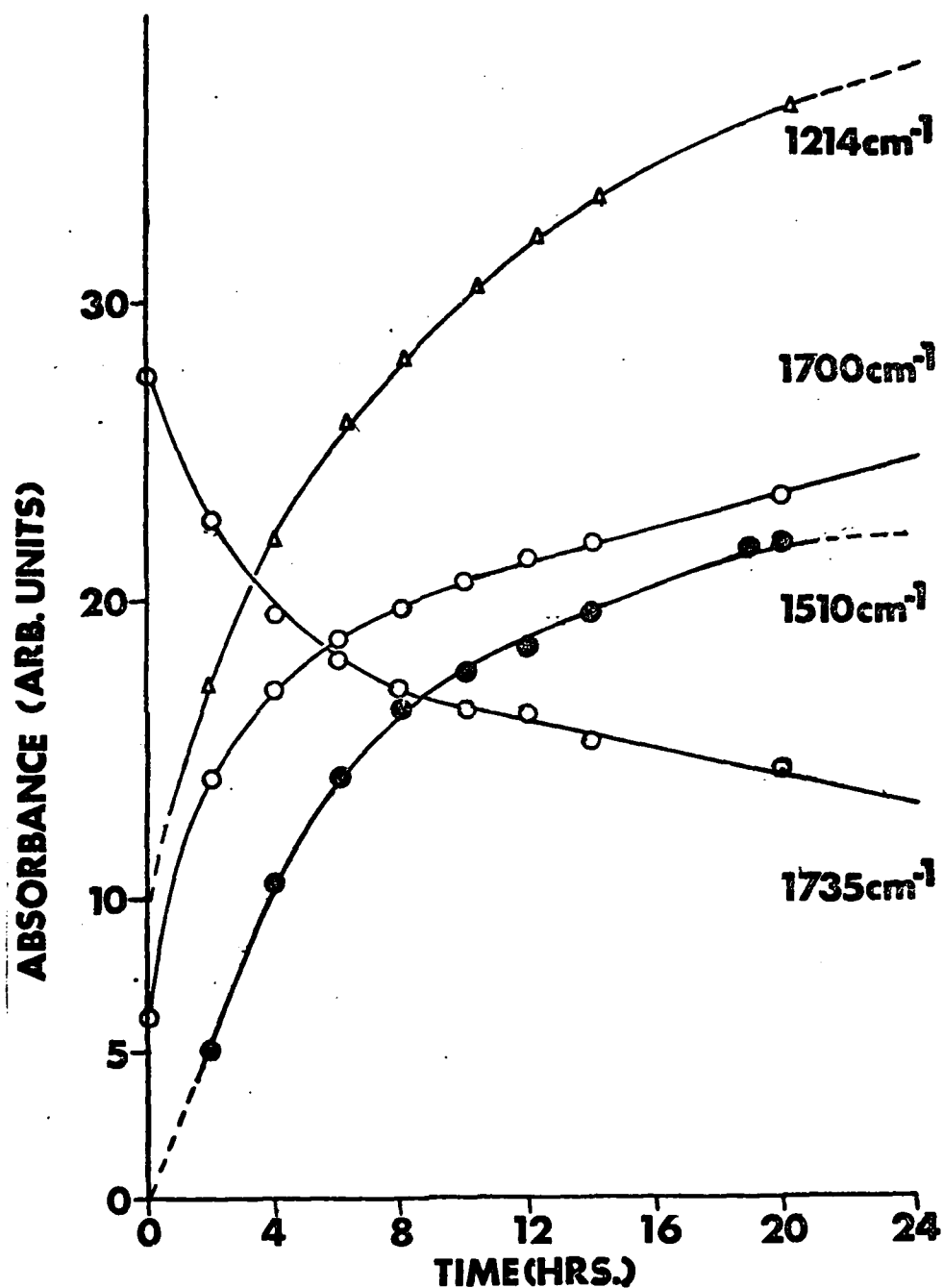


Figure 10. Graph of absorbance (in arbitrary units) plotted against time for four infrared bands occurring in the spectra of the PAN/MAA copolymer at 130°C under a reduced pressure of 5×10^{-2} torr.

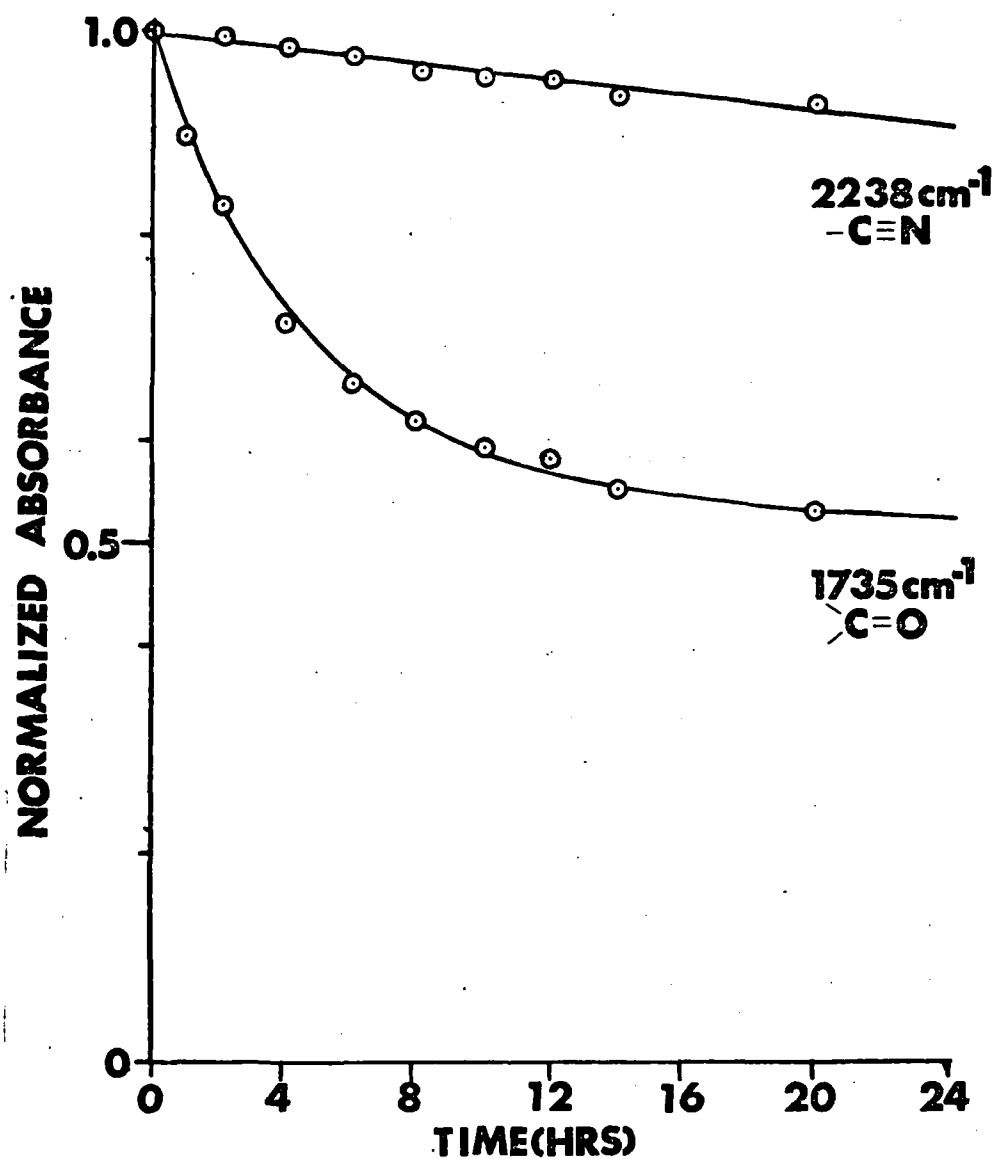


Figure 11. Graph of the normalized absorbances of the nitrile and carbonyl bands of the PAN/MAA copolymer plotted against degradation times at 130°C under a reduced pressure of 5×10^{-2} torr.

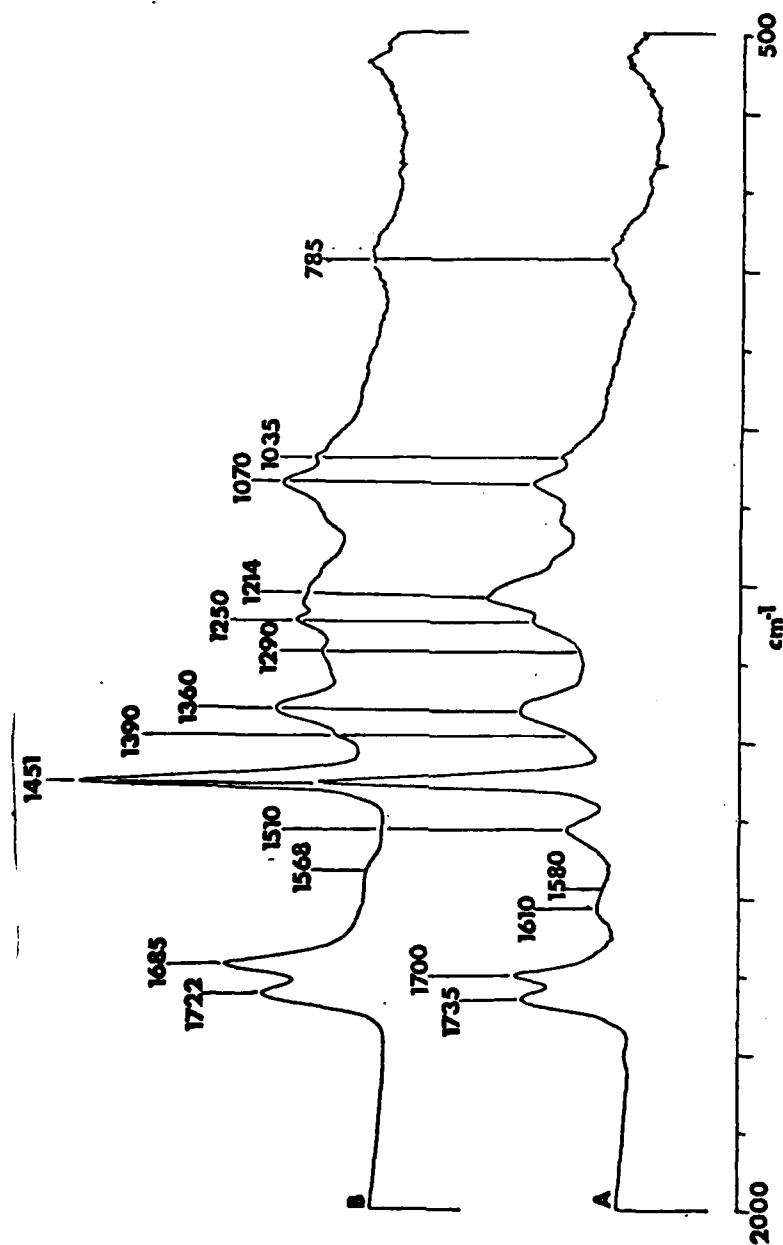
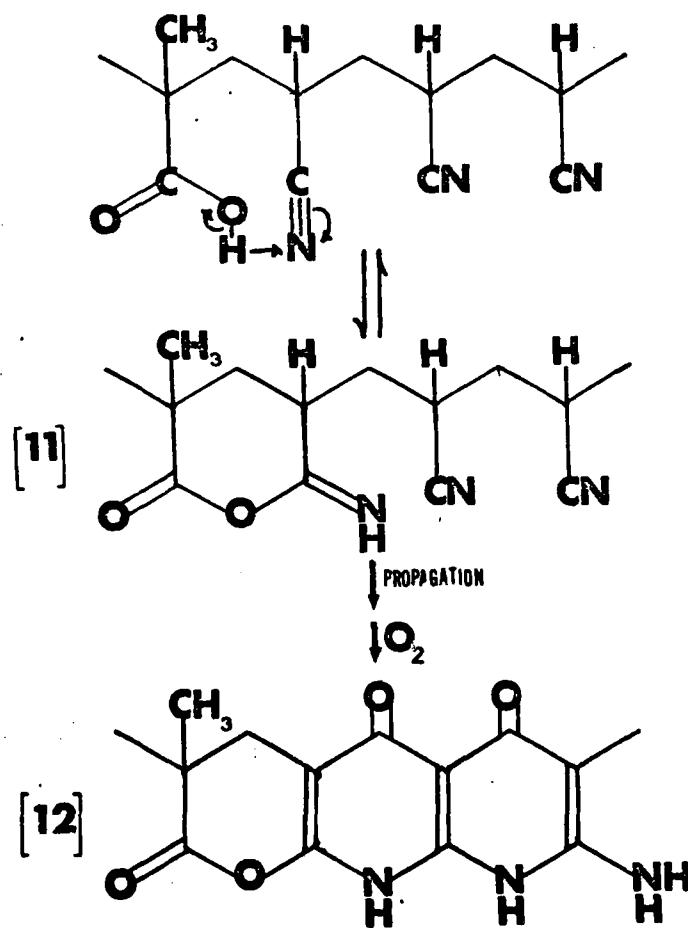


Figure 12. FTIR absorbance spectra in the range 500 - 2000 cm⁻¹. A) The PAN/MAA copolymer degraded for six hours at 130°C under a reduced pressure of 5 x 10⁻² torr and recorded at room temperature and B) Identical film after deuterium exchange.

are given in the experimental section) the infrared spectrum shown at the top of Figure 12 was obtained. A comparison of the protonated and partially deuterated spectra is informative. Bands associated with the undegraded acrylonitrile units at 1451, 1360, 1250, 1070, 1035 and 785 cm^{-1} are unaffected by the deuteration experiment. However, the infrared bands at 1735 and 1700 cm^{-1} shift in frequency to 1722 and 1685 cm^{-1} respectively. The relatively weak bands at $1610/1580\text{ cm}^{-1}$ associated with the cyclic pyridone structure characteristic of degraded PAN units also shift to lower frequencies consistent with the results obtained from the degradation of α -deuterated PAN (19). The 1510 cm^{-1} infrared band completely disappears upon deuterium exchange and the relative intensity of the 1214 cm^{-1} is sharply reduced. New bands at 1390 and 1290 cm^{-1} appear after deuterium exchange.

In order to rationalize the involvement of the MAA units in the cyclization process an intuitive mechanism may be considered in which the hydroxyl group of the acid simply attacks the nitrile carbon, accompanied by subsequent proton transfer [11]. Continued propagation and formation of pyridone type ring structures [11] would follow the mechanism suggested by Coleman and Petcavich (5) as shown in Scheme 13.

This type of reaction would result in the formation of a 6-amino-2-pyrone-type structure [12] as the first cyclization product which is inconsistent with spectral results. Structures of this type have carbonyl stretching frequencies in the region



Scheme 13

of approximately 1770 cm^{-1} (20), while a new major carbonyl band at 1700 cm^{-1} is observed. Furthermore, this type of reaction is inconsistent with known acid-nitrile reactions at elevated temperatures which yield predominantly imides (11).

A mechanism for the initial degradation of PAN/MAA copolymers consistent with the infrared spectral results is given in Figure 13. It should be recalled that a similar mechanism was proposed by Grassie and McGuchan (10) involving initial formation of an imide but there are significant differences in the subsequent reaction of further acrylonitrile units along the chain. The proposed mechanism may be described as follows:

(1) Initial cyclization of a MAA unit with an adjacent acrylonitrile unit to yield a glutarimide structure [I]. The imidic proton is acidic [II] and nucleophilic attack of the intermediate acyl anion upon the next nitrile group occurs.

(2) Cyclization of further acrylonitrile units [III] now proceeds via an anionic mechanism in a manner previously described for PAN homopolymer (Figure 1) followed by imine-enamine tautomerism [IV] and reaction with oxygen to yield pyridone type structures [V].

The FTIR spectra support the formation of the final product [V]. As previously mentioned, the infrared bands occurring at 1610 and 1580 cm^{-1} are characteristic of the pyridone type structure formed in degraded PAN homopolymer (5) which upon deuteration, shift to approximately 1603 and 1568 cm^{-1} (19).

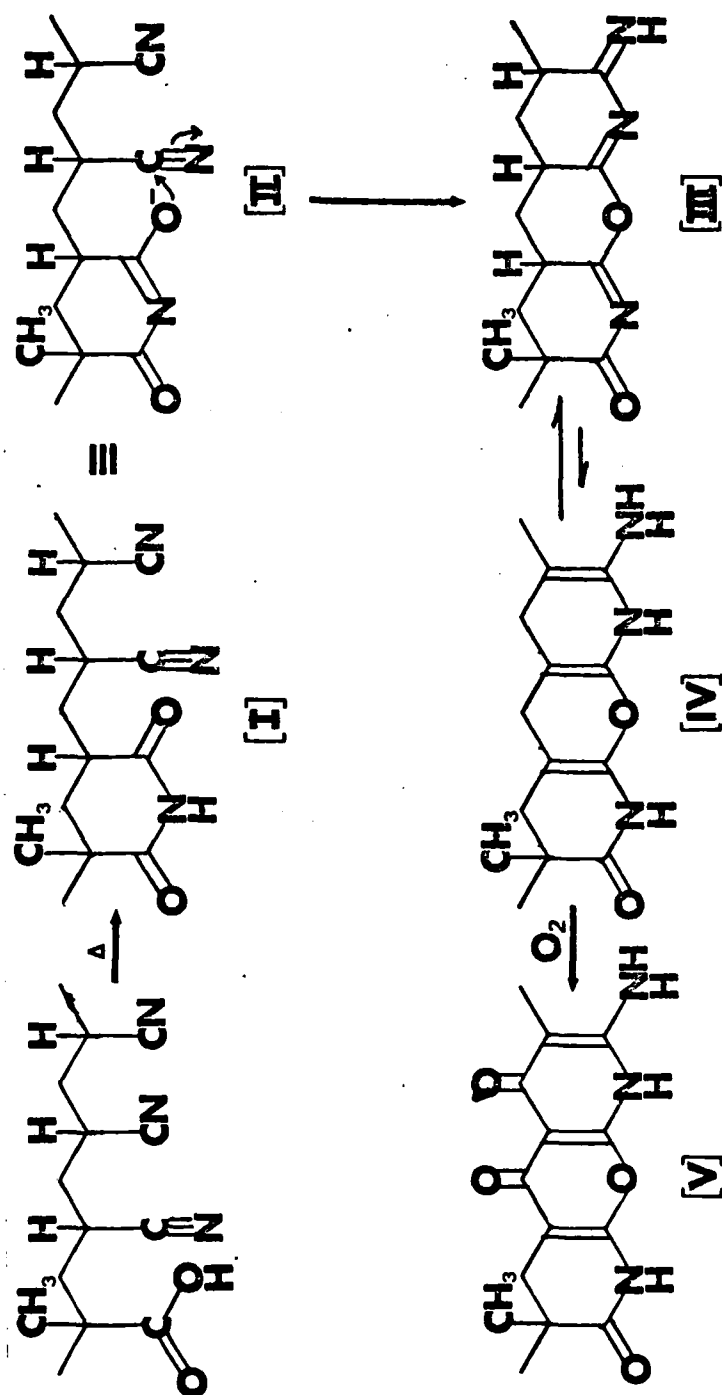
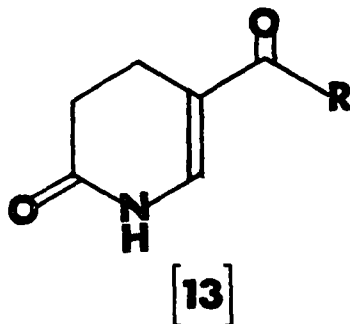


Figure 13. Scheme depicting the chemical reactions occurring during the degradation of a PAN/MAA copolymer at 130°C under a reduced pressure of 5×10^{-2} torr.

These bands have been assigned to mixed modes containing contributions from the $C=O$ and $C=C$ stretching and NH bending vibrations. Evidence for these assignments was presented based on the infrared studies of the model compound $\Delta(8,9)$ -octahydro-7-quinoline (21).

On careful examination of the infrared band centered at 1700 cm^{-1} it is revealed that a shoulder at approximately 1710 cm^{-1} is present (see the difference spectra shown in Figure 9). These bands may be reasonably assigned to mixed modes containing contributions from $C=O$, $C=C$ stretching and NH bending vibrations of the 5-acrylated-3,4-dihydro-2-pyridone structure [13].



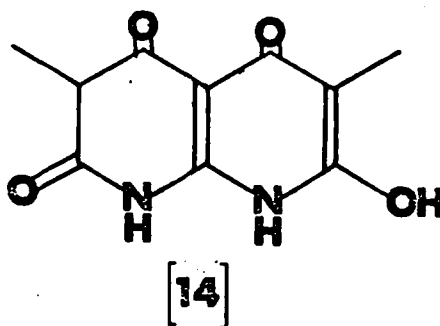
Support for this assignment is obtained from the infrared data of Kato, et al., (22) who studied a variety of 5-acrylated-3,4-dihydro-2-pyridones and assigned infrared bands in the $1705 - 1680\text{ cm}^{-1}$ range to the $C=O$ stretching frequencies. Upon deuterium exchange (see Figure 12) the 1700 cm^{-1} band shifts to 1685 cm^{-1} . This is reasonable, as the mode at 1700 cm^{-1} will contain contributions from the $N-H$ bending vibration and will be exchanged to $N-D$ upon

deuteration. This is analogous to the amide I vibration observed in the spectra of proteins (23). In this case the 1650 cm^{-1} band is assigned to a mixed mode; predominantly a C = O stretching and NH in plane bending vibration.

The infrared bands occurring at 1510 and 1214 cm^{-1} which follow the same growth pattern as the 1700 cm^{-1} band (see Figure 10) can also be considered analogous to the amide II and III vibrations respectively (23). These are assigned to mixed modes containing significant contributions from C - N stretching and N - H bending vibrations (see Structure [13]). After deuterium exchange the 1510 cm^{-1} band is completely eliminated and a new band is observed at 1390 cm^{-1} . The affect of deuterium exchange on the 1214 cm^{-1} is more complex. A reduction of intensity is observed and a new band at 1290 cm^{-1} is formed. This region of the spectrum is complicated by the presence of C - O stretching vibrations and the form of the normal mode is presumable more intricate. Furthermore, the C - O stretching vibration of the 4H-pyran-4-one structure (see [V], Figure 13) would occur in the $1200 - 1220$ region of the spectrum (24,25).

A final comment concerning the mechanism proposed by Grassie and McGuchan (10) is relevent. These authors also suggest the initial formation of an imide [6]. However, their reaction scheme involves propagation by iminol tautomers [7] resulting from continuous rearrangement of imidates formed by reaction of iminol and nitrile as shown in Scheme 1. The final degraded structure [8] of Grassie and McGuchan is not consistent with FTIR spectral

results. The appearance of the bands at 1700 and 1510 cm^{-1} and their behavior upon deuterium exchange cannot be accounted for on the basis of structure [8]. However, in fairness to the authors, they did not consider the subsequent imine-enamine tautomerism and oxidation which would lead to the following:



Frankly, it is difficult to distinguish between structures [14] and [V] (Figure 7). The precise mechanism of the formation of the glutarimide is still in doubt (11,26,27). Most studies of the reaction of acids and nitriles have been performed on low molecular weight compounds where free rotation of the constituent groups is feasible. In the case of the PAN/MAA copolymer, the initial acid and nitrile groups can freely rotate but after formation of the first cyclized product this is no longer true. Accordingly, structure [V] is favored. It should be noted that the 4-pyrone structure presented in [V] is considered to be very stable. However, on the basis of the spectral evidence obtained, structures similar to that suggested in [14] above cannot definitely be ruled out.

C. Thermal Degradation of PAN/AM Copolymers

Under Reduced Pressure

Given the relatively rapid rate of degradation of this copolymer at 200°C, it was decided to lower the degradation temperature to a level at which the spectral changes could be readily followed. A temperature of 160°C was found to be optimum. Figures 14 and 15 show the infrared spectra of the PAN/AM copolymer recorded as a function of time at 160°C under a reduced pressure of 5×10^{-2} torr. The initial spectrum was recorded as soon as the sample had attained the degradation temperature of 160°C. No significant degradation is observed. As degradation proceeds there is a reduction in both the nitrile stretching absorbance at 2238 cm^{-1} associated with the acrylonitrile (AN) units and the carbonyl stretching absorption at 1685 cm^{-1} associated with the AM units in the polymer chain. Concurrently, the appearance of bands at 1610 and 1580 cm^{-1} , which are characteristic of PAN homopolymer degradation (5), is observed. An infrared band at 1220 cm^{-1} also appears and increases steadily throughout the degradation time. This band is not observed during the degradation of PAN homopolymer and is believed to result from a reaction which directly involves the AM units in the cyclization of AN units.

In order to reveal any infrared bands that may be associated with the degraded materials but might be masked by bands of the unreacted polymer, a spectral digital subtraction technique was employed. Figure 16 illustrates difference spectra that were

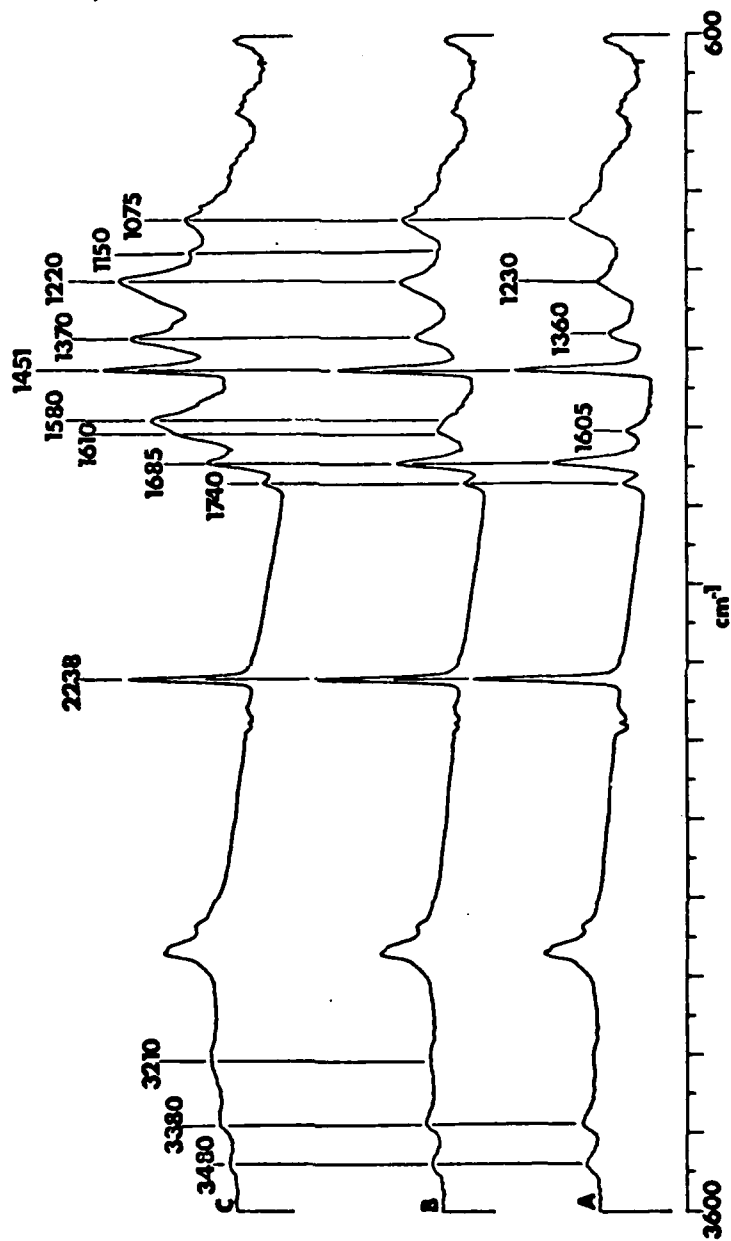


Figure 14. FTIR absorbance spectra in the range 600 - 3600 cm^{-1} of a PAN/AM copolymer film at 160°C under a reduced pressure of 5×10^{-2} torr.
 A) Initial spectrum at 160°C, B) degraded 2 hours and C) degraded 3 hours.

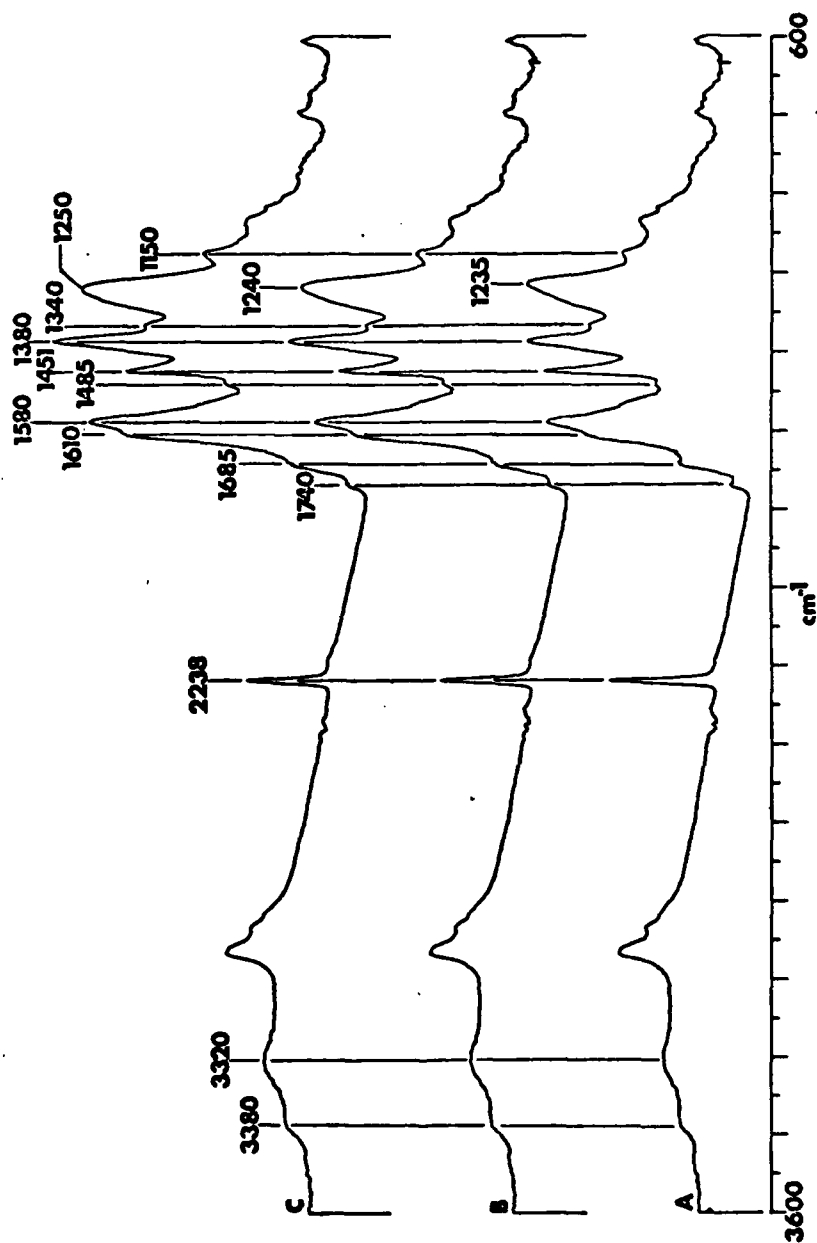


Figure 15. FTIR absorbance spectra in the range $600 - 3600 \text{ cm}^{-1}$ of a PAN/AM co-polymer film at 160°C under a reduced pressure of 5×10^{-2} torr.
 A) Degraded 4 hours, B) degraded 6 hours and C) degraded 8 hours.

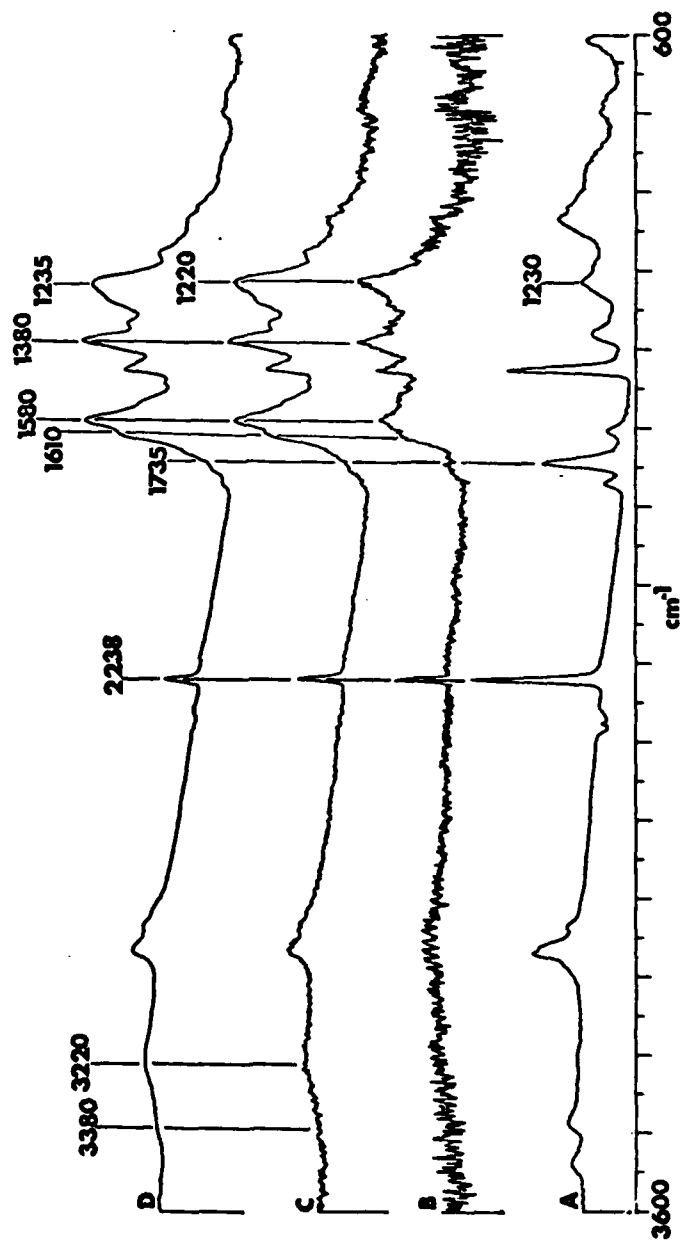


Figure 16. FTIR absorbance spectra in the range $600 - 3600 \text{ cm}^{-1}$ of a PAN/AM co-polymer film at 160°C and 5×10^{-2} torr. A) Original spectrum at 160°C , B) difference spectra, 1 hr. - original, C) difference spectra, 2 hr. original and D) difference spectra, 4 hr. - original.

obtained by subtraction of the initial spectrum from that of the degraded spectra after 1, 2 and 4 hours at 160°C and under a reduced pressure of 5×10^{-2} torr. The criterion used for this subtraction was to eliminate the AM carbonyl stretching absorbance at 1685 cm^{-1} . In addition to infrared bands characteristic of the cyclic pyridone structure in degraded PAN homopolymer (5), the band observed at 1220 cm^{-1} has now been accentuated. No other new bands are observed in the difference spectra.

A mechanism consistent with these spectral results is presented in Figure 17. The essential features of this mechanism are:

(1) Formation of the iminoglutarimide structure [Ia] from reaction of an acrylamide unit with an adjacent nitrile unit. The reaction of amides with nitriles to yield imino-imides is well known (11,28). For example, o-cyanobenzoamide is converted to imino-phthalimide when heated under vacuum.

(2) Anionic propagation by cyclization of AN sequences [IIa].

(3) Rearrangement of structure [IIa] via amide-iminol like tautomerism [IIIa]. This type of tautomerism is feasible only after cyclization of several AN units has occurred since a conjugated system is required to stabilize the iminol form (29).

(4) Rearrangement of structure [IIIa] via imine-enamine tautomerism in a manner similar to that previously suggested for PAN homopolymer (5).

(5) The intermediate enamine tautomer [IVa] then reacts with trace amounts of O_2 to yield the final structure [Va].

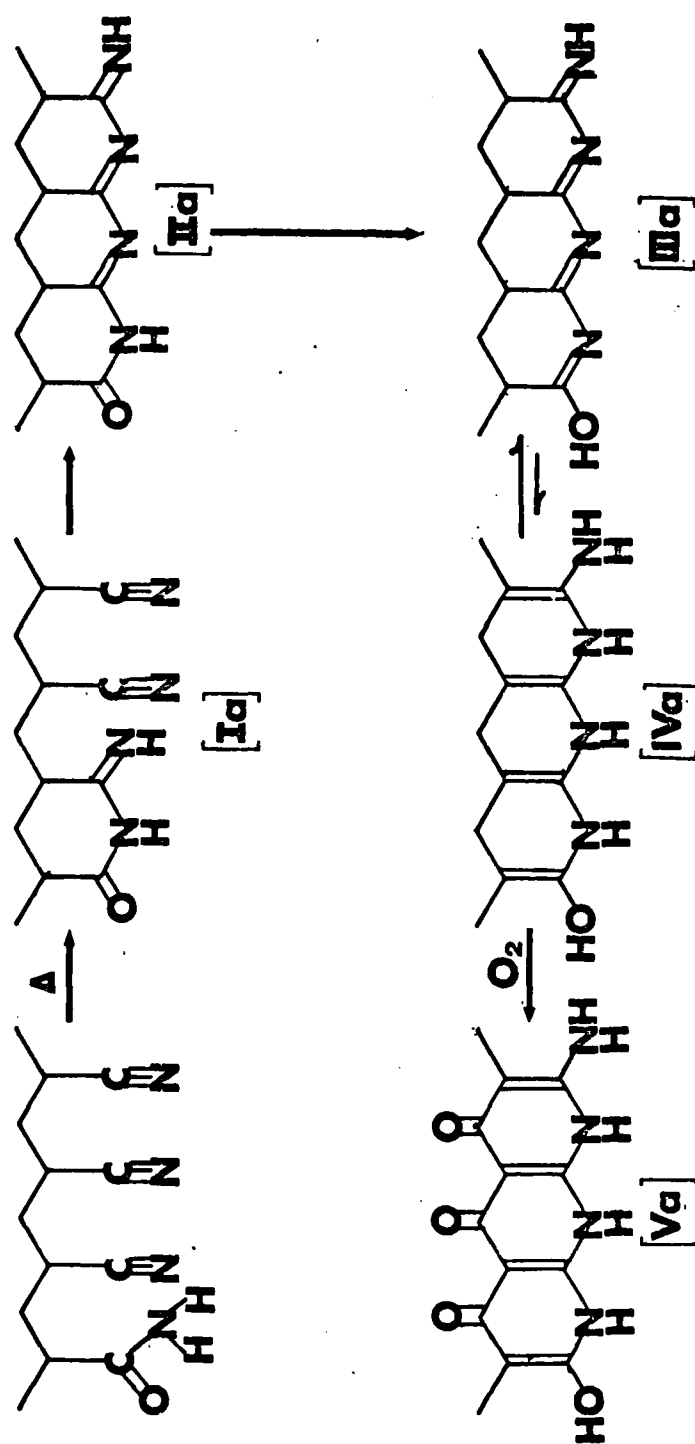
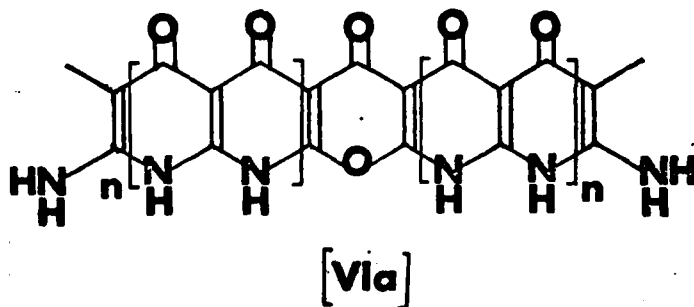


Figure 17. Scheme depicting the chemical reactions occurring during the degradation of a PAN/AM copolymer at 160°C under a reduced pressure of 5×10^{-2} torr.

It should be noted that while initiation via the exocyclic imine of structure [Ia] is preferred due to superior nucleophilicity, cyclization may also be initiated by the exocyclic hydroxyl group of structures [IIIa].

The FTIR spectra support the formation of structure [Va]. As previously shown (5) the bands occurring at 3380, 3230, 1610, 1580, 1385, 1260, 1150, 750 and 610 cm^{-1} are characteristic of the pyridone type structure formed in degraded PAN homopolymer at 200°C under reduced pressure. The absence of an absorption at 1700 cm^{-1} is significant and indicates that the amide-iminol tautomerism [IIIa] occurs in the degradation reaction based on the following argument. If this tautomerism did not occur then an infrared band at 1700 cm^{-1} , associated with the carbonyl structure [IIa], which would increase in intensity as the degradation reaction proceeded in a similar manner to that described for the degradation of the PAN/MAA copolymer should be present.

As mentioned previously cyclization of AN units may also be initiated by the exocyclic unit shown in structure [IIIa] of Figure 4. This would lead to typical final sequences as shown in [VIa] below.



The infrared band observed at 1220 cm^{-1} may be reasonably assigned to a predominantly C - O stretching vibration associated with the 4-H-4-pyranone structure depicted in [VIa]. This is consistent with the assignment of a similar band noted for the degradation product of the PAN/MAA copolymer. However, a similar absorption would be expected for the C - O deformation associated with the exocyclic hydroxyl group shown in [Va] (30), therefore it is feasible that both structures [Va] and [VIa] exist during the degradation reaction.

It was previously mentioned that Grassie and McGuchan (10) also studied the effects of inclusion of AM units upon the degradation of PAN. The authors suggested a free radical mechanism leading to a final degradation product [9] as shown in Scheme 6. The final product [9] is clearly inconsistent with the spectral results. Structures of this type would exhibit carbonyl stretching frequencies in the $1720 - 1740\text{ cm}^{-1}$ region of the spectrum which are not observed. However, if imine-enamine tautomerism and subsequent oxidation of structure [9] is included, structures similar to those of [Va] and [VIa] would result and it would be difficult to definitely choose between the three based on the present spectral evidence. However, it will be recalled that the free radical mechanism of Grassie and McGuchan was suggested for pyrolysis temperatures in excess of 200°C where homolytic cleavage is feasible. Therefore, at the relatively low temperature of 160°C and under reduced pressure, the cyclization mechanism depicted in Figure 17 is favored.

A final comment concerning the relative rates of degradation of the PAN/MAA and PAN/AM copolymers is in order. Comparisons of these relative rates at 200, 160 and 130°C have already been discussed. Of interest is the enhanced rate of degradation of the PAN/AM copolymer compared to that of the PAN/MAA copolymer after the induction period especially at 160°C (see Figure 6). After two hours more AN units are involved in the degradation reaction of the PAN/AM case. This behavior could be explained on the basis of the two different mechanisms suggested for these two copolymers. Propagation of the cyclization reaction may occur on either side of an AM unit in the PAN/AM copolymer from the exocyclic imine and hydroxyl groups formed at the degradation temperature (see Figure 17). In contrast, for the PAN/MAA copolymer, propagation can only occur on one side of an MAA group. Further reaction is blocked by the fact that the methyl group cannot tautomerize and the carbonyl group cannot initiate additional cyclization reactions.

D. Thermal Degradation of PAN/VAc Copolymer

Under Reduced Pressure

Figures 18 and 19 show FTIR spectra recorded at 200°C under a reduced pressure of 5×10^{-2} torr as a function of time for a film of the PAN/VAc copolymer. It should be emphasized that the initial spectrum (Figure 18A), recorded as soon as the sample had attained 200°C, shows no evidence of degradation. Bands at 1610/

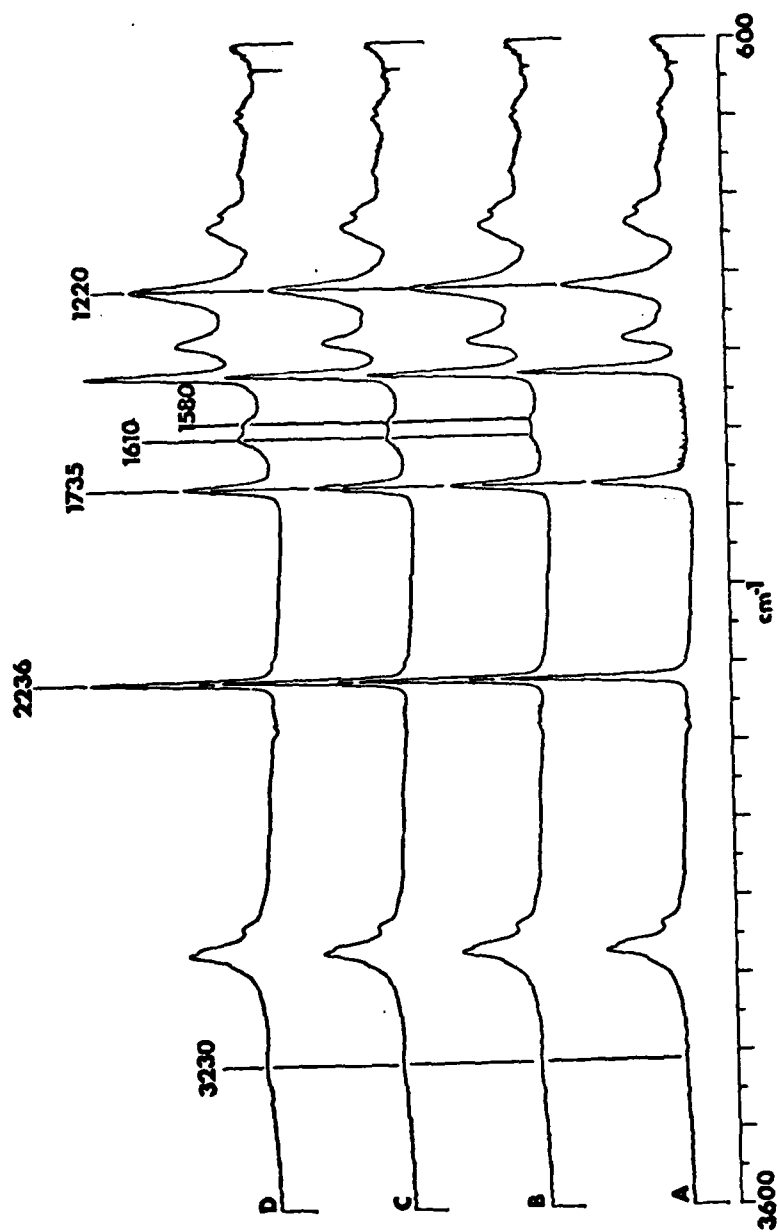


Figure 18. FTIR absorbance spectra of the PAN/VAc copolymer in the range 600 - 3600 cm⁻¹ as a function of time at 200°C under a reduced pressure of 5 x 10⁻² torr. A) Initial spectrum, B) degraded 15 minutes, C) degraded 30 minutes, and D) degraded 1 hour.

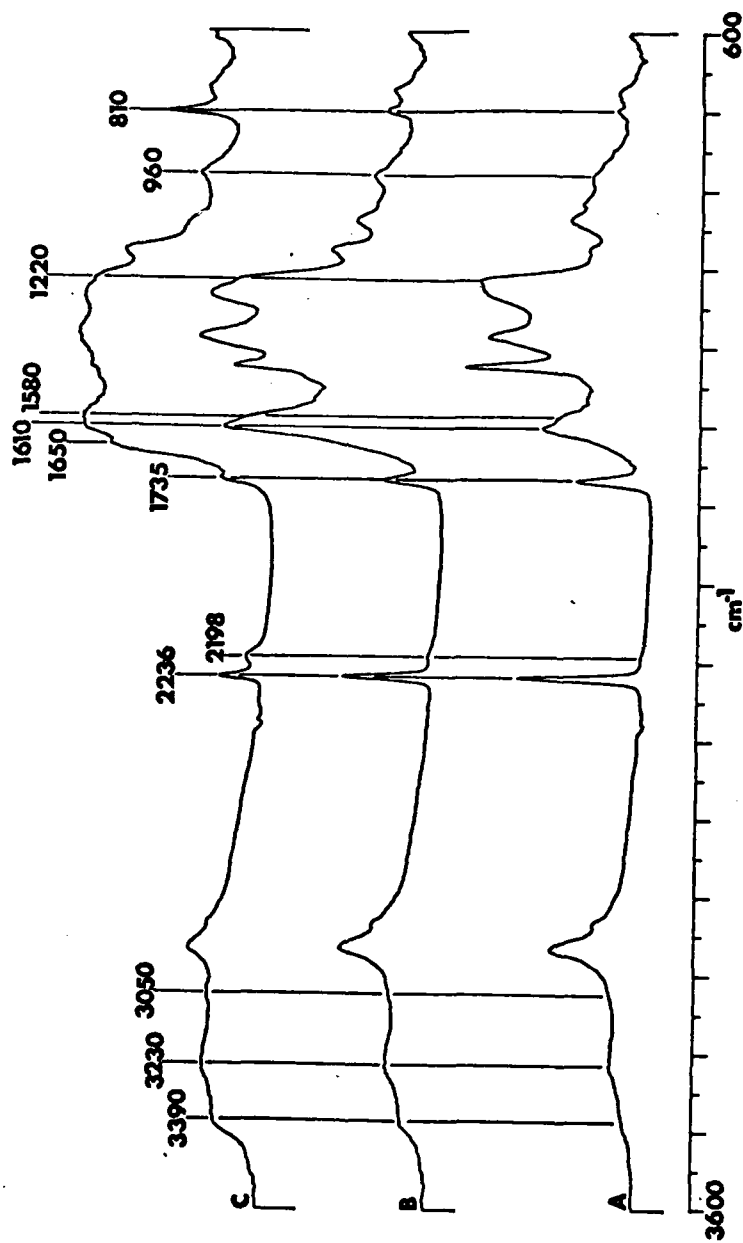


Figure 19. FTIR absorbance spectra of the PAN/VAc copolymer in the range 600 - 3600 cm^{-1} as a function of time at 200°C under a reduced pressure of 5×10^{-2} torr. A) Degraded 2 hours, B) degraded 4 hours and C) degraded 10 hours.

1580 cm^{-1} characteristic of PAN homopolymer degradation (5), are completely absent. This is in marked contrast to the results obtained for the PAN/MAA and PAN/AM copolymers. After 15 minutes at 200°C, there is evidence of the 1610/1580 cm^{-1} bands (Figure 18b) and these bands increase in intensity throughout the range of degradation times of 30 mins to 10 hours (Figures 18 and 19). Between 4 and 10 hours further infrared bands are discernible at 3050, 1650, 960 and 810 cm^{-1} which are in addition to those infrared bands attributable to the undegraded acrylonitrile units and pyridone type structures associated with the degraded product. For expository purposes, a comparison between spectra of undegraded PAN homopolymer; PAN homopolymer degraded for 24 hours and the PAN/VAc copolymer degraded for 4 hours, all taken under identical experimental conditions, is presented in Figure 20.

A mechanism for the degradation of PAN/VAc copolymers at 200°C and under a reduced pressure of 5×10^{-2} torr, which is consistent with these FTIR spectral observations, is shown in Figure 21. The initial steps of this mechanism are markedly different from those suggested for the PAN/MAA and PAN/AM copolymers where the comonomers initiates cyclization of the acrylonitrile units and are incorporated in a cyclic species. In the case of the PAN/VAc copolymer, elimination of the acetate anion occurs which initiates cyclization of acrylonitrile units. This is analogous to the well known base catalysed degradation of PAN (3) and, in fact, the acetate anion may be considered to be the $\text{X}^{\ominus}$ anion shown in Figure 1. It should be recalled that the inclusion of VAc into

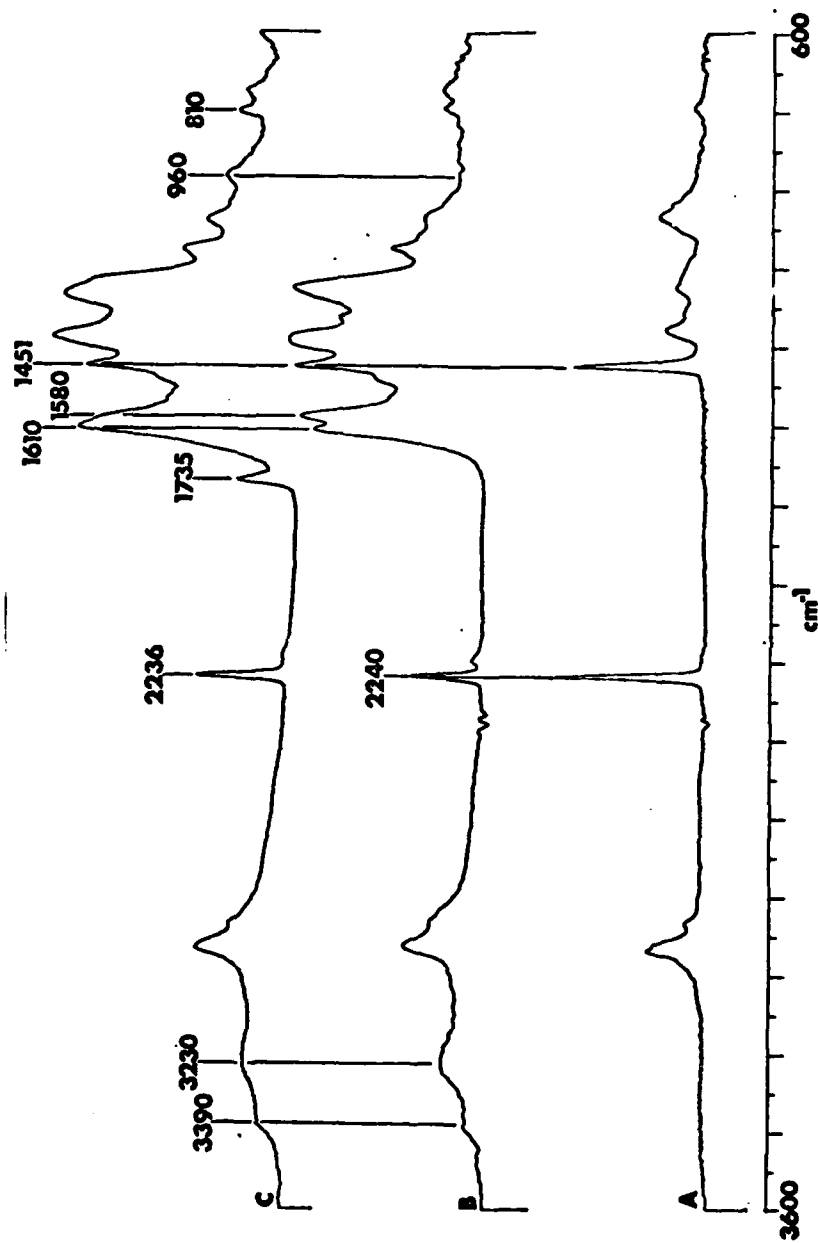


Figure 20. FTIR absorbance spectra comparing a degraded PAN homopolymer to a degraded PAN/VAC copolymer. A) Initial PAN homopolymer spectra at 200°C and 5×10^{-2} torr, B) PAN homopolymer after 24 hours at 200°C and 5×10^{-2} torr and C) PAN/VAC copolymer degraded for 4 hours at 200°C and 5×10^{-2} torr.

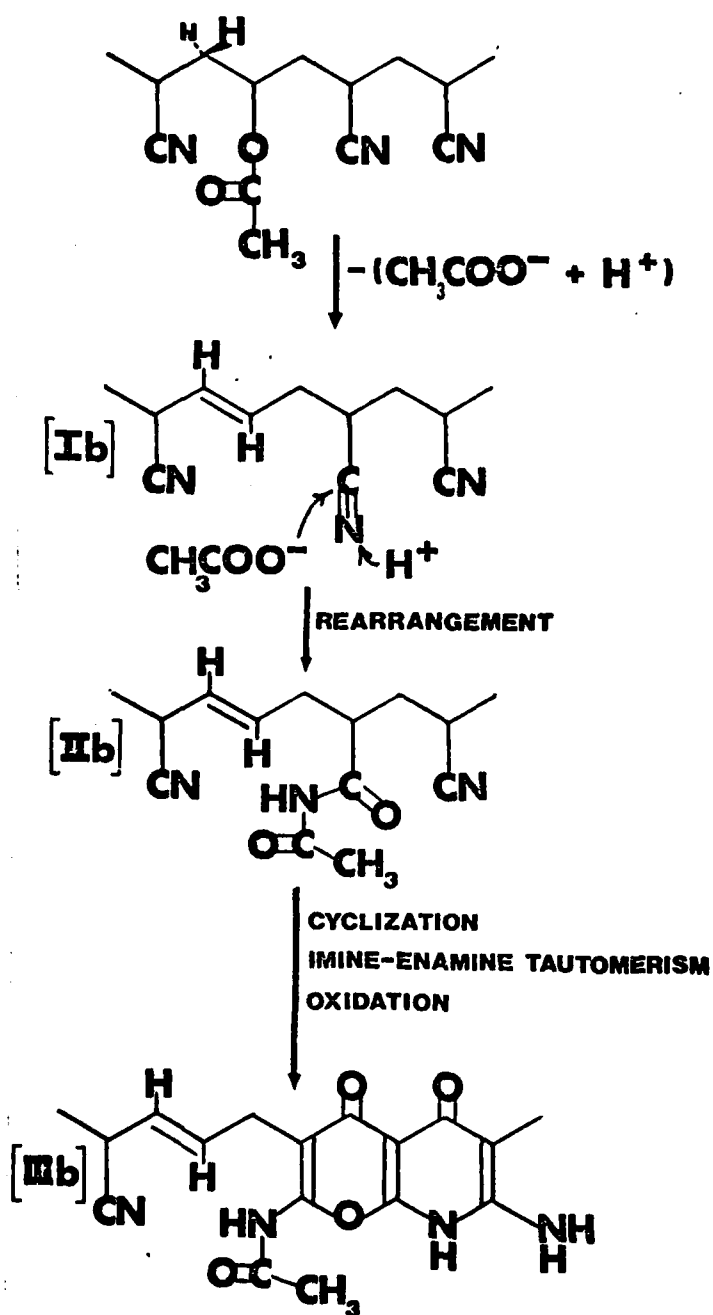


Figure 21. Degradation scheme depicting the proposed chemical reactions occurring in the PAN/VAc copolymer at 200°C under a reduced pressure of 5×10^{-2} torr.

the PAN polymer chain does significantly increase the rate of degradation over that of pure PAN homopolymer under identical experimental conditions. However, inclusion of MAA or AM units in the PAN chain has a much greater effect on the rate of degradation. The elimination reaction and formation of acetate anion is relatively slow and is the rate determining step. Acetate esters are known to undergo such elimination reactions on heating. The reaction is believed to proceed through a cyclic transition state in which the C - O bond is broken first leading to the formation of transient ion pairs (31). Grassie (32) has demonstrated that poly(vinyl acetate) (PVAc) is thermally stable up to temperatures of 190°C under reduced pressure. Above 190°C acetic acid is evolved which finally produces a conjugated poly(ene) sequence in the backbone. This type of mechanism (commonly called a 'zipper' mechanism) involves the elimination of acetic acid from PVAc to yield an initial olefinic bond which activates adjacent vinyl acetate groups leading to conjugated sequences. However, in the case of the PAN/VAc copolymer which contains only approximately 3 mole % of VAc, the probability of two or more sequences of VAc in the chain is insignificant. Therefore the formation of conjugated polyenes along the polymer chain is not anticipated. In essence the mechanism may be summarized as follows:

(1) Elimination of an acetate group resulting in the formation of a trans-olefinic bond in the main chain. This may occur on

either methylene groups (which are in identical environments) adjacent to the acetate group.

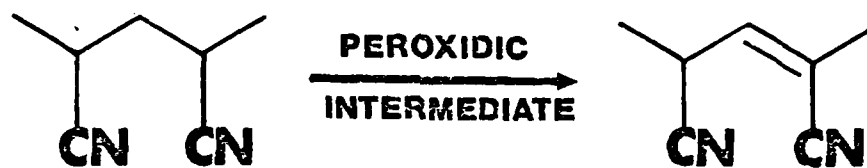
(2) Attack of the acetate anion on an adjacent acrylonitrile group yielding initially an imino anion which immediately rearranges to form an imide [IIb] in a manner consistent with the well known elevated temperature reaction of nitriles and acids (11). It is feasible that steps 1) and 2) occur through a cooperative process involving adjacent nitrile groups. However, this is not essential as acetic acid could diffuse throughout the film and attack an acrylonitrile group at random.

(3) Cyclization of acrylonitrile units down the chain now proceeds via an anionic mechanism in a manner described for PAN homopolymer (5) followed by imine-enamine tautomerism and reaction with oxygen to yield pyridone type structures [IIIb]. These should only be considered to be typical structures as rearrangement of labile protons may take place.

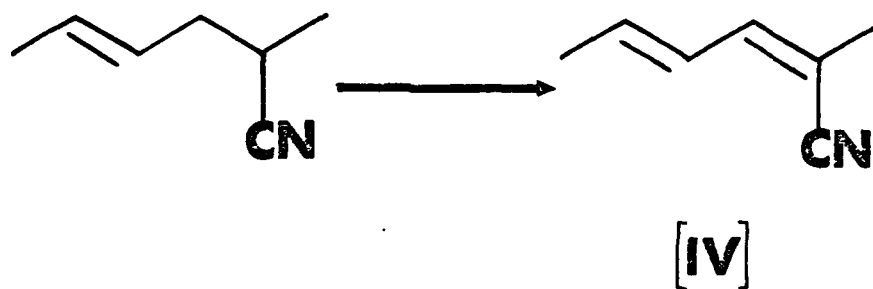
The FTIR studies support the final product shown as structure [IIIb]. In the initial stages of degradation up to one hour at 200°C under reduced pressure (see Figure 18) the only definitive changes observed in the infrared spectrum are the growth of the bands at 1610/1580 cm^{-1} which are characteristic of the pyridone structure. Concurrently, there is a reduction in the absolute intensity of the 2236 cm^{-1} band associated with unreacted acrylonitrile groups as indicated by the graph shown in Figure 5. Between two and ten hours additional new bands at approximately 3380, 3230, 3050, 2198, 1650, 1385, 1260, 1150, 1070, 960, 810,

750 and 610 cm^{-1} are observed. From a comparison of the infrared spectra of undegraded PAN homopolymer; PAN homopolymer degraded for 24 hours and PAN/VAc copolymer degraded for 4 hours shown in Figure 20 it is immediately apparent that only the bands at 3050, 1650, 960 and 810 cm^{-1} are unique in the spectra of the degraded PAN/VAc copolymer. These bands may readily be assigned to olefinic C - H stretching, C = C stretching and C - H out-of-plane bending vibrations associated with substituted olefinic structures (33). Whereas the 3050, 1650 and 960 cm^{-1} bands can be confidently assigned to the disubstituted trans-olefinic structure depicted in structure [IIIb], the 810 cm^{-1} band cannot be assigned with such confidence. A similar band was observed in the infrared spectrum of PAN homopolymer degraded in air (5) and was assigned to a =CH out-of-plane deformation associated with 1,1,2-trisubstituted olefins. Conley and Bieron (15) have suggested that oxidative dehydrogenation can occur yielding conjugated polyenes with pendent nitriles as shown in Scheme 14. In the case of the PAN/VAc copolymer, elimination of the acetate group results in the formation of a double bond. This double bond will activate the adjacent methylene hydrogens which are well known to be susceptible to free radical attack. In analogy to the scheme shown above a conjugated polyene could be formed as indicated in Scheme 15.

The structure (IVb) is very stable and is consistent with spectral results (the 810 cm^{-1} band being assigned to the 1,1,2-trisubstituted olefin). However, it should be emphasized that Brandrup and Peebles (34) have criticized mechanisms of the



Scheme 14



Scheme 15

type shown above, therefore this interpretation can only
be considered tentative.

CONCLUSIONS

FTIR studies of the degradation of PAN and three copolymers of acrylonitrile containing approximately four weight percent of VAc, AM and MAA, have demonstrated that inclusion of the comonomers has a marked affect on the rate of degradation at elevated temperature and under reduced pressure. From rate studies performed at 200°C, it is apparent that the rate of degradation is dependent upon the specific chemical type of comonomer included in the PAN polymer chain. The rate of degradation increases in the order $PAN < PAN/VAc < PAN/AM \approx PAN/MAA$.

Mechanisms which satisfactorily explain the observed spectral changes occurring during degradation of each copolymer are given. The mechanisms for each copolymer are markedly different, but in each case the comonomer is incorporated in the final degraded product. In the case of MAA and AM, the comonomers initiate cyclization by reaction with an adjacent nitrile group and are incorporated as a cyclic structure. The VAc comonomer is eliminated in the form of transient ions and diffusible acetic acid, both of which initiate nitrile groups at random and are incorporated as exocyclic groups. It is considered that these results are pertinent to the production of PAN polymers which are employed as precursors to the formation of carbon fibers, and are also extensively used in the textile industry.

RECOMMENDATIONS FOR FUTURE WORK

As previously stated, to improve the properties of carbon fibers derived from PAN precursors it is necessary to optimize the number of nitrile units that are cyclized during low temperature treatment. The FTIR studies presented in this thesis have demonstrated that inclusion of some comonomers into the PAN chain markedly accelerates cyclization.

Future studies, which may lend insight to the production of superior carbon fibers, would include the following:

(1) Determine the effects of Acrylic Acid, Itaconic Acid and Amideoxime 'comonomers' on the degradation mechanism. It has been suggested that in the MAA copolymer, two sided initiation through tautomerism of the terminal carbonyl groups is blocked by the presence of the α -methyl group. An acrylic acid comonomer, which has no α -methyl group, may undergo tautomerism resulting in an exocyclic hydroxyl group. This hydroxyl would then initiate cyclization. In the case of itaconic acid comonomers, initiation may be independent of the tactic position relative to an adjacent nitrile since this comonomer is a vinylidene dicarboxylic acid. Finally, amideoxime comonomers have been shown to be similar to carboxylic acid comonomers in as far as both lower the cyclization temperature, however at higher pyrolysis temperatures the copolymers of amideoxime display a lower weight loss.

(2) Examine the effects of varying comonomer concentration on the degradation rate. Should one of the above mentioned comonomers

exhibit superior thermal properties, experiments (i.e. synthesis, degradation studies, etc.) should be performed to determine the optimum comonomer concentration to maximize cyclization.

(3) Determine the effect of tacticity on the degradation mechanism. It is believed that the cyclization reactions occurring during degradation involve only small blocks of isotactic nitrile sequences. If this be the case, than isotactic PAN would be extremely useful as a precursor material.

Attempts should be made to polymerize tactic PAN by several methods such as Ziegler-Natta catalysis, urea canal complex, in a liquid crystal media, and in the presence of crown ethers. The polymers could then be characterized by FTIR, ^{13}C -NMR, and thermal analysis. Degradation studied should then be performed to determine the kinetics and structure of the degraded product.

(4) Determine the effects of chain orientation on the degradation mechanism. Uniaxially oriented films should be prepared and degradation studies performed using FTIR. This type of experiment would further resolve the question of a tacticity dependence for the cyclization reaction since orientation would reduce chain rotation and thus slow cyclization of atactic sequences.

REFERENCES

1. P. A. Thrower, Earth and Mineral Sciences News Letter, The Pennsylvania State University, University Park, PA, 48, 9, June 1979.
2. J. E. Bailey and A. J. Clark, Nature, 234, 529 (1971).
3. L. H. Peebles, Jr., Encyclopedia of Polym. Sci. and Tech., Suppl. Vol. 1, Wiley, New York, 1976.
4. M. M. Coleman and P. C. Painter, J. Macromol. Sci. - Revs. Macromol. Chem., C16, 197 (1977).
5. M. M. Coleman and R. J. Petcavich, J. Polym. Sci., Polym. Phys. Ed., 16, 821 (1978).
6. N. Grassie and J. N. Hay, J. Polym. Sci., 56, 189 (1962).
7. Ibid., 30, 37 (1958).
8. Ibid., 27, 207 (1958).
9. J. G. Grasselli, The Standard Oil Co. of Ohio, Technical Report No. 3381, May 1967.
10. N. Grassie and R. McGuchan, Polym. J., 8, 257 (1972).
11. E. N. Zil'berman, Russ. Chem. Rev., 331 (1960).
12. J. F. Walker, Formaldehyde, Reinhold, New York (1944).
13. N. Grassie and R. McGuchan, Europ. J. Polym. Sci., 9, 113 (1973).
14. R. Silverstein, G. Bassler and T. Morrill, Spectrometric Identification of Organic Compounds, Wiley, New York (1974).
15. R. T. Conley and J. F. Bieron, J. Appl. Polym. Sci., 7, 1757 (1963).
16. G. G. Cameron and D. R. Kane, Polymer, 9, 461 (1968).
17. N. Grassie and R. McGuchan, Europ. J. Polym. Sci., 8, 865 (1972).
18. N. Grassie and D. R. Bain. J. Polym. Sci. A1, 8, 2653 (1970).
19. R. J. Petcavich, P. C. Painter, and M. M. Coleman, J. Polym. Sci. - Polym. Lett. Ed. 17, 165 (1979).

20. B. E. Zaitsev and Y. N. Sheinker, Izves Akad. Nauk. SSSR, Otdel, Khim., Nauk, 11, 2070 (1962).
21. C. A. Grob and H. J. Wilkens, Helv. Chim. Acta, 48, 808 (1965).
22. L. Kato, Y. Yamanaka and S. Kawamata, Chem. Pharm. Bull., 12, 2411 (1969).
23. T. Miyazawa, T. Shimanouchi and S. Mizushima, J. Chem. Phys. 29, 611 (1968).
24. Y. Mikawa, Bull. Chem. Soc. Jap., 29, 110 (1956).
25. R. G. Snyder and G. Zerbi, Spectrochim. Acta, Part A, 23, 391 (1967).
26. W. S. Durrell, J. A. Young and R. D. Dresdner, J. Org. Chem., 28, 831 (1963).
27. R. A. Olofson, The Pennsylvania State University, Private Communication.
28. O. Allendroff, Chem. Ber., 24, 2346 (1891).
29. J. March, Advanced Organic Chemistry: Reactions Mechanisms, and Structure, McGraw-Hill, New York, 1968.
30. R. E. Richards and H. W. Thompson, J. Chem. Soc., London, 1260 (1947).
31. P. Sykes, Mechanisms in Organic Chemistry, Longsman, Green and Co. Ltd., London, 1961.
32. N. Grassie, Trans. Faraday Soc., 48, 379 (1952).
33. N. B. Colthup, L. H. Daly and S. E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1975.
34. J. Brandrup and L. H. Peebles, Jr., Macromolecules, 1(1), 64 (1968).

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