

Examination of the Oxidative Degradation of Polyacrylonitrile Using Infrared Spectroscopy*

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INTRODUCTION

In the past several years, much effort has been expended in an effort to adequately explain the formation of color and the thermal degradation reactions of polyacrylonitrile polymers. Houtz¹ observed that discoloration of polyacrylonitrile was accelerated by heat and oxygen. However, unlike vinyl polymers, the molecular weight did not decrease on heating, indicating that chain scission to form volatile fragments does not take place. From these data, the formation of conjugated cyclic systems through the interaction of neighboring nitrile groups was postulated as a possible mechanism for the degradation. This basic mechanism with only slight modifications has been utilized by other investigators in an effort to adequately account for the observed changes in the physical properties of polyacrylonitrile under a variety of degradation conditions.²⁻⁵ Straus and Madorsky⁶ observed that polyacrylonitrile showed unusual stability in the temperature range between 250° and 455°C. This stability was found characteristic of polymers which do not undergo direct depolymerization to monomer, but rather lose side groups from adjacent carbons on the chain to form conjugated double bond systems. Until 1958, it was generally accepted that the cyclic structure generally was responsible for polymer discoloration. Schurz⁷ attacked this mechanism on the basis of the fact that the physical properties of the degraded polymer, particularly, the spectral characteristics do not agree with those expected for conjugated pyridinoid systems. An alternate mechanism was claimed by this investigator to more adequately explain the observed changes in the degraded polyacrylonitrile. The postulated reaction scheme involved the formation of azomethine linkages by condensation of a nitrile group from an adjacent chain with a tertiary hydrogen of the polymer chain activated by the alpha-nitrile group. Grassie⁸ pointed out, in taking exception to the Schurz postulate, that coloration develops from yellow to orange to red, suggesting

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a lengthening of the conjugated structures. Infrared analysis supports the change from nitrile to substituted imine to poly-imine structures. The solubility changes are presumably a function of the rigid configuration of the newly formed structure, rather than crosslinking. The ultraviolet bands could be consistent with a cyclic structure which is not fully aromatic, and therefore, in agreement with the proposed mechanism.

A number of discrepancies were observed in both of the postulated mechanisms on recent examination of air oxidized polyacrylonitrile films. Although an intense absorption was observed in the carbon-nitrogen double bond absorption region, no change in the absorption of the nitrile functional group to indicate a loss in this functional species was observed. In addition, the cyclic mechanism does not adequately explain the accelerated color formation in an oxygen containing atmosphere. In view of these data, it was of interest to investigate in some detail the oxidative degradation of this polymer system. It was proposed to follow the functional group changes using direct infrared spectrophotometric techniques on thin films. Under rather mild thermal degradation conditions in air, it was anticipated that the initial degradation reactions could be evaluated. From these reactions some additional knowledge of the nature of the early course of degradation might assist in evaluating the proposed mechanisms for the eventual total degradation of polyacrylonitrile. Any reaction producing multifunctional species via a radical oxidation process would be expected to be very complex after extended periods at reaction temperatures. Therefore, it was deemed necessary to study by this method only those initial degradation reactions which take place at a relatively short period of time, and which would tend to introduce additional labile systems into the polymer unit. The object of such a study was to show the presence of additional functional groups introduced oxidatively into the polymer system for which the proposed degradation schemes do not account and yet would definitely alter the overall path of degradation.

EXPERIMENTAL

The infrared instruments used for this study were a Baird, Model AB-2, Beckman IR-4 and Beckman IR-5A double beam, recording infrared spectrophotometers. The technique used for the measurement of absorbance values was the baseline method described by Wright.⁹ The samples of pure polyacrylonitrile, obtained as films from dimethylformamide solution, was supplied by the Film Department, E. I. du Pont de Nemours & Company, Buffalo, New York.

Degradation Techniques

A. Intermittent Monitoring of Polyacrylonitrile Films. Two types of ovens were used to age polymer samples. Initially, polymers were aged in commercial forced-draft ovens. The temperature was accurately controlled by direct heating using a variable transformer. Although this type

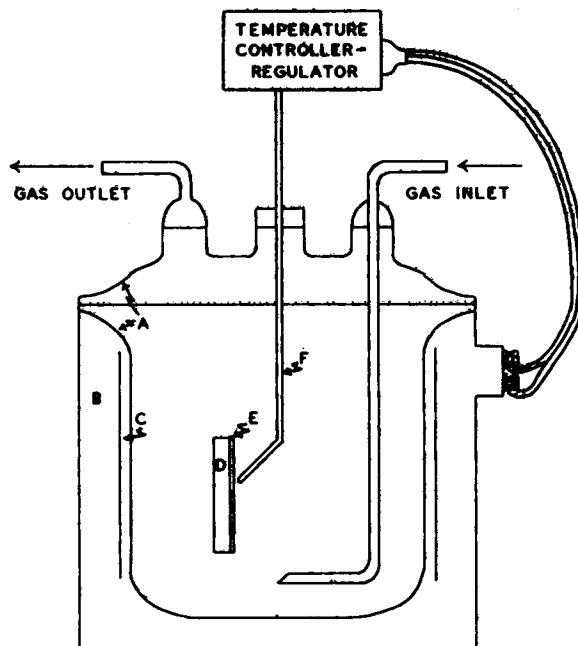


Fig. 1. Oven utilized for controlled oxidation studies.

of unit was found satisfactory for aging in air, a specially constructed oven was later adopted in order to better control the aging parameters. The oven, shown in Figure 1, consists of a resin kettle (A) with a demountable top, insulated with an asbestos filled aluminum jacket (B). Embedded in the asbestos was a chromel wire, B and S 26 gauge heating wire coil (C). The polymer sample (E), coated on a sodium chloride plate (D), or clamped in an aluminum holder was placed in a position close to the regulating thermocouple (F). By means of the four port openings in the top of the kettle, the intake and exit of the aging atmosphere could be accurately controlled. The temperature was controlled using a West Instrument Company proportioning temperature controller-regulator system.

Using these two types of ovens, intermittent heating was carried out in the following manner. The polymer sample, held in the appropriate sample holder, was inserted into the oven. After a specific time interval, the sample was removed and desiccated until cool. Then the infrared spectrum was determined and the entire process repeated until all the necessary spectral data were determined.

B. Difference Spectral Monitoring. A variation of recording the spectra after intermittent heating was the use of difference spectrum determination. If a polymer film of the same thickness is inserted in the reference beam, as in the sample beam of the spectrophotometer, no spectrum will be observed, due to the null principle of the double beam

optical system. Therefore, a straight line spectrum was observed with nonaged films in the reference and sample beams. If the sample film was aged, the only positive changes in absorption noted were due to the ingrowth of functional groups not present in the original polymer. Conversely, inverted peaks in the spectrum denoted the disappearance of functional groups originally contained in the polymer. By using this method, the infrared spectrum of a given sample was very sensitive to changes in functionality during the thermal aging process.

C. Continuous Monitoring of Polyacrylonitrile Films. An alternate method of aging polymers was also developed to supplement aging in stationary ovens. A heated cell was constructed which allowed heating and spectral examination simultaneously at the desired reaction temperature.¹⁰ In the study of the reaction rates in air, at elevated temperatures, the cell was heated to the desired temperature under an atmosphere of nitrogen to prevent oxidation of the film prior to the initial determination of its spectrum. After the introduction of the sample into the spectrophotometer, the spectrum of particular regions of interest could be recorded as rapidly as desired. Using this type of heating and monitoring unit, it was possible to measure the rate of reaction as a function of the ingrowth of degradation bands at very close intervals.

At very high temperatures a possible experimental error exists using this system. If the polymer sample becomes a radiating source when heated, it is possible that the observed band could be an additive due to the transmitted and radiated energy at a particular frequency. By increasing the intensity of the radiation after it has passed through the sample, this stray radiation would decrease the value of I_0/I and therefore alter the recorded absorbance. At the temperature employed in this study (100° to 200°C.), this source of error was insignificant in the experimental results.

Film samples of polyacrylonitrile of suitable thickness for infrared analysis were held in specially designed aluminum holders, similar to the commercial holders used in microcell construction. Individual sample holders insure proper alignment of the sample in the beam of the spectrophotometer after each aging period. In addition, these holders could be handled conveniently without contact with the film sample. In order to eliminate any possible catalytic effect by the aluminum surface, thin layers of asbestos were used as spacers.

Experimental Procedures

Samples of polyacrylonitrile films were heated by the intermittent technique at 100°C., 150°C., and 200°C. in forced draft ovens. The temperature change during the heating cycle was $\pm 2^\circ\text{C}$. However, there is no doubt that by using this technique, a portion of the oxidation is continuing during the heating and cooling of the samples prior to spectral examination. Similar experiments were carried out for extended periods *in vacuo* (0.05 mm.) and in nitrogen atmospheres.

A single film sample was heated in air at 200°C. for 45 min., spectrally examined, and heated *in vacuo* at 160°C. for 22 hrs. and again spectrally examined. Difference spectrum were determined at 150°C. and 200°C. and continuous monitoring was carried out at 200°C. in order that all the necessary data could be gathered in a 6 hr. period of continuous examination. The infrared spectrum was recorded between 3 and 7 μ approximately every four minutes.

Results and Discussion

The course of oxidative degradation of polyacrylonitrile was observed at three temperatures, 100°C., 150°C., and 200°C. The results obtained by intermittently monitoring the spectral changes occurring for film samples aged at the three temperatures are numerically (as absorbance) presented in Tables I, II, and III. The band changes at each of the temperatures

TABLE I
Intermittent Heating of Polyacrylonitrile at 100°C. Ingrowth of Absorption Bands^a

Time/hr.	Infrared spectral data				
	3300 cm. ⁻¹	2240 cm. ⁻¹	2215 cm. ⁻¹	1710 cm. ⁻¹	1600 cm. ⁻¹
1		0.530			
65		0.548		0.065	0.072
300		0.502		0.095	0.086
465		0.510	0.046	0.201	0.258
475	0.096	0.478	0.045	0.229	0.288
488	0.108	0.514	0.046	0.246	0.360
512	0.117	0.500	0.058	0.282	0.382
535	0.134	0.529	0.050	0.307	0.442
586	0.149	0.559	0.040	0.326	0.511
629	0.179	0.570	0.044	0.432	0.720
725	0.362	0.600	0.108	1.04	

^a Film thickness 0.043 mm.

TABLE II
Intermittent Heating on Polyacrylonitrile at 150°C. Ingrowth of Absorption Bands^a

Time/hr.	Infrared spectral data				
	3300 cm. ⁻¹	2240 cm. ⁻¹	2215 cm. ⁻¹	1710 cm. ⁻¹	1600 cm. ⁻¹
1		0.620		0.115	0.190
2		0.625	0.048	0.101	0.194
5	0.091	0.650	0.040	0.141	0.291
9	0.049	0.755	0.040	0.158	0.336
14	0.054	0.629	0.018	0.221	0.610
24	0.636	0.622	0.101	0.976	
29	0.645	0.660	0.102		
48	0.832	0.642	0.142		
93		0.603	0.131		
140		0.322	0.208		
187		0.272	0.233		
211		0.272	0.233		

^a Film thickness 0.043 mm.

TABLE III
Intermittent Heating of Polyacrylonitrile at 200°C. Ingrowth of Absorption Bands^a

Time/hr.	Infrared spectral data				
	3300 cm. ⁻¹	2240 cm. ⁻¹	2215 cm. ⁻¹	1710 cm. ⁻¹	1600 cm. ⁻¹
0.5		0.561			0.169
1.0	0.097	0.536	0.054	0.171	0.355
1.5	0.120	0.552	0.054	0.177	0.415
2.0	0.115	0.573	0.049	0.209	0.484
3.0	0.215	0.603	0.052	0.445	1.63
4.0	0.348	0.658	0.138	0.797	
7.0	0.814	0.638	0.218		
10.	1.08	0.555	0.232		
13.		0.505	0.272		
16.		0.526	0.296		
20.		0.505	0.276		

^a Film Thickness 0.043 mm.

are remarkably consistent in that all the bands appearing in the spectrum of degraded polyacrylonitrile appear at essentially equivalent time intervals, dependent only upon the degradation temperature. This indicates the mechanism of the degradation is the same over the temperature range studied.

As indicated in Table IV, the time necessary to degrade three identical samples of polyacrylonitrile to the same spectral state of degradation is roughly as expected from consideration of the Arrhenius equation.



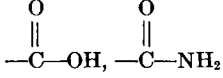
TABLE IV
Degradation Versus Time of Heating

Temperature	Time
100°C.	550 hr.
150°C.	11 hr.
200°C.	2 hr.

The purpose of presentation here is to present the reader with the relative time intervals in which particular bands might appear. For example, Table V indicates the ingrowth of bands observed on aging polyacrylonitrile at 150°C. A band appearing after one hour at 150°C. might be expected to appear after 50 hrs. at 100°C.

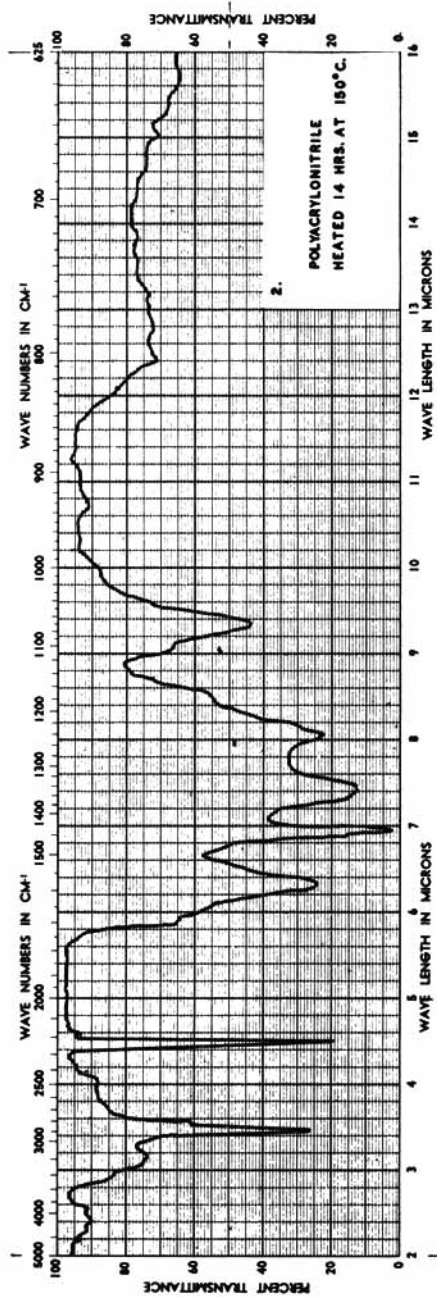
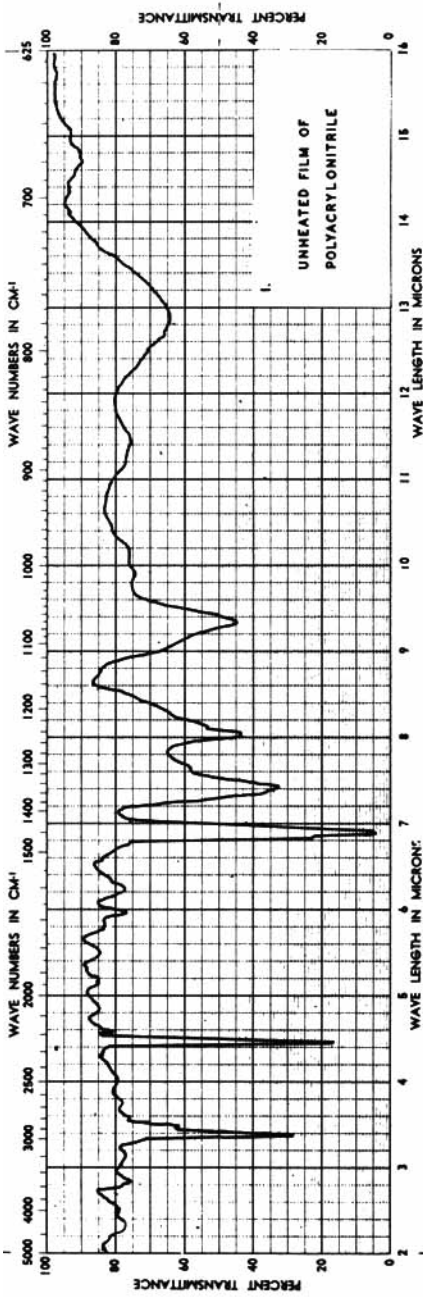
It was found that the degradation at 100°C. was much too slow for practical observation. Conversely, degradation at 200°C. was too rapid if the intermittent monitoring technique was to be used. The spectral changes which have occurred after 14 hrs. of oxidation at 150°C. (Spectrum 2, Fig. 2) are best visualized by comparison with a nonoxidized film spectrum (Spectrum 1, Fig. 2); as can be seen, the changes can be observed quite satisfactorily. However, at longer time intervals the spectrum becomes quite complex with broad, indistinguishable bands making interpreta-

TABLE V
 Growth of Infrared Bands on Oxidation at 150°C.

Band frequency	Assignment	Intensity	Time of first appearance
1600	$-\text{C}=\text{C}-$	Strong	1st hr.
1380	$-\text{CH}_2-$	Weak to Medium	14th hr.
810	$=\text{C}-\text{H}$	Weak	14th hr.
1685		Medium to Strong	2nd hr.
1710		Medium to Strong	5th hr.
3300-3100		Medium to Strong	10th hr.
2215	$-\text{C}=\text{CH}-\text{C}\equiv\text{N}$	Weak to Medium	24th hr.

tion impossible. It was of interest, therefore, to develop another method which would enable the deduction of functional changes occurring at these time intervals. A significant, although not completely satisfactory, improvement was obtained by employing the difference method as spectrally exemplified in Spectrum 3, Figure 2. It is notable in this spectrum that examination of the 5μ region shows that the base line remains the same, even though functional group changes do take place. Major changes, such as absorption band ingrowth at 3.0 and 6.3μ can readily be detected. More significantly, small changes in spectral properties, such as the band shift at 7.2μ , can also be observed.

In the light of these general considerations, the details of the interpretation of the spectral changes can be discussed. The most important observation is that the intensity of the sharp carbon-nitrogen triple bond stretching vibration at 2240 cm.^{-1} (4.5μ) does not change during the early stages of degradation. This absorption band remains constant during the entire primary oxidation process. The band ingrowth at 6.3μ proceeds to infinite absorbance before the band at 4.5μ begins to decrease. The absorption band at 1600 cm.^{-1} (6.3μ) can be best interpreted as a carbon-carbon double bond stretching vibration. The enhanced intensity would be expected if the double bond introduced into the polymer skeleton is conjugated with another unsaturated group. The shift of this frequency to 1600 cm.^{-1} is consistent with a neighboring electron-withdrawing group (such as the nitrile group) in conjugation with the double bond. Bellemy¹¹ lists the frequency of a conjugated carbon-carbon double bond stretching vibration as near 1600 cm.^{-1} with enhanced intensity. The intensity of this band is significant in that, it cannot be attributed to cyclic structure as



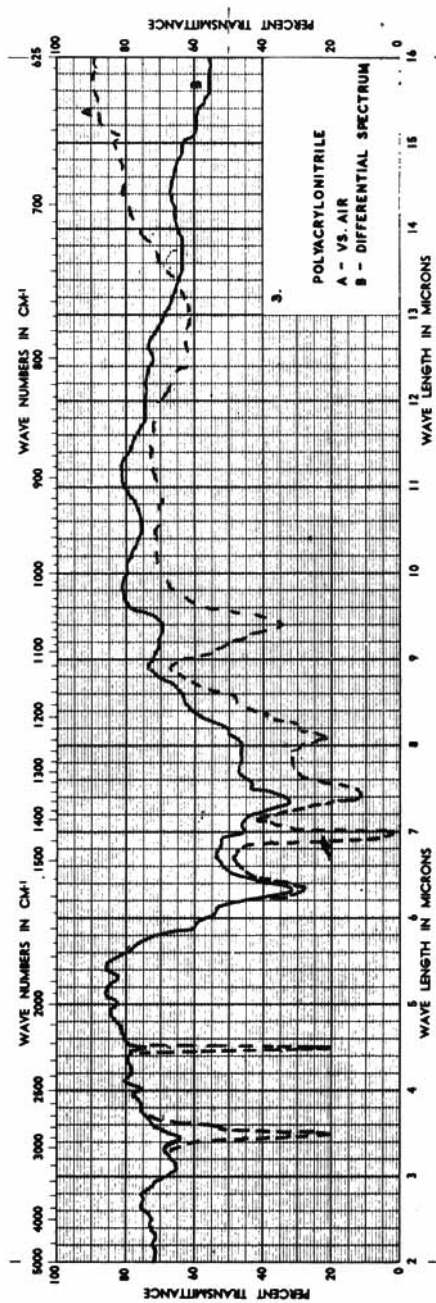


Fig. 2. Typical infrared spectra.

proposed in the Houtz mechanism.¹ At this stage of degradation little or no loss of nitrile can be detected and the intensity of the band is already such that it has proceeded to infinite absorbance. In the comparison with spectrally known hetero-aromatic systems, although comparable bands of weak intensity appear in this region, bands of great intensity, 100 times that of the nitrile, are absent. However, on comparison with conjugated systems of nonaromatic types, good agreement with both the observed band positions and relative intensities is obtained.

This interpretation is further substantiated by a weak absorption at 1380 cm.^{-1} , which although undetected in the spectrum of the degraded sample when compared to air as a reference, was present in the difference spectrum using unaged polyacrylonitrile film in the reference beam. Similarly, a weak band at 810 cm.^{-1} , was also distinguishable using the difference technique.

These three bands, the carbon-carbon double bond stretching frequency at 1600 cm.^{-1} , the carbon-hydrogen in-plane deformation band at 1380 cm.^{-1} , and the out-of-plane deformation band at 810 cm.^{-1} are in good agreement for a 1,1,2-trisubstituted olefinic linkage. Therefore, this structural moiety represents the initial product detected in the course of the degradation.

At later stages of oxidative degradation, it is evident that secondary oxidations and group interactions are taking place. The simultaneous ingrowth of absorption bands at 1685 cm.^{-1} ($5.95\ \mu$), 1710 cm.^{-1} ($5.85\ \mu$) and $3300\text{--}3100\text{ cm.}^{-1}$ ($3.0\text{--}3.2\ \mu$) indicate the appearance of acid, amide, or acid and amide functional groups. After 4 hrs. at 200°C . an absorption

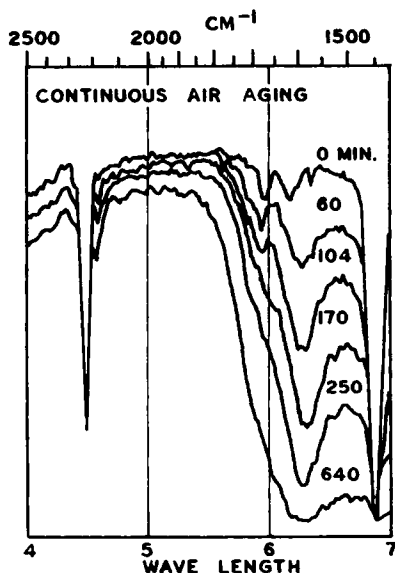


Fig. 3. Typical spectral changes between 4 and $7\ \mu$ at 200°C .

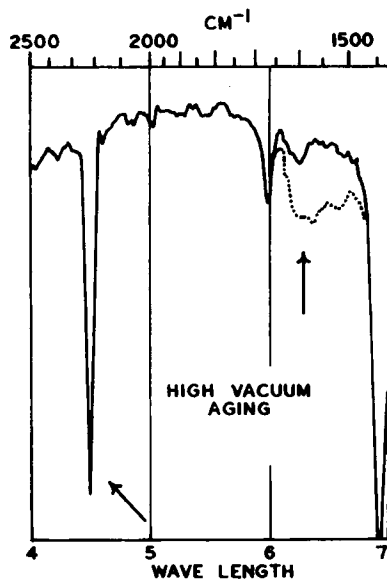


Fig. 4. Aging *in vacuo* at 160°C.: (—) after 1 hr.; (- -) after 22 hrs.

band at 2215 cm.^{-1} (4.55μ) begins to slowly grow in intensity. This ingrowth is accompanied by a corresponding decrease in the intensity of the nitrile absorption at 2240 cm.^{-1} (4.5μ). It is evident that the appearance of this band is merely a shift of the nitrile absorption due to the changing structure of the polymer at skeletal positions adjacent to this group. For example, the conjugation of the nitrile group with the olefin would be expected to cause a shift of this type and magnitude in the observed frequency.

If the physical changes of the polymer are observed, the most striking feature is the color sequence involved. The unaged film is colorless but upon heating it goes through a color change of light yellow, to yellow, to light orange, to reddish orange, to red, to deep red. A film sample heated at 200°C. for 10 hrs. will appear black, only if it is held to a bright light does it appear to be a very deep red. After 30 hrs. at 200°C., the film is very brittle and cracks easily.

When polyacrylonitrile films were heated at 160°C. *in vacuo* or nitrogen, for extended periods of time, no significant changes in the infrared spectrum of the aged film are detectable. Only after approximately 150 hrs. can small changes be detected. These are most probably due to the absorption of small quantities of oxygen on the film surface when the aging oven was opened in order to spectrally examine the film. Reevacuation of the system undoubtedly leaves a residual amount of oxygen in the oven. The color change during this process is also very slight and the aged film is a very pale yellow.

Heating a film of polyacrylonitrile in air at 200°C. for 45 min. gave a

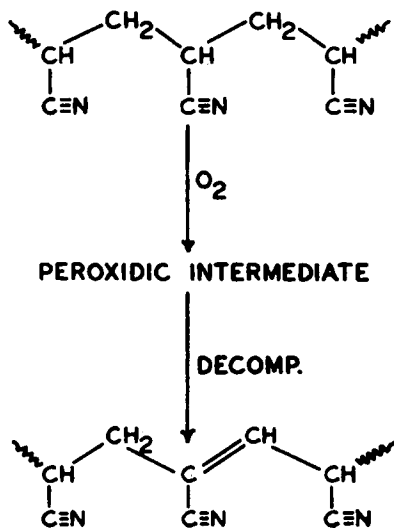


Fig. 5. Initial oxidation step in polyacrylonitrile degradation.

typical oxidized film spectrum. The film was then heated for extended periods *in vacuo* at 160°C. No further change in absorption of the 1600 cm.^{-1} band was observed. Therefore, it must be concluded that no rapid chemical degradation of polyacrylonitrile takes place *in vacuo* at 160°C. regardless of the condition of the sample prior to treatment. Similar treatment of a film sample using a nitrogen atmosphere instead of an evacuated system showed continued oxidative changes for 2 hrs. after the nitrogen purging of the oven was started.

These results can be summarized briefly as follows: (a) the nitrile absorption band in the infrared region does not change during the initial oxidation stage of the degradation indicating the nitrile group is not involved in this process; (b) the initial degradation product is a 1,1,2-disubstituted olefin; (c) the reaction being observed is dependent upon the presence of oxygen as shown by vacuum and inert atmosphere studies; (d) the secondary reactions are sufficiently removed on a time scale to allow suitable spectral observation of the functional group changes taking place.

It is concluded from these data that the cyclic mechanism proposed by Houtz¹ and accepted by others²⁻⁵ is not an accurate scheme in explaining the reactions taking place in the early stages of the oxidative degradation. The postulate involving crosslinking through azomethine linkages as proposed by Schurz⁷ is also inaccurate. Both of these reaction schemes involve the nitrile group to account for the thermal degradation. Since the initial reaction is nitrile independent these routes of degradation must be negated as proposals which account for these early oxidation steps. As secondary reactions such proposals may be plausible although they are difficult to substantiate using infrared spectral techniques. Also the experimental conditions employed in this study are considerably less

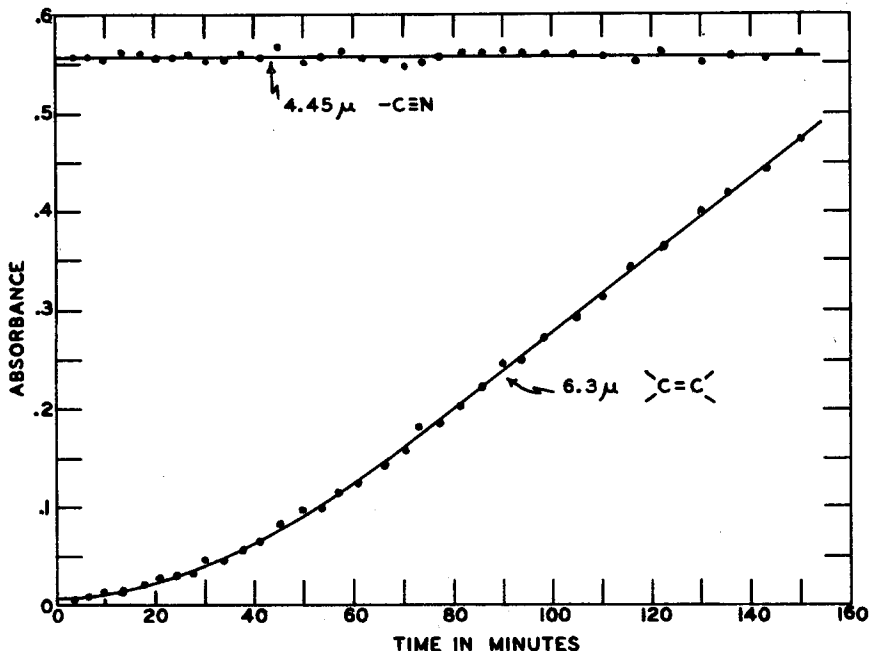


Fig. 6. Continuous heating and infrared monitoring of polyacrylonitrile oxidation in air at 200°C.

severe than those used by Houtz¹ and Vosburgh,¹² hence, the observation of a condensed pyridinoid structure is not likely. In view of the rather conclusive evidence¹² for these structural moieties, this present study must not be considered as a complete elucidation of the mechanism of oxidative degradation. Rather, the route by which initial degradative species are produced, and under which increased severe conditions produce more complex degradation products better defines the reaction.

Since the most oxidatively susceptible linkage in the polymer backbone is the tertiary hydrogen activated by the adjacent electron-withdrawing nitrile group, it would be consistent to propose as a more reasonable initial degradation route the reactions shown in Figure 5.

The results obtained by the continuous heating of polyacrylonitrile are graphically plotted Figure 6. After approximately 70 min. of oxidation the reaction rate becomes constant for the remainder of the observable portion of the initial oxidation cycle. The portion of the cycle (Fig. 6) was taken as that period of degradation in which the complex band structure in the spectrum did not overlap the bands being measured.

The results of these data can be interpreted in the following manner. The initial step in the degradation of polyacrylonitrile is the attack of oxygen on the polymer surface. In the first ten minutes, no decomposition to product can be detected since the concentration is very small and insensitive to infrared detection.¹³ The first appearance of product at 1600

cm.^{-1} (6.3μ) occurs after ten minutes and the concentration of oxygenated intermediates on the surface continues to increase with subsequent decomposition in a slow reaction to stable products. A changing rate is observed during this period since the polymer surface is not fully saturated and rate of product formation will be dependent on the concentration of the oxygenated intermediates. At approximately 70 min., the polymer surface becomes fully saturated with the oxygenated species. Based on previous evidence¹⁴ that polymers of similar types readily absorb oxygen, it is consistent that the absorption of oxygen and its reaction is faster than the peroxidic decomposition to stable products. Therefore, the concentration of oxygen-containing intermediates will remain constant during

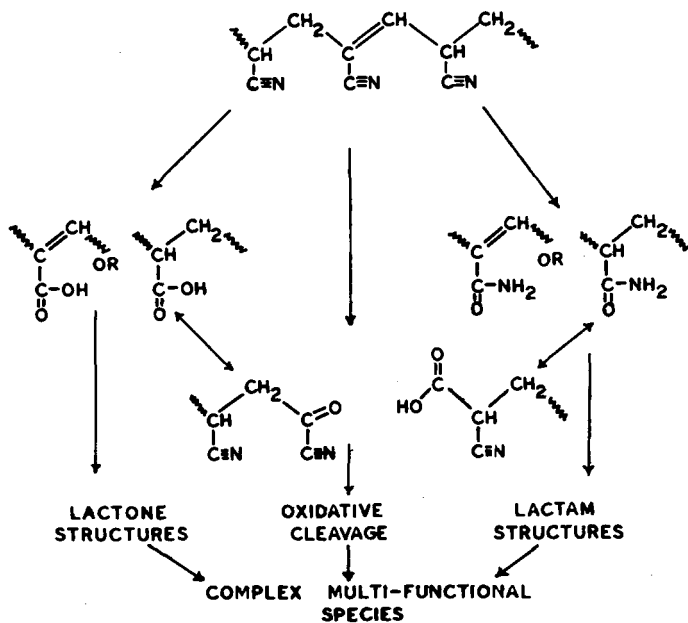


Fig. 7. Postulated secondary oxidation and degradation reactions.

the initial degradation reaction. The rate of decomposition to product will then be proportional to constant, and the reaction will be zero order with respect to polymer.

Once the labile double bond is introduced into the structure, a number of subsequent secondary reactions are possible. The absorption bands at 1685 cm.^{-1} (5.95μ) and 1710 cm.^{-1} (5.85μ) can be attributed to carbon-oxygen double bonded stretching frequencies, which together with the $3300\text{--}3100 \text{ cm.}^{-1}$ band (3.0 to 3.2μ), support acid and amide formation. These absorption bands also could arise from cyclic structures of a non-conjugated type. In addition to the nitrile-nitrile interactions proposed in previous mechanisms, a number of other possible secondary products which may also promote oxidative degradation through interaction with

the nitrile group are shown in Figure 7. With the inclusion of oxygen into the system together with olefinic species, the route by which the system further degrades becomes extremely complex and upon further degradation the broadly defined spectrum obtained sheds no light on these processes. However, extension of this mechanism using copolymeric systems might greatly assist in the evaluation of these oxidation routes. These studies may also assist in explaining the incomplete conversion of this system to a fully aromatic species and the inclusion of oxygen into the final product of air degradation.

The route by which color is formed in these polymers is perhaps the most difficult to substantiate or refute from this work. Since the most likely formation of a conjugated chromophore is via interaction of the nitrile group with other susceptible linkages, studies under oxygen in heated cell units in the ultraviolet region would greatly assist in an evaluation of color formation at the early stages of degradation. These and related studies are in progress and will be reported at a later date.

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Synopsis

The oxidative thermal degradation of polyacrylonitrile has been examined using infrared spectroscopy. It was found that the generally accepted mechanism for the thermal degradation of polyacrylonitrile in air, which involves direct interaction of neighboring nitrile groups, and alternate proposals, involving azomethine crosslinks through reaction of the nitrile group and a neighboring tertiary hydrogen atom, do not satisfactorily represent an initial degradation scheme accounting for the observed infrared spectral changes. Rather, it must be concluded that these reactions take place after the initial degradation, to produce highly complex pyridinoid systems, and are not observable under the experimental conditions employed here. By detailed interpretation of the spectral changes using, in part, a difference spectral examination technique, an alternate route for the oxidative degradation involving the introduction of double bonds

in the polymer chain could be formulated. This reaction can best be visualized as occurring via the attack of molecular oxygen at the activated tertiary carbon-hydrogen bond adjacent to the electron-withdrawing nitrile group. The nitrile group was shown to remain unreacted during the course of the initial oxidation. After the introduction of the double bond, a number of secondary degradative reactions, of which the previously proposed routes of degradation are representative, take place; these include degradation reactions of the nitrile groups to form acid and amide groups. It was observed that the accumulation of oxygenated intermediates on the surface of the polymer film is a rapid reaction and that the initial degradation process is controlled by the concentration of these species.

Résumé

La dégradation thermique oxydative du polyacrylonitrile a été étudiée par spectroscopie infrarouge. On a trouvé que le mécanisme généralement accepté pour la dégradation thermique du polyacrylonitrile à l'air par interaction directe des groupes nitriles vicinaux, ainsi que les autres schémas basés sur la formation de ponts azométhine à partir des groupes nitriles et des hydrogènes tertiaires vicinaux, ne représentent pas de façon satisfaisante un schéma de dégradation initiale tenant compte des variations observées dans le spectre infrarouge. On est de plus amené à conclure que ces réactions se déroulent après une dégradation initiale. Elles donnent naissance à des systèmes pyridinoides très complexes ne pouvant être observés dans les conditions expérimentales de ce travail. À la suite d'une interprétation détaillée des modifications spectrales grâce, en partie, à une technique d'examen des différences spectrales, un mécanisme différent faisant intervenir l'introduction de doubles liaisons dans la chaîne polymérique a pu être formulé pour la dégradation oxydative. Cette réaction peut être adéquatement représentée par l'attaque de l'oxygène moléculaire sur le lieu carbone-hydrogène tertiaire activé adjacent au groupe nitrile électrocapteur. On a pu montrer que le groupe nitrile ne réagissait pas durant l'oxydation initiale. À la suite de l'introduction de la double liaison, une série de réactions de dégradation secondaires se produit. Elles sont représentées par les schémas de dégradation antérieurs. À ceux-ci doivent être jointes les réactions de dégradation des groupes nitriles avec formation de groupes acides et amides. On a observé que l'accumulation des intermédiaires oxygénés sur la surface du film polymérique est une réaction rapide et que le processus de dégradation initial est contrôlé par la concentration de ces intermédiaires.

Zusammenfassung

Der thermisch-oxydative Abbau von Polyacrylnitril wurde infrarotspektroskopisch untersucht. Es zeigte sich, dass der allgemein angenommene Mechanismus des thermischen Abbaus von Polyacrylnitril in Luft mit direkter Wechselwirkung benachbarter Nitrilgruppen, sowie andere Vorschläge mit einer Azomethinvernetzung durch Reaktion der Nitrilgruppe mit einem benachbarten tertiären Wasserstoffatom ein den beobachteten Infrarotänderungen entsprechendes Schema für das Anfangsstadium des Abbaus nicht befriedigend erklären können. Es muss vielmehr angenommen werden, dass diese Reaktionen erst nach dem Anfangsstadium des Abbaus unter Bildung hochgradig komplexer pyridinähnlicher Systeme stattfinden, und unter den hier angewendeten Versuchsbedingungen nicht zu beobachten sind. Durch genaue Interpretation der spektralen Veränderungen mit teilweiser Benützung eines spektralen Differenzverfahrens konnte ein alternativer Weg für den oxydativen Abbau mit Einführung von Doppelbindungen in die Polymerkette formuliert werden. Diese Reaktion kann man sich am besten als einen Angriff des molekularen Sauerstoffs an der aktivierten tertiären, der elektronenentziehenden Nitrilgruppe benachbarten Kohlenstoff-Wasserstoffbindung vorstellen. Die Nitrilgruppe bleibt während des Anfangsstadiums der Oxylation unverändert. Nach der Einführung der Doppelbindung findet eine Anzahl sekundärer

Abbaureaktionen statt, wie sie für die früher vorgeschlagenen Abbauwege charakteristisch sind; dazu gehören Abbaureaktionen der Nitrilgruppen unter Bildung von Säure- und Amidgruppen. Die Anhäufung von sauerstoffhaltigen Zwischenprodukten an der Oberfläche des Polymerfilms ist eine rasche Reaktion und das Anfangsstadium des Abbauvorganges wird durch die Konzentration dieser Produkte bestimmt.

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