drolysis by concentrated hydrochloric acid but liberated gases from an aqueous solution of sodium nitrite. The elemental analysis indicated a high oxygen content, which yielded the formula $C_8H_{15}N_3O_3$.

Anal. Calcd for $C_8H_{15}N_3O_3$: C, 47.76; H, 7.46; N, 20.90; O, 23.88. Found: C, 47.26; H, 7.50; N, 21.06; O, 24.48.

The oxygen was actually determined. The molecular weight in a vapor phase osmometer was determined as 201 in acetone.

4. Fraction, Residue of Distillation. After removal of all components by high-vacuum distillation, major amounts of a brown-black residue remained which apparently was polymeric, since fibers could be pulled from the melt. The polymer was purified by precipitation in acetone and high-vacuum treatment in a molecular still to remove all low-boiling components.

The polymer was soluble in water and partially soluble in DMSO. The nmr spectrum showed one doublet at 81 cps and the ir band showed broad absorption bands in the C=N region around 1600 cm^{-1}.

The elemental analysis of the polymer indicated a high nitrogen and oxygen content.

Anal. Calcd for $(C_4H_7NO)_x$: C, 56.47; H, 8.2; N, 16.47; O, 18.82. Found: C, 55.95; H, 7.9; N, 17.05; O, 19.7.

Hydrolysis with concentrated hydrochloric acid yielded isobutyric acid; treatment with basic hydrogen peroxide destroyed the brown color. The product obtained was highly hygroscopic but could not be identified. Based on these facts, the polymer was identified as a polynitrone.

Acknowledgment. We wish to thank Professor W. H. Urry for many helpful discussions.

On the Chromophore of Polyacrylonitrile. VI. Mechanism of Color Formation in Polyacrylonitrile

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Contribution No. 482 from the Chemstrand Research Center, Inc., Durham, North Carolina. *Received October 27, 1967*

ABSTRACT: The formation of color in polyacrylonitrile is shown to be due to the formation of partially hydrogenated naphthyridine-type rings produced by linking up of adjacent nitrile units. This structure absorbs oxygen rapidly but not completely to form polynitrone $(-C{=}N(\rightarrow O)-)_n$ units. The polymerization of the nitrile units is initiated by products resulting from oxygen attack, by defects in the polymer chain, and by nucleophilic agents. Oxygen forms a hydroperoxide at the methylene carbon which forms a ketonitrile by elimination of water. A similar β-ketonitrile is produced by polymerization of the growing chain radical through a pendant nitrile group on the formed polymer. The cyanoenamine produced first is hydrolyzed to a β-ketonitrile when polymerization is conducted in an acidic aqueous medium. These defects may initiate the polymerization of adjacent nitrile groups. The amount of color formed is directly proportional to the number of these defects in the absence of other initiators. The fluorescence of polyacrylonitrile, described by many observers, is shown to be due to the presence of these ketonitrile groups in the polymer chain.

The thermal discoloration of polyacrylonitrile has received considerable attention during recent years. The main interest of previous publications was to establish the nature of the chromophore causing the color of the heat-treated polymer.[2–11] Since this work relied mostly on spectral evidence, no final conclusion could be drawn. Furthermore, relatively little work had been done on the mechanism of initiating the chromophore formation. The action of amines,[12] bases,[13,14] and the tertiary hydrogen atoms of the polymer itself[15] was considered. The initiating action of the latter was inferred by Grassie and Hay because all polyacrylonitriles developed color despite extensive purification of the monomer while polymethacrylonitrile did not discolor at high temperatures when it was prepared from purified monomers and extraneous material was excluded.[15,16]

In contradiction to this, we would like to show that the monomeric unit of polyacrylonitrile itself will not initiate the color formation reaction, but that it is converted into species which will initiate the color formation.

This paper summarizes the work carried out in this laboratory on the formation of color in polyacrylonitrile

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[2] (a) R. C. Houtz, *Textile Res. J.*, **20**, 786 (1950); (b) J. R. McCartney, *Mod. Plast.*, **30**, No. 11, 118 (1953).

[3] W. J. Burlant and J. L. Parsons, *J. Polymer Sci.*, **22**, 249 (1956).

[4] N. Grassie and I. C. McNeill, *ibid.*, **27**, 207 (1958).

[5] J. Schurz, *ibid.*, **28**, 438 (1948).

[6] W. Skoda, J. Schurz, and H. Bayzer, *Z. Phys. Chem.* (Leipzig), **210**, 35 (1959).

[7] R. T. Conley and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 1757 (1963).

[8] A. A. Berlin, A. M. Dubinskaya, and Y. S. Moshkovskii, *Vysokomolekul. Soedin.*, 1938 (1964).

[9] W. Fester, *Textil Rundschau*, **20**, 1 (1965).

[10] L. H. Peebles, Jr., and J. Brandrup, *Makromol. Chem.*, **98**, 189 (1966).

[11] L. H. Peebles, Jr., *J. Polymer Sci.*, *A-1*, **5**, 2637 (1967).

[12] E. M. LaCombe, *ibid.*, **24**, 152 (1957).

[13] H. Stübchen and J. Schurz, *Monatsh. Chem.*, **89**, 234 (1958).

[14] T. Takata, I. Hiroi, and M. Taniyama, *J. Polymer Sci.*, A2, 1567 (1964).

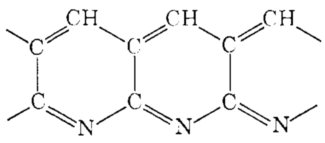
[15] N. Grassie and J. N. Hay, *ibid.*, **56**, 189 (1962).

[16] N. Grassie and I. C. McNeill, *ibid.*, **39**, 211 (1959).

and presented in earlier papers of this series.[10,11,17–20] It describes the nature of the chromophore and the major initiators and gives reaction paths for color formation. Details of the origin of these defects and the evidence for them has been presented in previous papers.

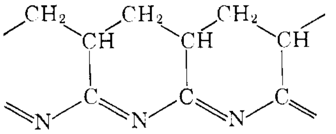
Results and Discussion

1. The Structure of the Chromophore of Discolored Polyacrylonitrile. The first step in an analysis of the thermal discoloration of polyacrylonitrile (PAN) must deal with the chemical nature of the chromophore. Five different structures of this chromophore have been advanced. They include the completely aromatic naphthyridine structure by Houtz[2a]



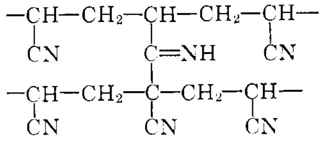
I

the partly hydrogenated rings of McCartney,[2b] Burlant and Parsons,[3] and Grassie and McNeill[4]



II

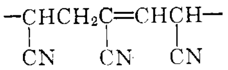
and the azomethine structure of Schurz.[5,6]



$$\begin{array}{l}-\underset{\displaystyle CN}{CH}-CH_2-\underset{\displaystyle |}{\underset{\displaystyle C{=}NH}{CH}}-CH_2-\underset{\displaystyle CN}{CH}-\\ -\underset{\displaystyle CN}{CH}-CH_2-\underset{\displaystyle CN}{C}-CH_2-\underset{\displaystyle CN}{CH}-\end{array}$$

III

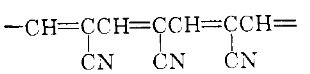
A single double bond conjugated with a nitrile group structure was suggested by Conley and Bieron as a precursor to the chromophore[7]



$$-\underset{\displaystyle CN}{C}HCH_2\underset{\displaystyle CN}{C}{=}CH\underset{\displaystyle CN}{C}H-$$

IVa

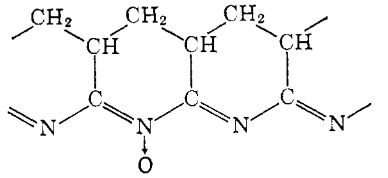
This idea was extended by Berlin[8] and Fester[9] to a system of conjugated double bonds with pendant nitrile groups.



$$-CH{=}\underset{\displaystyle CN}{C}CH{=}\underset{\displaystyle CN}{C}CH{=}\underset{\displaystyle CN}{C}CH{=}$$

IVb

Peebles and Brandrup confirmed structure II but showed that it was partially oxidized to an imine–nitrone copolymer.[10]



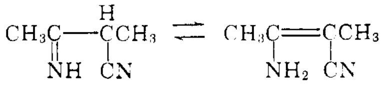
V

The first four structures have been assigned to the chromophore mainly from spectral evidence of the colored polymer. Since C=O, C=C, and C=N absorb at approximately the same wavelengths in the ultraviolet and in the infrared spectra and since the spectra of the polymer always show broad absorption bands rather than sharp, well-defined absorption peaks, distinction between these possibilities was not possible by spectral means alone.

Vosburgh[21] demonstrated that at least two forms of colored polyacrylonitrile exist. When polyacrylonitrile (or an acrylic copolymer) is heated to 250° in an air atmosphere for 4 hr, the material becomes black and will not burn when placed in a bunsen burner flame. The formation of the nonflammable material is accompanied by a very large release of energy which, unless carefully dissipated, will ignite the unconverted material. At lower temperatures, the material will also turn black, but will not form the nonflammable material.

The fully aromatic structure of Houtz (I) is believed to represent the structure of the nonflammable polymer because material can be volatilized from the polymer above 200°, but very little is lost below 200°.[3,22] We restrict ourselves to the chromophore formed below 150°, thus eliminating from consideration the nonflammable material formed at 250°. Therefore, structure I can be eliminated as a candidate for the low-temperature, thermally produced chromophore of PAN.

The hypothesis of Schurz (structure III) was tested by the preparation of 2-imino-3-cyanobutane (VI) as a model for the azomethine link. These compounds are known to exist predominantly as enamines (VII)



$$CH_3\underset{\displaystyle NH}{\underset{\displaystyle \|}{C}}-\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}CH_3 \rightleftharpoons CH_3\underset{\displaystyle NH_2}{C}{=}\underset{\displaystyle CN}{C}CH_3$$

VI VII

and to possess a strong uv absorption.[23] The absorption band of 2-imino-3-cyanobutane was observed at 255 mμ.

Polyacrylonitrile absorbs at 265 mμ if prepared in bulk or nonaqueous media, owing to the enamine structure. But it was shown earlier that this link is introduced into the polymer by polymerization through a pendant nitrile group and that it has only negligible chromophoric properties.[18] The model compound is perfectly white and in addition is easily hydrolyzed to a ketonitrile by short-time contact with acid[18] while the chromophore of PAN is not hydrolyzed under this and even more severe conditions.[10,11] Finally, thermal oxidation of model compounds of PAN, such

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(17) J. R. Kirby, J. Brandrup, and L. H. Peebles, Jr., *Macromolecules*, **1**, 53 (1968), paper II in this series.

(18) J. Brandrup, J. R. Kirby, and L. H. Peebles, Jr., *ibid.*, **1**, 59 (1968), paper III in this series.

(19) J. Brandrup and L. H. Peebles, Jr., *ibid.*, **1**, 64 (1968), paper IV in this series.

(20) J. Brandrup, *ibid.*, **1**, 72 (1968), paper V in this series.

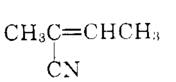
(21) W. G. Vosburgh, *Textile Res. J.*, **30**, 882 (1960).

(22) Based on work carried out in this laboratory,[10] we would expect that the fully aromatic structure probably also contains some nitrone groups, since they were shown to be present in model compounds and since elemental analysis of PAN for C, H, and N becomes more and more incomplete, see Table II.

(23) S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961).

as 2,4-dicyanopentane and isobutyronitrile, does not produce the hydrolyzable azomethine structure. These compounds were heated to 145° under oxygen and nitrogen and the uv absorption was measured. Discoloration occurred only under oxygen while the compounds were stable under nitrogen for more than 1 week. Heating under oxygen produced a gradual intensification of the absorption in the region of 220–300 mμ, but no definite peak developed that could be ascribed to an azomethine group. Azomethine formation should also occur under nitrogen and be visible in the uv spectrum. Furthermore, the color developed could not be removed by treatment with hydrochloric acid. Thus, direct experimental proof against the Schurz hypothesis is given, whereas earlier only indirect arguments were given.[14,24]

Conley and Bieron suggested structure IVa based on the investigation of the infrared spectra of heat-treated PAN films and assumed it to play a role in the thermal degradation.[7] They found that the intensity of the nitrile absorption band at 2240 cm^{-1} did not change as the color developed and concluded that the nitrile groups did not participate. The appearance of a second nitrile band at 2215 cm^{-1} indicated conjugation with another double bond. As was shown earlier,[19] the extinction coefficient of the chromophore must be very large, since less than 1% of heat-degraded model compound turned the remaining unchanged material deep brown. This indicates that only minor amounts of nitrile groups have to participate in this reaction. Recently, a decrease in the infrared band was observed in the thorough investigation by Noh and Yu.[25] In addition, the band for a conjugated nitrile group at 2215 cm^{-1} is explained by the formation of a ketonitrile group as shown earlier[17] and discussed below, the enol form of which has a nitrile group absorption at 2215 cm^{-1}. The remaining bands at 1600 and 1380 cm^{-1} are explained by the nitrone formation in the chromophore, as shown below.[10] Fnially, structure IVa cannot be used to explain the uv spectra of PAN observed, since the model compound, 2-cyano-2-butene,

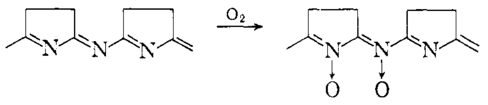


$$\underset{\displaystyle\text{CN}}{\text{CH}_3\text{C}}{=}\text{CHCH}_3$$

does not absorb in the near-ultraviolet spectrum.[17] Therefore, only structure IVb, a system of conjugated (–C=C–)$_x$ bonds, and structure II, a system of conjugated (–C=N–)$_x$ bonds, remain to be investigated.

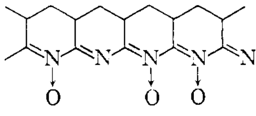
Evidence for structure IVb was based on the apparent constancy of the nitrile band at 2240 cm^{-1} whereas Grassie and also Noh and Yu observed a decrease of this band and adopted structure II. Clearly, spectral evidence alone is insufficient to distinguish between these two possibilities. This led to the search for a chemical means of distinguishing between these structures.[10] Conjugated (–C=N–)$_x$ systems were prepared by the polymerization of saturated nitrile compounds by either base (succinonitrile) or heat (isobutyronitrile and 2,4-dicyanopentane). Heat-treated poly(vinyl chloride) and β-carotene were chosen as conjugated (–C=C–)$_x$ systems. These materials were subjected to a large number of chemical reactions and it was found that treatment with basic hydrogen peroxide bleaches and destroys a (–C=N–)$_x$ system but not a (–C=C–)$_x$ system, while palladium on charcoal catalyzes the hydrogenation of a conjugated (–C=C–)$_x$ system but not a (–C=N–)$_x$ system.[10]

Since PAN degraded by heat or base always behaved like a (–C=N–)$_x$ system, it seemed justified to eliminate structure IVb and to adopt structure II. But it was realized that large amounts of oxygen are built into the chromophore. The analysis of heat-treated PAN for C, H, and N is always found to be incomplete.[3,10] Polyisobutyronitrile had a formula $(\text{C}_4\text{H}_7\text{NO})_n$[10,20] and the oxygen content of polysuccinonitrile varied with the polymerization conditions.[10] In addition, a polysuccinonitrile prepared in the absence of air absorbed oxygen very fast (Figure 3 in ref 10). Since the conjugation is not destroyed by this oxygen absorption and the nmr spectrum shows that the carbon skeleton remains unchanged, the formation of a nitrone was suggested.[10]



This structure similarly explains the infrared and nmr spectra of heat-treated PAN, it explains the increasing incomplete C, H, and N analysis with increased heat treatment, and it explains the change in solubility behavior of heat degraded PAN, since polynitrones are insoluble in all organic solvents, but slightly soluble in water, formic acid, and dimethyl sulfoxide.[10,20]

Based on this evidence, it is considered that the chromophore of heat-treated PAN must contain nitrone links. Since the oxygen uptake of polysuccinonitrile was not complete, it is felt that apparently not all –C=N– links react and the final chromophore therefore must be a random copolymer of imine and nitrone bonds. Thus, the chemical proof of the polyimine nature of the chromophore in heat-treated PAN and in base-degraded PAN establishes a sound base for work on the mechanism of color formation as it occurs in the polymer.



The work with model compounds[10,19,20] also demonstrates that the amount of chromophore required to produce color is quite small. A 1% solution of polysuccinonitrile in methanol is black, hence the amount of chromophore in slightly colored polymer must also be quite small. Thus we must look for minor but important reactions.

2. The Mechanism of Chromophore Formation. Scattered information about the formation of the chromophore has accumulated over the years. The action of amines was described by LaCombe,[12] of acids and phenols by Grassie,[16] and of base by Mc-

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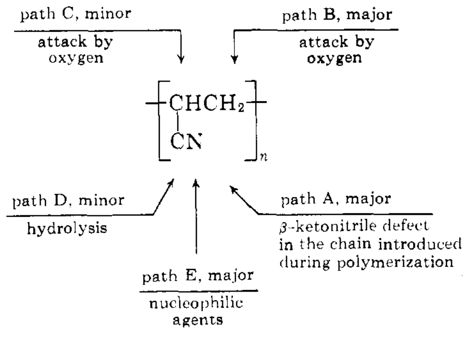
(24) N. Grassie, J. N. Hay, and I. C. McNeill, *J. Polymer Sci.*, 31, 205 (1958).

(25) I. Noh and H. Yu, *Polymer Letters*, 4, 721 (1966).

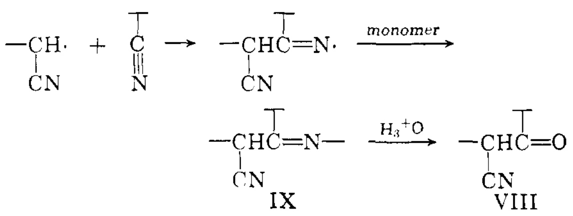
Cartney,[2b] Schurz,[5,6] Beaman,[26] and Overberger.[27] The initiating action of all of these reagents was explained as a nucleophilic attack of the reagent on a single nitrile group in the polymer.[16] The reactive species formed would then continue the nitrile addition reaction.[26,27]

Grassie and Hay also invoked the tertiary hydrogen atom as described above, based on the instability of purified PAN and the stability of polymethacrylonitrile. In other words, they concluded that the thermal instability would be an inherent property of PAN itself. While this latter conclusion must be confirmed based on the evidence cited below, the reason given by Grassie cannot be accepted. Several nitrile-containing molecules (2,3-dicyanobutane, 2,4-dicyanopentane, 2,5-dicyanohexane, and isobutyronitrile) were heated at 145° under nitrogen or oxygen for several days.[19] All of these compounds proved to be absolutely stable under nitrogen after more than 1 week at 145°, while the presence of oxygen caused peroxide and ketone formation, which initiated color formation.[19] These experiments clearly demonstrate that the tertiary hydrogen atoms of nitrile-containing compounds are stable and have no initiating properties. A different mechanism must therefore be responsible for the discoloration under nitrogen of polymers containing the same basic structure. The search for this mechanism revealed that the formation of color in PAN is a very complex process and virtually every part of the polymer molecule is affected. The heat treatment of model compounds under nitrogen showed that the PAN structure *per se* is heat stable and that an initiator is needed to start the polymerization of the nitrile groups. These initiating species are introduced into the PAN molecule in different ways, as shown in Scheme I. In this scheme, nucleophilic agents (path E) initiate the conjugated polyimine chain which are created in paths A–D.

Scheme I
Mechanism of Thermal Degradation of Polyacrylonitrile



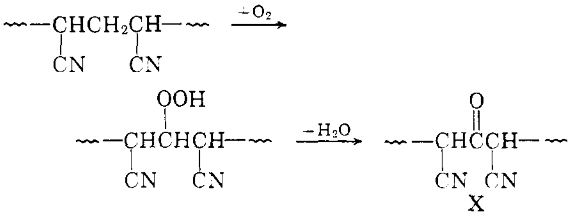
Path A is the creation of a β-ketonitrile VIII in the chain by addition of a growing polymer chain end to a nitrile group of a polymer molecule followed by hydrolysis of the enamine group IX.[18] The cyanoenamine (IX) is stable in organic solvents and can be observed by its strong uv absorption at 265 mμ (absorption I).[17] The β-ketonitrile (VIII) is a weak acid and can be titrated. In its ionized form it has a strong uv absorption at 275 mμ (absorption II) which can be used to determine the ketonitrile content of polymers photometrically.[17]



$$-\underset{\mathrm{CN}}{\mathrm{CH}}\cdot + \overset{\top}{\mathrm{C}}{\equiv}\mathrm{N} \rightarrow -\underset{\mathrm{CN}}{\mathrm{CH}}\overset{\top}{\mathrm{C}}{=}\mathrm{N}\cdot \xrightarrow{\text{monomer}} -\underset{\mathrm{CN}}{\mathrm{CH}}\overset{\top}{\mathrm{C}}{=}\mathrm{N}- \xrightarrow{\mathrm{H_3{}^+O}} -\underset{\mathrm{CN}}{\mathrm{CH}}\overset{\top}{\mathrm{C}}{=}\mathrm{O}$$

IX VIII

Path B is the major route of thermal oxidative degradation. The oxidative attack at the β-hydrogen atoms in preference to the α-hydrogen atoms is directed by the polar CN group (and differs from oxidative attack on hydrocarbon polymers). This information was established by studies on compounds of the structure $CH_3CHCN(CH_2)_nCHCNCH_3$ (n = 0, 1, 2) where the compound with the highest number of n is the least stable.[18] The hydroperoxide breaks down with elimination of water to form a β-ketodinitrile (X).

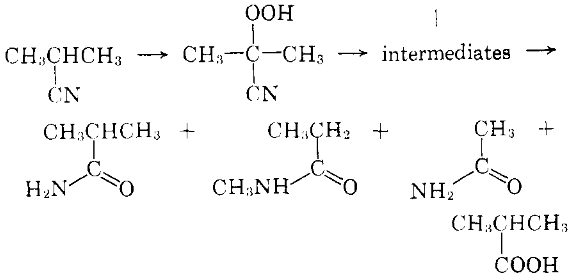


$$\sim\underset{\mathrm{CN}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{CN}}{\mathrm{CH}}\sim \xrightarrow{+\mathrm{O_2}} \sim\underset{\mathrm{CN}}{\mathrm{CH}}\overset{\mathrm{OOH}}{\mathrm{CH}}\underset{\mathrm{CN}}{\mathrm{CH}}\sim \xrightarrow{-\mathrm{H_2O}} \sim\underset{\mathrm{CN}}{\mathrm{CH}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\mathrm{CN}}{\mathrm{CH}}\sim$$

X

The β-ketodinitrile (X) content was determined after different times of heat treatment by the amount of absorption II developed; the hydroperoxide was determined iodometrically.[18]

Path C. The attack of oxygen at the tertiary hydrogen atom to form a hydroperoxide is a minor route of thermal degradation in the case of polyacrylonitrile. This place of attack had received considerable attention in the polymer literature,[28] but is not substantiated here based on work with isobutyronitrile[20] and higher cyano-containing homologs.[19] Isobutyronitrile was heat treated under pressure at 150° to determine the products of thermal attack at the tertiary hydrogen atom. The main products among the 30 different compounds produced were amides, N-substituted amides, and acids.[20] They all are degradation products of a hydroperoxide initially formed. These products will remain part of the chain in the case of the polymer and cannot be isolated. This is in agreement with the experimental fact that essentially no



$$\mathrm{CH_3}\underset{\mathrm{CN}}{\mathrm{CH}}\mathrm{CH_3} \rightarrow \mathrm{CH_3}-\overset{\mathrm{OOH}}{\underset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{CH_3} \rightarrow \text{intermediates} \rightarrow$$
$$\mathrm{CH_3}\underset{\mathrm{H_2N-C=O}}{\mathrm{CH}}\mathrm{CH_3} + \mathrm{CH_3}\underset{\mathrm{CH_3NH-C=O}}{\mathrm{CH_2}} + \underset{\mathrm{NH_2-C=O}}{\mathrm{CH_3}} + \mathrm{CH_3}\underset{\mathrm{COOH}}{\mathrm{CH}}\mathrm{CH_3}$$

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(26) R. G. Beaman, *J. Amer. Chem. Soc.*, **70**, 3115 (1948).

(27) C. G. Overberger, E. M. Pearce, and N. Mayes, *J. Polymer Sci.*, **34**, 109 (1959).

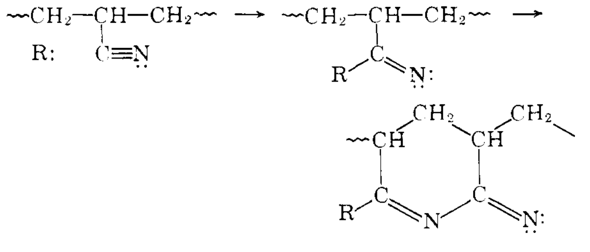
(28) H. C. Beachell and D. L. Beck, *J. Polymer Sci.*, **A3**, 457 (1965).

volatile products are obtained during heat treatment of PAN at 150° or below.[3] Evaluation of the rate of discoloration of isobutyronitrile[20] and the rate of oxygen uptake of 2,3-dicyanobutane[19] *vs.* 2,4-dicyanopentane yields a ratio of attack of β *vs.* α carbon atoms of approximately 3 to 1. This result is in agreement with substitution rules of organic chemistry.[29]

Path D, which is the hydrolysis of the nitrile group by acids and bases to form amide and carboxyl groups, is easily controlled by suitable choice of polymerization and use conditions. Grassie and McNeill[16] as well as Takata[14] have demonstrated the deleterious effects of amides and acids on the color stability of PAN.

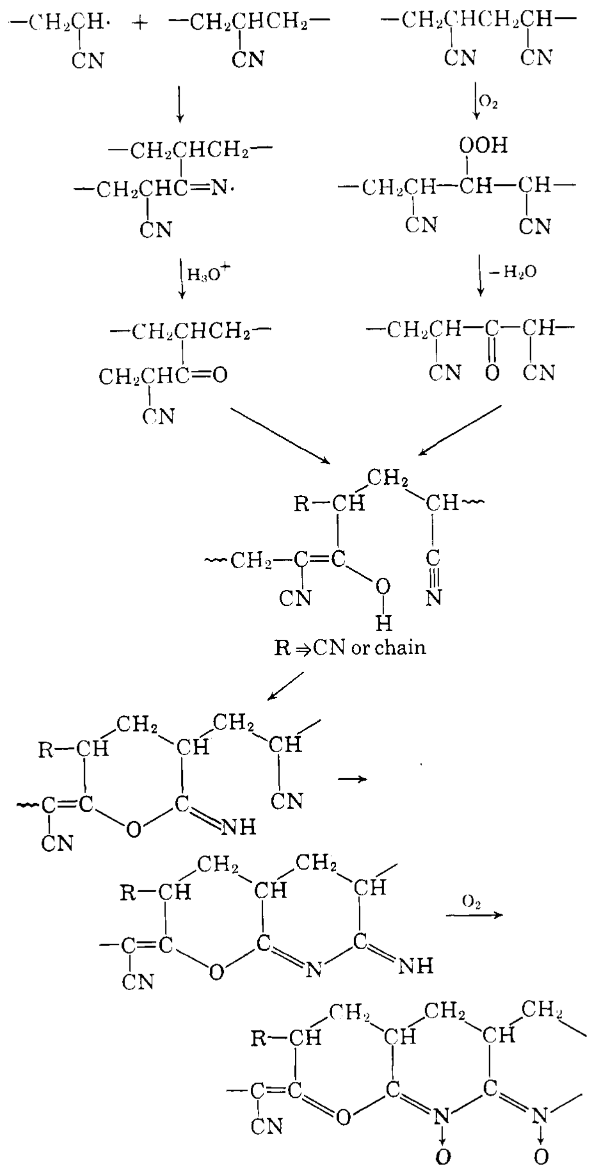
Path E is the major route of nucleophilic attack on the nitrile group. Paths A–D produce nucleophilic agents which all attack the polymer by path E to form chromophore.

Grassie and McNeill had shown that the effect of all initiators known could be explained by a nucleophilic attack on a nitrile group forming an active species able to continue the polymerization of nitrile groups.[15]



The action of amides, bases, and acids as nucleophiles is already fully substantiated by earlier work.[12,26,27] It remains to demonstrate the nucleophilic character of the ketonitriles produced in paths A and B. 2,5-Dicyanohexane was heat treated at 145° in the presence and absence of 2-cyanobutanone. The color developed was measured by dissolving aliquots in ethylene carbonate–propylene carbonate and measuring the absorbance of the solution at 225 mμ.[30] As seen in Figure 1, addition of 2-cyanobutanone eliminates the induction period required to form the *in situ* ketonitrile. Second, polymers containing different amounts of absorption II (β-ketonitrile) were heat treated for 8 hr at 145°. The color developed was measured as the yellowness index.[31] Figure 2 shows that a direct relationship exists between the amount of discoloration and the amount of β-ketonitrile present. The intercept on the yellowness axis means that color is formed in PAN even if no defect is present initially. This must be due to the formation of β-ketonitrile groups by oxygen attack at the β-carbon atom during the experiment. These two experiments clearly demonstrate the initiating ability of β-ketonitrile groups and we may write the sequence of reactions given in Scheme II.

SCHEME II



Ketonitriles formed either by addition of the growing end to the nitrile group or by oxygen attack at the β carbon will attack the next nitrile group able to form a six-membered ring.[32] This forms an active species able to promote polymerization of the nitrile group. The chromophore formed will partially pick up oxygen and form the imine–conitrone system.

3. The fluorescence of polyacrylonitrile has been known for a long time and was reported in connection with light-scattering work.[33a–c] It is considered to be an inherent property of PAN itself similar to the heat instability.[15] However, we observed that the fluorescence is not an inherent property of PAN but, instead, is connected with the defect present in PAN. In other words, the β-ketonitrile is the origin of the fluorescence. Since this defect is present in all PANs produced by free-radical catalysis, the fluorescence appeared as a property of PAN itself. The polymers described by Chiang, Rhodes, and Evans are prepared

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(29) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1958, p 200 ff.

(30) As a referee kindly pointed out, the absorbtivity shown in the figure is based on the content of starting material and is therefore not an absolute absorbtivity.

(31) D. B. Judd, "Color in Business, Science, and Industry," John Wiley and Sons, Inc., New York, N. Y., 1952, p 1651.

(32) The nucleophilic center of attack can be either the α-carbon or the enolate oxygen.

(33) (a) W. R. Krigbaum and A. M. Kotlier, *J. Polymer Sci.*, **32**, 323 (1958); (b) J. Bisschops, *ibid.*, **17**, 81 (1955); (c) L. H. Peebles, Jr., *ibid.*, **A3**, 361 (1965); (d) R. Chiang, J. H. Rhodes, and R. A. Evans, *ibid.*, *A1*, **4**, 3089 (1966).

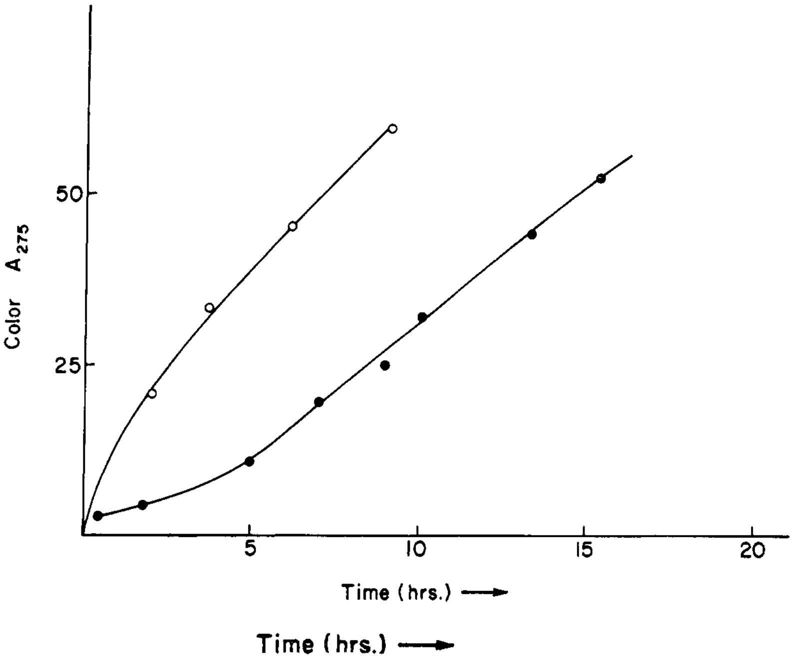


Figure 1. Thermal discoloration of 2,5-dicyanohexane at 145° under oxygen with (○) and without (●) addition of 16 wt % 2-cyanobutanone.

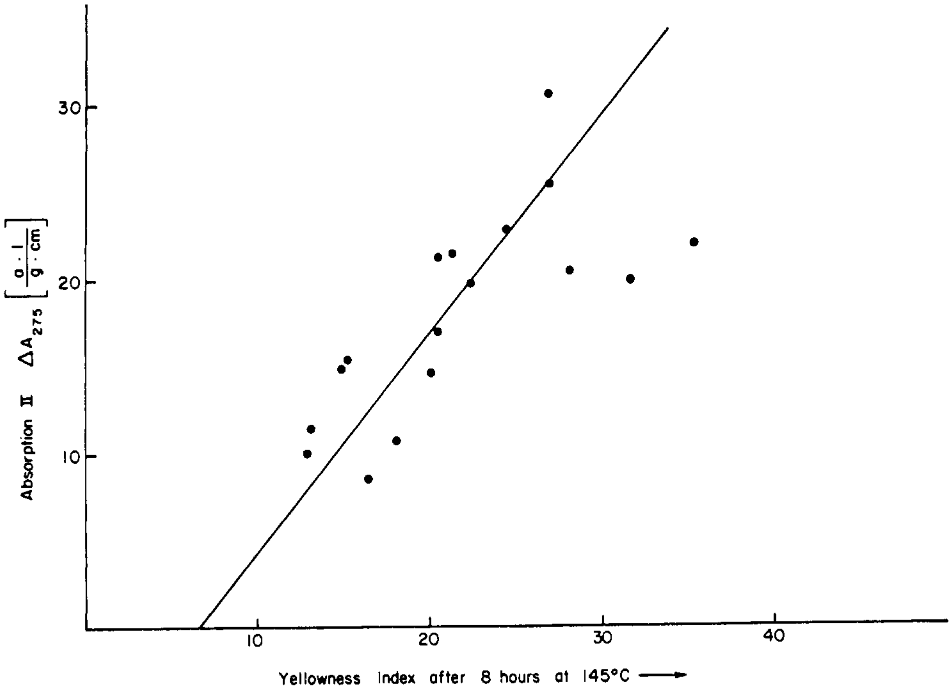


Figure 2. Dependence of the thermal discoloration of PAN on the amount of β-ketonitrile defect present in the polymer (absorption II).

by ionic coordinate catalysts and do not contain either the enamine or the ketonitrile. These polymers do not show fluorescence.[33d]

Fluorescence measurements were carried out in fluorescent grade DMF at room temperature. The results are shown in Table I. Excitation and emissions are given in millimicrons; the intensity is reported on a relative scale. It is clearly seen that the intensity decreases where the concentration of the β-ketonitrile decreases. Polymers which do not have the β-ketonitrile (made in organic solvents) do not fluoresce. Acetylation of PAN partially removes the β-ketonitrile and accordingly decreases the fluorescence. Hydrolysis of a polymer made in organic solvents changes the enamine into a β-ketonitrile. A corresponding increase in fluorescence is observed.

The model compound 2-cyanobutanone excites and emits at the correct wavelength but its intensity is much smaller even if measured in highly-viscous media. The viscosity influences mobility which determines the lifetime of the excited species and thereby the ratio of fluorescent emission *vs.* radiationless energy loss. Since the mobility of the model compounds will always be larger than that of a segment in a model

TABLE I
FLUORESCENCE OF PAN *vs.* β-KETONITRILE CONTENT

Sample	β-Ketonitrile content, ΔA_{275}[a]	Excitation, mμ	Emission, mμ	Relative intensity
1. Redox polymer, prepared in water	0.216	345	400	0.9
2. Redox polymer, prepared in water	0.147	345	400	0.315
3. Redox polymer, prepared in water	0.108	345	400	0.12
4. AIBN polymer, prepared in EC–PC	. . .	365	410	0.041
5. Sample 4, hydrolyzed with HCl	0.141	365	405	0.25
6. Sample 1, acetylated	. . .	345	400	0.17
7. Sample 1, base added	0.216	345	400	0.58
8. 2-Cyanobutanone in 10% poly(vinyl alcohol) solution		345	400	0.04
9. 2-Cyano-3-amino-2-butene		320	365	0.01

[a] β-Ketonitrile content determined by change in absorbance at 275 mμ upon addition of base.

chain, the difference in intensity observed cannot be too important.

Furthermore, Fujisaki[34] reported similar dependencies for the fluorescence of PAN on the molecular weight as we have observed for the β-ketonitrile.[18]

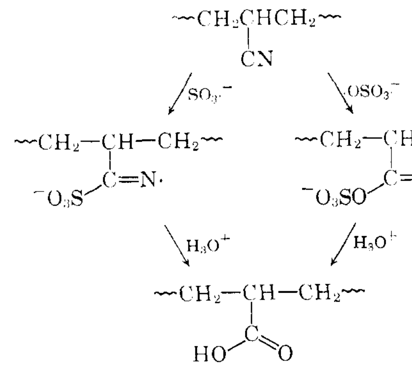
Therefore, we conclude that the fluorescence is caused by the β-ketonitrile in the chain. The amount of fluorescence observed will be a direct measure of the β-ketonitrile content and therefore of the heat stability of PAN polymers.

4. Formation of Nonchromophoric Weak Acid Groups in the Polymer. As was shown earlier,[17] the photometric titration of PAN solutions in ethylene carbonate–propylene carbonate indicated the presence of more than one kind of weak acid group which were characterized as chromophoric and nonchromophoric weak acid groups. The former was identified as being due to a β-ketonitrile structure; the latter was called a carboxyl group by Glenz and Beckmann[35] and Philipp, Reichert, Tryonadt, and Gröbe[36] which supposedly originated by hydrolysis of the nitrile groups. We wish to draw attention to two other possible structures responsible for the presence of nonchromophoric weak acid groups and an alternate method for the formation of carboxyl groups.

Titration of model compounds showed that 2,3-dicyanobutane, a model for a head-to-head structure, and 2-cyano-2-butene, a model for a defect suggested by Conley and Bieron, can be titrated as weak acid groups.[17,37]

An alternate method for the formation of carboxyl groups might be the following. The chromophoric weak acid group was explained as being due mainly to addition of the growing chain end to a nitrile group in the polymer. In general, any radical will undergo a similar pattern of reactions—of propagation, transfer, or termination. Other radicals present in the system, therefore, should be able to add to nitrile groups in the polymer. In the case of a redox system, sulfate and sulfonate radicals will be present in the system. Attack of those radicals on the nitrile group may yield the structures given in Scheme III. These structures will partially undergo hydrolysis in the acidic aqueous medium of the polymerization and yield carboxyl groups. This is a free radical induced hydrolysis of nitrile groups yielding carboxyl groups. These three possibilities were not pursued further and are offered here as speculation only.

SCHEME III



5. Conclusions. The scheme of color formation in PAN developed here is in agreement with most experimental facts and in addition it explains a number of hitherto unexplained properties of PAN.

1. The thermal instability of PAN in an inert atmosphere was explained by Grassie and McNeill as a self-initiation of the repeat unit by the labile α-hydrogen who therefore concluded that the repeat unit *per se* is unstable. While self-initiation through the α-hydrogen could not be confirmed, it was shown that PAN always contains defects (enamines, ketonitriles) introduced by an addition of the growing chain end to a nitrile group in the polymer molecule. The presence of these groups simulates the instability of the repeat unit itself. Since these groups are always present, their importance to thermal instability could not be resolved by investigating the polymer only.

2. The ultraviolet spectrum of PAN is consistent with the presence of enamine and ketonitrile groups.[17,18]

3. The molecular weight of polyacrylonitrile remains essentially constant[24] and no major amounts of volatiles are formed.[3,19] This is explained by oxygen attack at the β-carbon instead of the α-carbon, which forms keto groups in a position β to the nitrile groups. Especially it explains the formation of this keto group without the evolution of HCN, which is only observed in small amounts below 200° after extended reaction periods.[3,19]

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(34) Y. Fujisaki, *Chem. High Polymers* (Tokyo), **18**, 581 (1961).

(35) O. Glenz and W. Beckmann, *Melliand Textilber.*, **38**, 296, 783 (1957).

(36) B. Philipp, H. Reichert, A. Tryonadt, and V. Gröbe, *Faserforsch. Textiltech.*, **15**, 304 (1964).

(37) Many multinitrile compounds can act as acids, among them, *e.g.*, cyanoform: R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953).

Table II
Polyacrylonitrile Heated for Various Times at 145°

Heating time, hr	%				
	C	H	N	O^a	Total
Calcd	67.92	5.66	26.42	. . .	100.0
0	67.92	5.66	25.97	0.6	100.11
24	67.58	5.70	25.86	0.72	99.86
48	67.51	5.65	25.50	1.04	99.70

[a] Determined analytically.

4. It had been observed that the elemental analysis becomes increasingly incomplete with increasing coloration.[2a,3,38,39] This was confirmed in this laboratory, as shown in Table II, where the oxygen content of heated samples increases with time. This is explained by the formation of polynitrones.[10]

5. The hitherto unexplained fluorescence is caused by the presence of ketonitrile groups in the polymer.

Acknowledgment. We wish to thank Miss M. W. Huffman and Mr. D. C. Westall for experimental assistance.

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The Ultraviolet Degradation of Terpolymer Scissioning Systems

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ABSTRACT: A mathematical model has been developed to describe the uv degradation of terpolymer scissioning systems. Nearest neighbor and anomalous link (*e.g.*, head-to-head or branching) effects have been ignored in order to preserve simplicity and analytical tractability. Equations relating the fraction of various linkages and of each component in terms of reactivity ratios and monomer feed fractions are presented. A method of estimating individual scissioning constants from terpolymer experimental data is presented and the significance of the estimates is discussed. Suitable experimental designs are discussed and the simplex lattice design is suggested. Variance contours for variations on this design are presented.

The deleterious effect of ultraviolet radiation on polymers is one of the main problems barring these materials from many applications. The systematic study of uv degradation is therefore a project of considerable academic and industrial interest.

One area, in particular, that has generated a substantial amount of work is the development of a quantitative theory of uv degradation.

Previous work[1–4] has demonstrated the applicability of high-energy radiation theory to uv degradation systems with suitable modification for attenuation (film thickness)[5–7] and wavelength effects[8] (activation spectra). A theory of copolymer degradation[9] has led to characterization of polymer systems.

This paper extends previous work[9] to the scissioning behavior of terpolymer systems.

For scissioning systems a variable of fundamental importance is the number of scissions per molecule (S). On the assumption of a random scission mechanism this is given by eq 1, where $\bar{k}$ = over-all scissioning constant scissions/mer time^{-1}, P_0 = degree of polymerization, and t = exposure time.

$$S = \bar{k}P_0t \qquad (1)$$

Copolymers contain linkages of various types, each with a given kinetic constant for degradation. (In a copolymer of monomers A and B at least three types, A–A, A–B, and B–B are present.) It can be shown that when $\bar{k}t \ll 1$, the observed kinetic constant for degradation is the linear sum of inter-mer scission constants (*e.g.*, k_{aa}, k_{bb}, k_{ab}), each weighted by the frequency of occurrence in the copolymer (f_{aa}, f_{bb}, f_{ab}). In order to describe the degradation system it is first necessary to calculate (or measure) these linkage fractions, second to estimate and generate confidence intervals for scission constants for various linkages, and last to test the model for fit. The following discussion is divided into five sections: (I) calculation of inter-mer linkage fractions, (II) a description of the variation of the average kinetic constant with composition, (III) estimation and testing of inter-mer scission constants for the model, (IV) comments on experimental design, and (V) critique of the model.

I. Calculation of Inter-Mer Linkage Fractions

In a terpolymer of monomers A, B, and C, there are six linkages of concern, f_{aa}, f_{ab}, f_{ac}, f_{bb}, f_{bc}, and f_{cc}. The various amounts of each linkage in a terpolymer

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(4) H. Jacobs and R. Steele, *J. Appl. Polymer Sci.*, **3**, 239 (1960).

(5) A. R. Schultz, *J. Chem. Phys.*, **29**, 200 (1958); *J. Phys. Chem.*, **65**, 967 (1961).

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