fairly dilute solutions depends on the identity of the solvent, but the comparisons involved not only different solvents but also PIB's from different sources, even though nominally of similar molecular weight. The present study, involving comparisons between two PIB–solvent systems with the same PIB, indicates that the spin–spin relaxation is insensitive to the nature of the solvent above the θ temperature.

Discussion

In the theory of the nuclear magnetic relaxation of very simple systems,[18] it is predicted (and found experimentally) that $T_1 = T_2$ when the frequency of molecular reorientation is sufficiently great, that is, when the temperature is high enough. There is no trend toward coalescence of T_1 and T_2 in the present studies, however, as is demonstrated in Figure 8. This separation of T_1 and T_2 has been observed before in molten PIB[13] and in PIB solutions.[1,5] Evidently the spin–lattice and spin–spin relaxations are controlled by different processes, but the details are obscure. Viewing the relaxation as a mechanism controlled by thermal activation of the familiar Arrhenius form, it follows that the activation energy for the T_2 process in Figure 8 is about 3.5 kcal/mol (and is similar for the T_1 and T_2 processes in all the dilute solutions studied here). In contrast, the activation energy for viscous flow is several times as large.[19] This disparity points again to the character of the motion involved in the T_2 process, presumed to depend on segmental reorientation. The barriers to intramolecular rotation in PIB appear to be rather small.[20] Thus, the temperature coefficient of the nuclear magnetic relaxation reflects this segmental reorientation, not the grosser motion involved in viscous flow.

Acknowledgment. We are grateful to our colleagues, Dr. D. C. Douglass, Dr. S. Matsuoka, and Dr. D. W. McCall, for sharing with us their discussions of relaxation in polymers. In addition, we thank Dr. McCall for his helpful comments on this paper.

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(18) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

(19) M. F. Johnson, W. W. Evans, I. Jordan, and J. D. Ferry, *J. Colloid Sci.*, **7**, 498 (1952).

(20) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961).

On the Chromophore of Polyacrylonitrile. II. The Presence of Ketonic Groups in Polyacrylonitrile

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Contribution No. 479 from the Chemstrand Research Center, Inc., Durham, North Carolina. Received October 27, 1967

ABSTRACT: Polyacrylonitrile prepared by free-radical catalysts contains an absorption of varying intensity in the 265–275-mμ region. The intensity of this absorption increases upon addition of base. This spectral behavior is explained in terms of a keto–enol equilibrium of a β-ketonitrile, where the enol anion is strongly colored.

Previously, we have shown that the chromophore of discolored polacrylonitrile consists of a random copolymer of conjugated imine and nitrone bonds.[2a] This is an extension of the structure suggested by McCartney,[2b] Burlant and Parsons,[3] and Grassie and McNeill.[4] The latter demonstrated that polymethacrylonitrile could be prepared in a stable form which would not discolor when heated, if the monomer was rigorously purified and the proper free-radical catalyst was used to initiate the polymerization.[5] They concluded that the polymerization of nitrile groups needs an initiator and showed that nucleophilic agents are capable of functioning as such. On the other hand, polyacrylonitrile cannot be obtained in a heat stable form. When heated to approximately 180°, it turns various shades of yellow to brown. Grassie and Hay concluded that the discoloration of polyacrylonitrile is an inherent property of the polymer molecule and suggested that the tertiary hydrogens in polyacrylonitrile (PAN) were sufficiently acid to start the polymerization of the nitrile groups.[6] Friedlander, Brandrup, Peebles, and Kirby[7] have shown that model compounds of PAN, which contain a 1,3 arrangement of nitrile groups, are heat stable under nitrogen, while PAN is not. Therefore, the $(-CH_2CHCN-)_x$ must be relatively heat stable and some other group as a defect must be present in the polymer which can act as an initiator of the discoloration reaction.

Evidence for various defects in PAN has been reported. Beevers,[8] Schurz, Zah, and Ullrich,[9] and

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(1) (a) Farbwerke Hoechst, Kunststoff-Forschung, Frankfurt am Main, Germany; (b) to whom all correspondence should be addressed.

(2) (a) L. H. Peebles, Jr., and J. Brandrup, *Makromol. Chem.*, **98**, 189 (1966); L. H. Peebles, Jr., *J. Polymer Sci., A-1*, **5**, 2637 (1967); (b) J. R. McCartney, *Mod. Plastics*, **30**, No. 11, 118 (1953); U. S. National Bureau of Standards Circular No. 525, Government Printing Office, Washington, D. C., 1953, p 123.

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

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(7) H. N. Friedlander, L. H. Peebles, Jr., J. Brandrup, and J. R. Kirby, *Macromolecules*, **1**, 79 (1968), paper VI in this series; J. Brandrup and L. H. Peebles, Jr., *ibid.*, **1**, 64 (1968), paper IV in this series.

(8) R. B. Beevers, *J. Phys. Chem.*, **66**, 1271 (1962).

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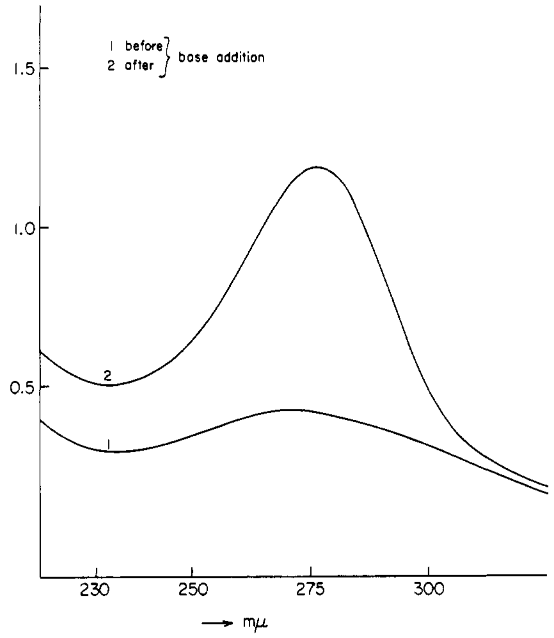

Figure 1. Typical ultraviolet spectrum of ion-exchanged polyacrylonitrile in ethylene carbonate–propylene carbonate before and after addition of base.

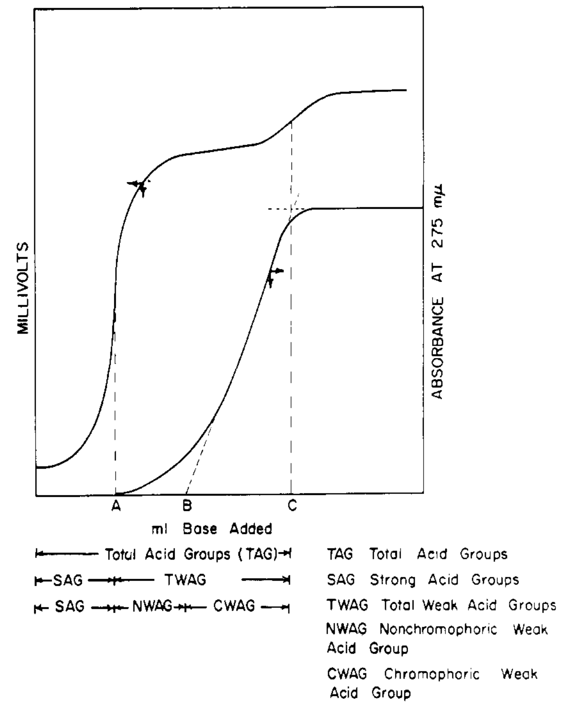

Figure 2. Typical titration curve for ion-exchanged acrylonitrile polymers showing photometric and potentiometric responses on addition of base.

Treiber, Berndt, and Toplak[10] have shown that an ultraviolet absorption band at 265–275 mμ exists in polyacrylonitrile, which is not present either in rigorously purified simple nitrile compounds,[9] in polymethacrylonitrile,[11] or in PAN prepared by ionic-coordinate catalysts of the type reported by Chiang, Rhodes, and Evans.[12] Potentiometric strong and weak acid groups have been determined in PAN by various laboratories.[13–15] The presence of potentiometric strong and weak acid groups and of an ultraviolet absorption at 275 mμ of varying intensity in ethylene carbonate–propylene carbonate (EC–PC) solutions of polyacrylonitrile was confirmed in these laboratories. In addition, we found that solutions which had only a negligible ultraviolet absorption at 265 mμ exhibited a tremendous increase in absorption intensity upon addition of base shifting in maximum to 275 mμ. This increase became smaller when the original absorption intensity was larger, which was interpreted as evidence for the presence of two different absorbing groups in the polymer chain. Since these groups may function as initiators for the discoloration of PAN, work was initiated to investigate the nature and origin of these defects in the polymer chain. This paper describes the nature of the group which causes the increase in absorption upon addition of base.

Results

Polyacrylonitrile prepared by a redox catalyst in water was dissolved in ethylene carbonate–propylene carbonate (EC–PC) and the ultraviolet spectrum was measured. The solutions became yellow when tetraethylammonium hydroxide was added. The increase in visible color is associated with a strong increase of the absorption maximum at 275 mμ in the uv spectrum, as shown in Figure 1. The increase in absorption is directly proportional to the amount of base added up to a maximum value beyond which addition of base apparently has no more effect. Since the increase in absorption is only observed after all strong acid groups are neutralized and since it corresponds to a simultaneous appearance of a weak acid group in the potentiometric titration curve, it was assumed that both titration curves measure the same weak acid group in the polymer. A typical titration curve is shown in Figure 2. The upper curve represents the potentiometric response as a function of the amount of base required to neutralize the strong acid groups at the inflection point A while the inflection point C indicates the volume of base required to neutralize all of the acid groups. The difference between A and C is associated with the total weak acid group content. The lower curve represents the increase in absorption at 275 mμ upon addition of base. The curvature in this photometric titration curve indicates that more than one weak acid group must be present. Therefore, the linear portions of this curve are extrapolated to determine the points B and C. The difference between B and C is interpreted to be due to a chromophoric weak acid group and the difference between A and B is due to a nonchromophoric weak acid group. The chromophoric weak acid group can also be determined by measuring the maximum absorptivity at 275 mμ after

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(10) E. Treiber, W. Berndt, and H. Toplak, *Angew. Chem.*, **67**, 69 (1955).

(11) J. Brandrup and L. H. Peebles, Jr., unpublished results.

(12) R. Chiang, J. H. Rhodes, and R. A. Evans, *J. Polymer Sci., A-1*, **4**, 3089 (1966).

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

(14) E. I. du Pont de Nemours and Co., British Patent 823,345 (Nov 11, 1959).

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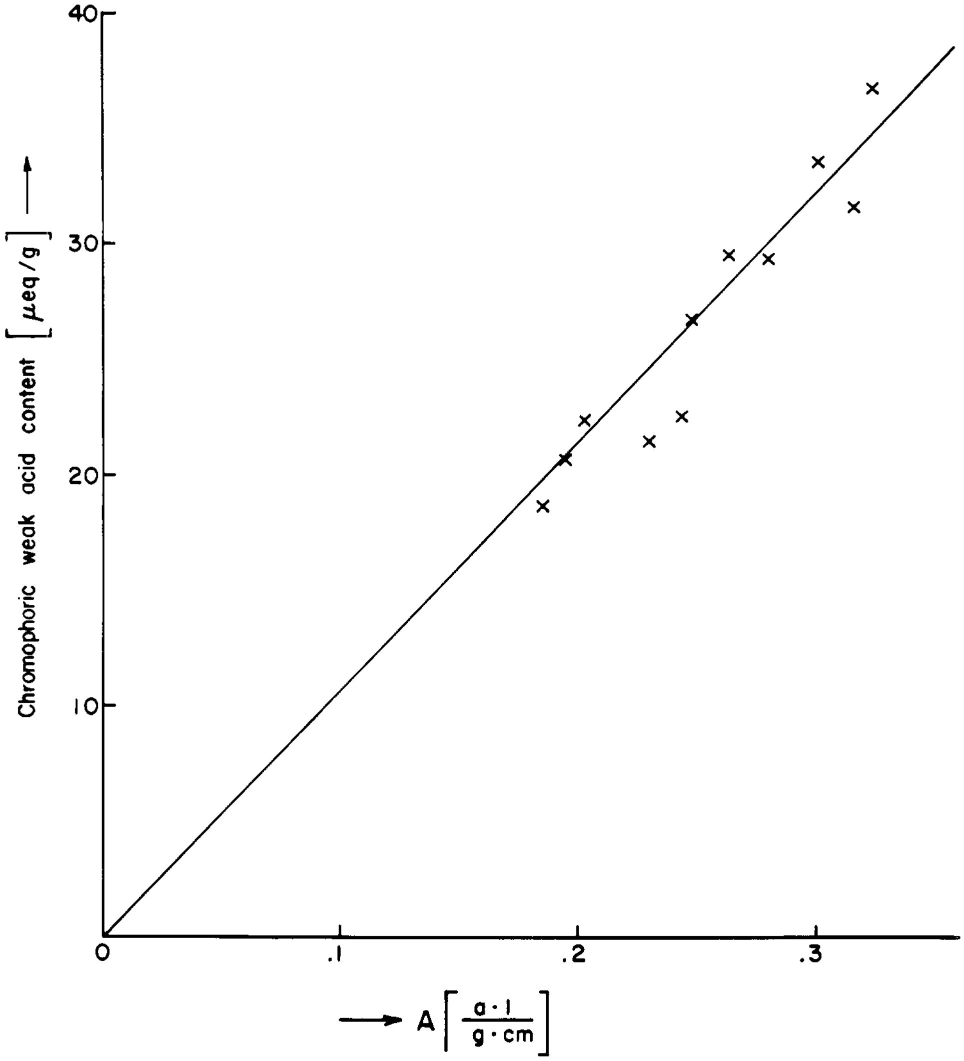

Figure 3. Validity of Beer's law for the defect observed in PAN. Potentiometric CWAG *vs.* change in uv absorption at A_{275}.

TABLE I

TYPICAL TITRATION VALUES FOR PAN POLYMERIZED BY $K_2S_2O_8$–$NaHSO_3$ IN WATER

[η], dl/g, in DMF at 25°	Strong acid groups, μequiv/g	Chromophoric weak acid groups, μequiv/g	Non-chromophoric weak acid groups, μequiv/g
0.94	63.2	21.4	8.3
1.81	26.2	18.1	6.1
1.83	26.9	15.9	7.0
3.13	10.4	10.5	5.2
3.95	10.2	11.6	5.4

base addition assuming Beer's law applies. When the chromophoric weak acid group content, determined by the method first described, is plotted *vs.* the maximum absorptivity, a straight line is obtained (Figure 3), which supports the assumption that the weak acid group and the photometrical titratable group are identical.

Extensive tests were carried out to see if the weak acid groups were impurities occluded in the polymer. Both weak acid groups were still present after repeated dissolution of the polymer and reprecipitation and after 48 hr extraction with methanol. This was taken as good evidence that these titratable groups must be an integral part of the polymer molecule. Typical titration data obtained for various polymers are listed in Table I.

Since there exists a one-to-one correspondence between the chromophoric weak acid content and the change in absorbance upon addition of base (Figure 3), it was concluded that both sets of information measure the same defect structure in the polymer. In other words, the defect should be a weak acid and a strong uv absorber in its ionized form. Candidates for the structure of the chromophoric weak acid group must meet the following conditions.

1. The increase in absorption only starts after neutralization of all strong acid groups.
2. An end point must be observed beyond which no further color formation occurs.
3. The reaction with base is reversible, since addition of a known amount of acid immediately bleaches the solution and the group can then be retitrated.

Table II

Compounds Checked for Their Titration Behavior in the Uv Region around 250–300 mμ

Compound	Potentiometric weak acid group	Uv absorbance	Change in absorbance after adding base
Ethyl acetate	Negative	Negative	Negative
Acrylonitrile	Negative	Negative	Negative
Vinyl acetate	Negative	Negative	Negative
Vinyl acetate heated 100°		Positive (277–287 mμ)	Negative
Acrylic acid	Positive	Negative	Negative
Acetonitrile	Negative	Negative	Negative
Isobutyronitrile	Negative	Negative	Negative
Malononitrile	Negative	Positive	Positive
Succinonitrile	Negative	Negative	Negative
Glutaronitrile	Negative	Positive	Negative
Methyl cyanoacetate	Negative	Positive	Positive (242 mμ)
Ethyl cyanoacetate	Negative	Positive	Positive (242 mμ)
Ethyl cyanoformate	Negative	Positive	Positive (250 mμ)
Cyanoacetic acid	Positive	Positive	Negative
α-Cyanoacetamide		Positive	Positive (260 mμ)
Succinimide		Positive (245 mμ)	Positive
Cyanoguanidine		Positive	Negative
Lactonitrile	Positive	Positive	Negative
Propionaldehyde cyanohydrin		Positive	Negative
Acetaldehyde cyanohydrin		Positive	Negative
Sodium 2-cyanoethanesulfonate	Not detd	Negative	Negative
Sodium 1-cyanopropanesulfate	Not detd	Positive (235 mμ)	Positive (?)
2-Cyanoethyl isopropyl sulfide		Negative	Negative
2-Cyanocyclopentanone	Positive	Positive (235 mμ)	Positive (268 mμ)
Ethyl malonate	Positive	Positive	Negative
Malonic acid		Positive	Negative
N-Methyleneglycinonitrile		Negative	Negative
Cyanuric acid		Negative	Negative
Cyanamide		Negative	Negative
2-Cyano-2-butene		Negative	Negative
Crotononitrile		Negative	Negative
β,β′-Iminopropionitrile		Negative	Negative
Hydracrylonitrile		Negative	Negative
Benzoylacetonitrile		Negative	Negative
Cumene	Negative	Negative	Negative
Benzyl cyanide	Negative	Negative	Negative

These conditions suggest that the change in absorption intensity must be an ionic reaction and most likely is related to a keto–enol equilibrium, the anion of which is a strong absorber.

Therefore, many enolizable compounds were examined under similar conditions to see if they exhibited both a change in uv absorption and a potentiometric weak acid group. Table II lists all the compounds screened in a qualitative fashion. The monomers and simple nitriles were included in the test to demonstrate that they do not have similar properties. Some of the compounds showed intense absorption maxima in the uv region but these maxima did not change by addition of base or acid. Cyano acid esters and amides and ketonitriles were the only compounds which showed a positive response. These compounds were included in a more thorough quantitative investigation of the titration behavior of various model compounds (Table III).

Models for one or two units in the chain (isobutyronitrile, 2,4-dicyanopentane) show no response at all, as expected. A compound representing a tail-to-tail linkage (2,5-dicyanohexane) is similarly inert. A compound representing a head-to-head linkage (2,3-dicyanobutane) shows one potentiometric weak acid group per molecule but no absorption in the uv spectrum. Conley and Bieron[16] suggested that double bonds might exist in PAN. Models for such structures (2-cyano-2-butene and crotononitrile) showed one weak acid group per molecule but no absorption in the uv spectrum. Hydroxyl end groups (hydracrylonitrile) also do not respond in these titrations.

Among these compounds, only two classes gave positive tests, ethyl cyanoacetate and ketonitriles. The ethyl cyanoacetate shows a much smaller change in absorptivity than is actually observed (*ca.* $^1/_{10}$). Thus, only one single class of compounds remains—ketonitriles—whose spectral behavior is similar to the properties of PAN (Figure 4). The absorption maximum and equivalent absorptivity of the titrated form of 2-cyanocyclopentanone was found to be 270 mμ and 12,000 l./equiv cm and that of 2-cyanobutanone to be 261 mμ and 13,700 l./equiv cm. The absorption maximum of the polymer is at 270–275 mμ and has an equivalent absorptivity of about 9650 l./equiv cm.

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

TABLE III

QUANTITATIVE DETERMINATION OF THE SPECTRAL CHANGES OCCURRING IN MODEL COMPOUNDS UPON ADDITION OF BASE

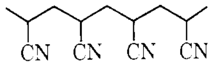
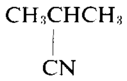
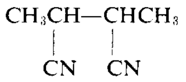
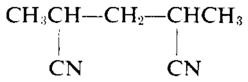
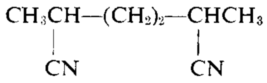
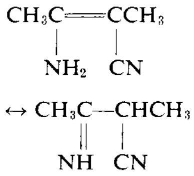
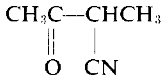
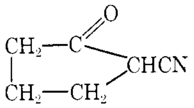
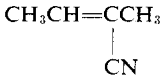
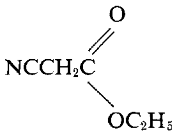
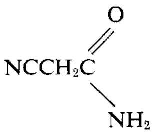
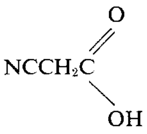
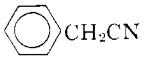
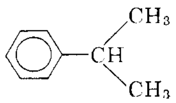
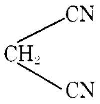
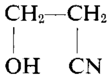
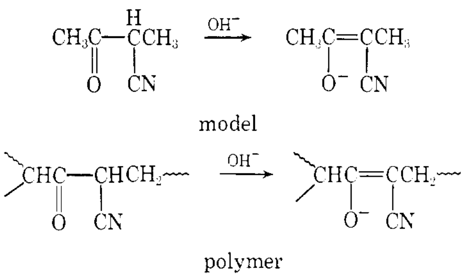
Compound			Absorptivity	
Name	Structure	Weak acid, equiv/molecule	Wavelength, mμ	Change in absorptivity after base addition, $\frac{\Delta al}{\text{equiv} \times \text{cm}}$
Polyacrylonitrile		1.2± 0.11	275	9,565
Isobutyronitrile	 $CH_3\underset{\mathrm{CN}}{\mathrm{CH}}CH_3$	...	...	...
2,3-Dicyanobutane	 $CH_3\underset{\mathrm{CN}}{\mathrm{CH}}—\underset{\mathrm{CN}}{\mathrm{CH}}CH_3$	0.92	...	...
2,4-Dicyanopentane	 $CH_3\underset{\mathrm{CN}}{\mathrm{CH}}—CH_2—\underset{\mathrm{CN}}{\mathrm{CH}}CH_3$	...	...	...
2,5-Dicyanohexane	 $CH_3\underset{\mathrm{CN}}{\mathrm{CH}}—(CH_2)_2—\underset{\mathrm{CN}}{\mathrm{CH}}CH_3$	...	...	...
2-Cyano-3-amino-2-butene	 $CH_3\underset{\mathrm{NH_2}}{\mathrm{C}}{=\!=}\underset{\mathrm{CN}}{\mathrm{C}}CH_3 \leftrightarrow CH_3\underset{\mathrm{NH}}{\mathrm{C}}—\underset{\mathrm{CN}}{\mathrm{CH}}CH_3$	0.48	255	No change
2-Cyanobutanone	 $CH_3\underset{\mathrm{O}}{\mathrm{C}}—\underset{\mathrm{CN}}{\mathrm{CH}}CH_3$	1.0	260	13,700
2-Cyanocyclopentanone		1.1	268	12,000
Crotononitrile	$CH_3CH{=}CHCN$	1.01	...	...
2-Cyano-2-butene	 $CH_3CH{=}\underset{\mathrm{CN}}{\mathrm{C}}CH_3$	0.94	...	...
Ethyl cyanoacetate		...	245	726
Cyanoacetamide		0.97	...	...
Cyanoacetic acid		...	...	...
Benzylcyanide		0.89	...	...
Cumene		...	...	...

Table III (*Continued*)

Compound: Name	Compound: Structure	Weak acid, equiv/molecule	Absorptivity: Wavelength, mμ	Absorptivity: Change in absorptivity after base addition, $\frac{\Delta al}{\text{equiv} \times \text{cm}}$
Malononitrile		. . .	. . .	. . .
Hydracrylonitrile	 $\underset{\mathrm{OH}}{\mathrm{CH_2}}-\underset{\mathrm{CN}}{\mathrm{CH_2}}$	. . .	. . .	. . .
Isobutyramide	. . .	. . .	. . .	. . .

Discussion

Polyacrylonitrile prepared by a redox system ($K_2S_2O_8$–$NaHSO_3$) in water contains an ultraviolet absorption at 275 mμ the intensity of which increases on addition of base. The increase in intensity can be used as a "self-indicator" to perform a "photometric" titration. Analysis of the photometric titration curve showed that two weak acids are present: a nonchromophoric and a chromophoric species. It is concluded that the chromophoric species is a β-ketonitrile group in the chain. Addition of base yields an enol anion which is colored and has a maximum absorption at 275 mμ (Figure 1) in the polymeric chain.



$$\mathrm{CH_3}\underset{\displaystyle \mathrm{O}}{\overset{}{\mathrm{C}}}-\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{CN}}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow{\mathrm{OH^-}} \mathrm{CH_3}\underset{\displaystyle \mathrm{O^-}}{\mathrm{C}}=\underset{\displaystyle \mathrm{CN}}{\mathrm{C}}\mathrm{CH_3}$$

model

$$\mathrm{{>}CH}\underset{\displaystyle \mathrm{O}}{\mathrm{C}}-\underset{\displaystyle \mathrm{CN}}{\mathrm{C}}\mathrm{HCH_2}\sim \xrightarrow{\mathrm{OH^-}} \mathrm{{>}CH}\underset{\displaystyle \mathrm{O^-}}{\mathrm{C}}=\underset{\displaystyle \mathrm{CN}}{\mathrm{C}}\mathrm{CH_2}\sim$$

polymer

The discoloration of PAN solutions by base, such as sodium hydroxide or amines, has been described.[2b,17] It always has been stated that part of the color formed is stable and cannot be removed by the addition of acid. The question arises whether the base discoloration of PAN reported in the literature is identical with the reversible increase in uv absorption described here. Grassie[5] and Takata[18] have shown that the discoloration of PAN by base is due to the polymerization of nitrile groups initiated by the nucleophilic action of the base forming a conjugated $(\text{–C=N–})_x$ system. This reaction was used by Peebles and Brandrup to polymerize succinonitrile to a polymer with a conjugated $(\text{–C=N–})_x$ backbone.[2a] It was observed that the reaction in PAN is solvent dependent and only occurs in dimethylformamide, dimethylacetamide, and dimethyl sulfoxide. Solvents like ethylene carbonate or propylene carbonate inhibit this base-initiated polymerization of nitrile groups.

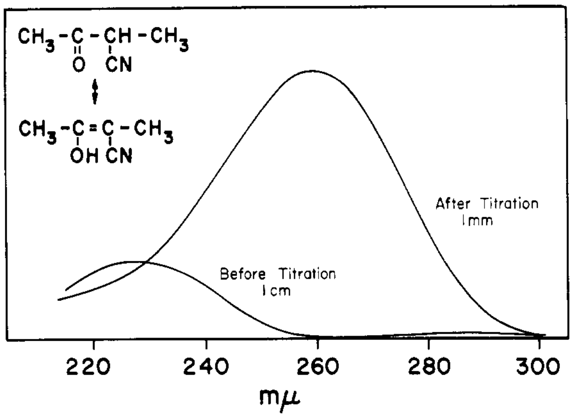


Figure 4. Ultraviolet spectrum of 2-cyanobutanone before and after titration with base.

Owing to the prevention of this reaction in these latter solvents, the photometric titration of the chromophoric weak acid group is possible. However, prolonged standing of the solutions which contain base produces a permanent color. This color cannot be removed by acid. Most likely this color is due to the formation of the usual chromophore $(\text{–C=N–})_n$.

Experimental Section

Polymers were prepared by a redox system ($K_2S_2O_8$–$NaHSO_3$) at 50° by the usual batch procedure. They were filtered, washed, extracted with methanol for 24 hr, and dried under high vacuum at 40°. Potentiometric titrations were carried out in purified ethylene carbonate–propylene carbonate solutions with tetramethylammonium hydroxide as titrant and with platinum electrodes.[15] The polymer solutions were ion exchanged with appropriate resins before titration.[15] Ultraviolet spectra were determined in a Cary spectrophotometer in EC–PC solutions at room temperature.

The preparation of nitrile-containing model compounds, 2,3-dicyanobutane, 2,4-dicyanopentane, and 2,5-dicyanohexane, is described in another paper of this series.[7b] 2-Cyano-3-amino-2-butene (I) was prepared according to Mohr.[19] 2-Cyanobutanone was prepared from I by hydrolysis with concentrated hydrochloric acid for 30 min at room temperature. The mixture was extracted with ether, dried with Na_2SO_4, and distilled, bp 65° (8 mm).

Anal. Calcd for C_5H_7NO: C, 61.9; H, 7.21; N, 14.43. Found: C, 61.02; H, 6.86; N, 14.10.

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(17) H. Stübchen and J. Schurz, *Monatsh. Chem.*, **89**, 234 (1958).

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

(19) E. Mohr, *J. Prakt. Chem.*, **90**, 189 (1914).

Ir and nmr spectra agree with the structure. The uv spectrum is seen in Figure 4. 2-Cyano-2-butene was prepared from the cyanohydrin of butanone.

Preparation of 2-Butanone Cyanohydrin. 2-Butanone (144 g, 2 mol) and 132 g (2 mol) of KCN were stirred at low temperature. Sulfuric acid (200 ml, 50%) was slowly added. The temperature was not allowed to rise above 20°.

It should be noted that a satisfactory reaction is obtained if (a) the temperature is not too low (below −10°) and (b) the acid is not added too fast. If the acid is added too fast, the reaction medium becomes acidic and the reaction stops. After the reaction was completed, the two layers were separated, acidified, extracted with ether, dried with $CaCl_2$, and distilled, bp 65° (4 mm).

Preparation of 2-Cyano-2-butene. $SOCl_2$ (60 ml) was added slowly with cooling to 90 ml of 2-butanone cyanohydrin in 270 ml of pyridine and 440 ml of dry ether. The mixture was refluxed for 3 hr. Water was added carefully and the ether was washed free from pyridine with dilute sulfuric acid. The ether was washed until neutral, dried with $CaCl_2$, and distilled, bp 110–140°. The original product contained some ketone which was removed by reaction with Girard's T reagent.

Anal. Calcd for C_5H_8N: C, 73.17; H, 9.76; N, 17.07. Found: C, 72.89; H, 9.40; N, 16.89.

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On the Chromophore of Polyacrylonitrile. III. The Mechanism of Ketone Formation in Polyacrylonitrile

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ABSTRACT: Polyacrylonitrile (PAN) made in organic solvents possesses an intense absorption at 265 mμ (absorption I). Short-time contact of the polymer with acid removes this peak, but produces another absorption at 275 mμ whose intensity is pH dependent (absorption II). Addition of base causes an intensity increase of the latter. This spectral behavior is caused by groups introduced by polymerization of the growing polymer radical through a pendant nitrile group on preformed polymer. The nitrile polymerization reaction which influences reaction kinetics in a manner comparable to a chain-transfer reaction naturally does not involve the tertiary hydrogen that is usually assumed to be the site of the chain-transfer-to-polymer reaction. In the first step of the nitrile polymerization reaction, an acid-sensitive enamine is produced (absorption I). This enamine is hydrolyzed to a ketonitrile which can be titrated by base photometrically (absorption II). Thus the determination of the change in absorption intensity at 275 mμ upon addition of base is a direct measure of the number of branch points in the polymer. The number of branch points determined this way ($5–10 \times 10^{-4}$) is in excellent agreement with constants determined by conventional kinetic methods (4.7×10^{-4}) by assuming chain transfer to polymer.

Polyacrylonitrile prepared by free-radical catalysis possesses an absorption in the ultraviolet region at 265 mμ (absorption I). This was discussed by Beevers[2a] and by Schurz, Zah, and Ullrich[2b] and is known as the "characteristic" absorption of PAN. We found that the intensity of this band becomes more and more pH dependent (intensity increase by base addition) with decreasing initial absorption intensity shifting at the same time to 275 mμ.[3] This was taken as evidence for the presence of two different defects in the polymer chain where the intensity of one group varies with pH (pH always greater than 5) (absorption II) and where the other does not (absorption I). These groups must be present in the polymer in different amounts depending on the condition of polymerization.

Paper II in this series shows that a photometrical titratable weak acid group is responsible for absorption II.[3] In its un-ionized form it is a β-ketonitrile group present as defect in the polymer; its enol anion form is responsible for the strong increase in absorption upon addition of base. This paper deals with the nature of the nontitratable, pH independent absorption (absorption I) and with the origin of both absorbing groups in the polymer.

Results

Acrylonitrile was polymerized in various solvents with various catalysts and over a range of temperatures (details below). The polymers were recovered, extracted with methanol, and dried. The ultraviolet spectrum of the polymers obtained was measured in ethylene carbonate–propylene carbonate (EC–PC) at room temperature. All of these polymers contained either an intense untitratable uv absorption at 265 mμ (absorption I, Figure 1) or a less intense uv absorption at 275 mμ whose intensity greatly increased upon addition of base (absorption II, Figure 2).

Apparently, all samples of polyacrylonitrile made in

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