Macromolecules 1986, *19*, 1851–1856

On Coloration of Polyacrylonitrile: A Nuclear Magnetic Resonance Study

V. R. Pai Verneker*[†] and B. Shaha[‡]

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, 560 012, India.

Received July 15, 1985

ABSTRACT: Coloration in polyacrylonitrile can be induced in three distinct ways: by heat treatment, by treatment with base, or during synthesis of the polymer itself using ionic initiators at relatively higher temperatures. The present investigation employing ^{1}H and ^{13}C NMR spectroscopy has revealed some common features in colored polyacrylonitrile irrespective of its mode of coloration. All colored polyacrylonitriles give an additional peak around δ 2.7 in ^{1}H NMR spectra and, except for heat-treated polyacrylonitrile, one extra group of peaks in the region δ 12–16 in ^{13}C NMR spectra. The former peak has been attributed to methine and/or methylene protons in branched and/or cyclized structures, while the latter peak has been attributed to methylene carbon atoms in the branched structure. Colorless polyacrylonitriles have been found to be predominantly heterotactic, while colored polyacrylonitriles have been found to have appreciable isotactic contribution.

Introduction

It is known that polyacrylonitrile (PAN) can be produced in essentially colorless form.[1] Thus, PAN obtained from acrylonitrile (AN) with free radical initiators like α,α'-azobis(isobutyronitrile) (AIBN), benzoyl peroxide (BPO), persulfate–metabisulfite, etc., or with energetic radiation like UV radiation is colorless. However, PAN obtained with anionic initiators is invariably colored unless prepared at low temperatures.[2,3] It is well-known that PAN shows peculiar discoloration effects on heat treatment or on treatment with bases.[4] Thus coloration in PAN may be attributed to three distinct causes: (a) coloration associated with synthesis of the polymer with anionic initiators, particularly at relatively higher temperatures; (b) coloration resulting from heat treatment of the polymer below its decomposition temperature; (c) coloration arising out of base treatment of the polymer.

Thermal[1,4–17] and alkali-induced degradation[1,18–25] of PAN has received considerable attention of researchers in the recent past, and aspects such as chain scission mechanism, thermal stability, generation of coloration, etc., have aroused significant interest among various investigators. Attempts made so far have been limited to the use of techniques like UV[4,11,17,20,22b] and IR[1,4,7,9,10,15–17,20,23] only to account for coloration in thermally and alkali degraded PAN, although techniques such as viscometry,[18,22a,23] XRD,[24] thermal conductivity,[24] etc., have also been used to study other aspects of the degradation phenomena. Peebles[25] in an excellent review has summarized the various attempts made by different workers in thermal and base degradation of PAN. It is, however, surprising to note that no attempt has so far been made as far as we know to study the degradation and coloration of PAN using an NMR technique, in spite of its high effectiveness toward elucidation of molecular microstructure, though the structure of PAN itself has been extensively studied by using ^{1}H NMR[26–38] and ^{13}C NMR[39–45] techniques. It may also be noted that no systematic attempt has so far been made in regard to the coloration in anionic PAN obtained at relatively higher temperatures. The present work is, therefore, an attempt to investigate the various aspects of coloration of PAN with ^{1}H NMR and ^{13}C NMR techniques.

Experimental Section

PAN was obtained by the use of a number of initiators—free radical as well as ionic. Among free radical initiators AIBN, BPO, and energetic radiation like UV radiation were employed. Among ionic initiators *n*-butyllithium and phenylmagnesium bromide were used. Metallic lithium and sodium were also used as initiators for a number of bulk and solution polymerizations of AN.

AIBN-initiated originally colorless PAN was rendered colored in the following ways: (a) by heating in vacuo (1×10^{-2} mmHg) at 100 °C for 936 h; (b) by treating a 1% polymer solution in dimethylformamide (DMF) with 10% sodium hydroxide (based on polymer weight) and keeping the mixture at 100 °C for 15 min.

^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker WH 270 MHz spectrometer operating at 270 and 67.89 MHz for ^{1}H and ^{13}C nuclei, respectively. The spectral width, pulse width, and acquisition time were 2994.012 Hz, 5 μs, and 1.368 s and 17241.379 Hz, 30 μs, and 0.475 s for ^{1}H NMR and ^{13}C NMR spectra, respectively. A ~0.5% polymer solution in Me$_2$SO-d_6, which also served as an internal lock, taken in a 4-mm-o.d. tube with Me$_4$Si as internal standard, was used for recording ^{1}H NMR spectra in the Fourier transform mode. For ^{13}C NMR spectra a ~5% solution in Me$_2$SO-d_6 taken in a 10-mm-o.d. tube was utilized with Me$_4$Si as internal standard in the Fourier transform proton-decoupled mode. A total of 25–500 transients was needed for a ^{1}H NMR spectrum, while 1000–30 000 transients were required for a ^{13}C NMR spectrum. Most of the ^{13}C NMR spectra were recorded at 373 K, while all other spectra were recorded at 300 K. The accuracy with respect to chemical shift values was within δ ±0.10, and the reproducibility of NMR stereoregularity was within ±5.9%.

Results and Discussion

The polymerization conditions and characteristics of the various PAN studied in the present investigation are summarized in Table I.

^{1}H NMR Studies. The chemical shifts and chemical shift assignments of the ^{1}H NMR spectra of the various PAN samples studied in the present investigation have been summarized in Table II. A survey of presently available literature reveals that all PAN studied so far by a ^{1}H NMR technique are colorless except those of Imai et al.[36] All these PAN give two groups of peaks in the ^{1}H NMR spectra centered around δ 2.0 and 3.1, corresponding to β-methylene and α-methine protons, respectively. In agreement with earlier work[26–35,37,38] all the free radical initiated PAN studied in the present investigation have been found to give these two groups of peaks (Table II, Figure 1a). Bulk-polymerized lithium initiated PAN (Li–PAN) obtained at −33 °C has also been found to give these two peaks (Figure 1b)—incidentally, they are all

---

[†] Present address: Martin Marietta Laboratories, Baltimore, MD 21227.

[‡] Present address: Department of Chemistry, M.B.B. College, Agartala, 799 004, India.

0024-9297/86/2219-1851$01.50/0

Table I
Polymerization of Acrylonitrile and PAN Characteristics

initiator	polym temp./ atm. (°C)	mol wt/sp viscosity	color
1% AIBN[a]	65/air	4.1×10^5	colorless
1% BPO	65/air	6.3×10^5	colorless
UV radiation	RT[b]/air	4.0×10^5	colorless
n-BuLi[c]	65/vacuo[d]	0.49[e]	yellow
n-BuLi[c]	-60/vacuo	5.2×10^5	colorless with yellow tint
C_6H_5MgBr[f]	45/air	0.13[e]	yellow
1% lithium	65/vacuo	9.77×10^3	orange
1% lithium	-33/vacuo	2.32×10^5	colorless
1% lithium (solution polymerized)	60/vacuo	0.055[e]	brown
1% sodium	65/vacuo	11.5×10^3	deep orange
1% sodium	-33/vacuo	23.8×10^3	yellow
1% sodium (solution polymerized)	60/vacuo	0.051[e]	brown

[a] Two more high molecular weight PAN samples were prepared with AIBN at room temperature. These were subjected to discoloration efffect by (a) heat treatment and (b) treatment with alkali. Their steric distribution, before discoloration, was analogous to that of AIBN initiated PAN (Table III) within experimental error. [b] RT = room temperature, 27 °C average. [c] AN, 1.0 g; initiator, 0.1 mL (15% solution in hexane). [d] 1×10^{-2} mmHg. [e] Specific viscosity of 1% solution in DMF at 30 ± 0.2 °C. [f] AN, 0.8 g. Initiator obtained out of 61.0 mg of Mg in 0.3 mL of bromobenzene and 10 mL of ether and kept at 45 °C for 1 h and 3 h at room temperature.

colorless. However, a typical anionic initiator like phenylmagnesium bromide initiated PAN obtained at 45 °C or *n*-butyllithium initiated PAN obtained at 65 °C has been found to give, in addition to these two groups of peaks, another group of peaks centered around δ 2.7 (Figure 1c, Table II). Similarly, bulk-polymerized sodium initiated PAN (Na–PAN) obtained at 65 through -33 °C have been found to give the peak around δ 2.7 in addition to those at δ 2.0 and 3.1 (Figure 2, parts a and b, Table II). (A triplet observed around δ 2.8 in bulk-polymerized Na–PAN obtained at 65 °C could be attributed to some impurity or side reaction. Please note that this peak is absent in Na–PAN obtained at -33 °C.) Bulk-polymerized Li–PAN obtained at 65 °C is similar to Na–PAN in this respect. All PAN showing the additional peak around δ 2.7 have been found to be colored various shades—from light yellows to dark red through orange. An interesting feature of this group of peaks is that the relative intensity of this peak compared to that of the peak around δ 2.0 or 3.1 decreases with a decrease in polymerization temperature (Figure 2, parts a and b). In agreement with earlier work[2,3] the intensity of coloration in these PANs decreased with a decrease in polymerization temperature (Table I). As already pointed out, Li–PAN obtained at -33 °C does not show this peak and is colorless. The intensity of this peak has also been found to be reduced significantly in *n*-butyllithium initiated PAN (almost colorless) obtained at -60 °C. Quite logically, one could then ascribe the peak around δ 2.7 observed in all colored PAN (obtained with ionic initiators at relatively higher temperature) to their coloration.

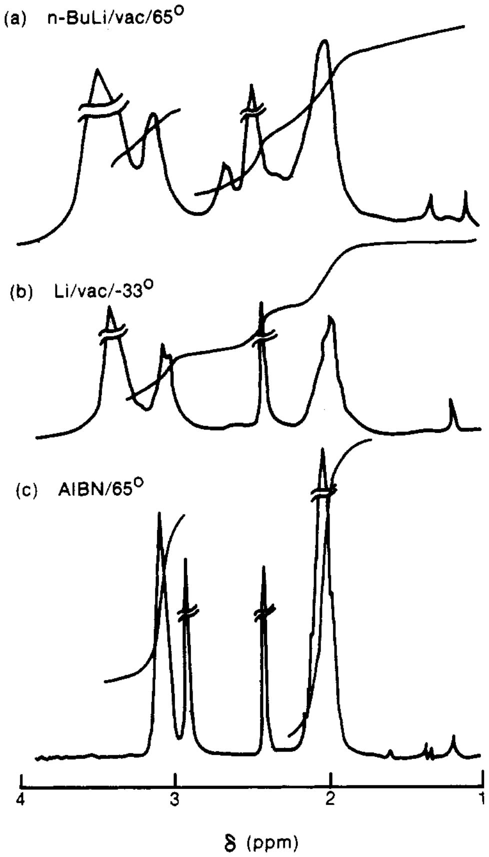


Figure 1. ^1H NMR spectra of PAN obtained with different initiators.

Solution-polymerized PAN obtained with lithium or sodium metal from high dielectric solvents like DMF or Me_2SO has been found to give all the three groups of peaks discussed so far. However, the intensity of the peak around δ 2.7 has been found to grow tremendously in solution-polymerized Na–PAN obtained from DMF with a simul-

Table II
^1H NMR Spectra of PAN: Chemical Shift Assignment

species	δ 1.15 terminal CH_3 in branches	δ 1.23 terminal CH_3	δ 2.0 CH_2 in backbone	δ 2.7 CH_2 or CH in cyclic structure	δ 3.1 CH in backbone	δ 8.31 imino
AIBN–PAN		×	×		×	
AIBN–PAN, heat treated	×	× (low)	×	×	×	×
AIBN–PAN alkali degraded	×	× (low)	×	×	×	×
BPO–PAN		× (low)	×		×	
UV–PAN		× (very low)	×		×	
n-BuLi–PAN, 65 °C	×	×	×	×	×	
n-BuLi–PAN, -60 °C	×	× (very low)	×	very low	×	
C_6H_5MgBr–PAN	×	×	×	×	×	×
Li–PAN, 65 °C			×	×	×	
Li–PAN, -33 °C		×	×		×	
Li–PAN, solution polymerized	× (low)	×	×	×	×	×
Na–PAN, 65 °C			×	×	×	
Na–PAN, -33 °C		× (very low)	×	×	×	
Na–PAN, solution polymerized	× (low)	×	×	×	×	×

Table III
^{13}C NMR Spectral Assignment and Stereoregularity of PAN

species	δ 12.2 CH_2 in branches	δ 14.2 CH_2 in branches	δ 27.0 CH	δ 32.6 CH_2	δ 120.0 nitrile	^{13}C NMR stereoreg, % iso	hetero	syndio
AIBN–PAN			×	×	×	29.28	49.69	21.03
AIBN–PAN, heat treated			×	×	×	12.58	72.96	14.46
AIBN–PAN, alkali degraded		×	×	×	×	41.31	39.52	19.13
BPO–PAN			×	×	×	24.93	47.01	28.06
UV–PAN			×	×	×	32.25	49.32	18.43
n-BuLi–PAN, 65 °C		×	×	×	×	30.16	53.24	16.60
C_6H_5MgBr–PAN		×	×	×	×	51.16	38.76	10.08
Li–PAN, 65 °C		×	×	×	×	43.33	38.81	17.86
Li–PAN, –33 °C			×	×	×	25.28	48.95	25.76
Li–PAN, solution polymerized	×	×	× (very low)	× (very low)	×	58.82	37.64	3.52
Na–PAN, 65 °C	×	×	×	×	×	45.99	44.34	9.67
Na–PAN, –33 °C		×	×	×	×	45.17	36.93	17.88
Na–PAN, solution polymerized	×	×	× (very low)	× (very low)	×	55.80	30.0	14.23

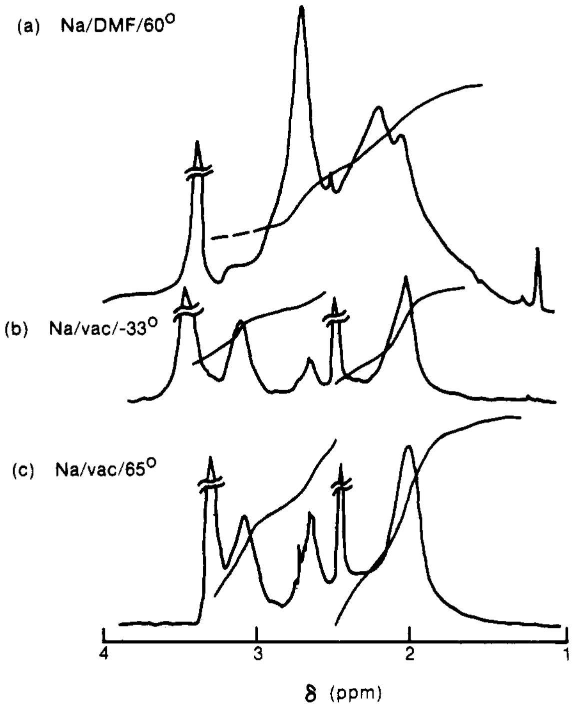


Figure 2. ^1H NMR spectra of sodium initiated PAN.

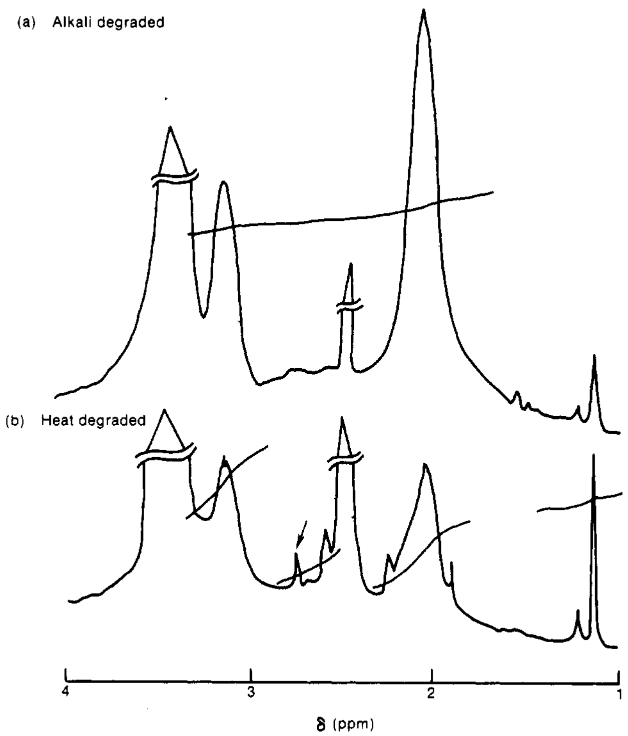


Figure 3. ^1H NMR spectra of (a) alkali-degraded PAN and (b) heat-treated PAN.

taneous appreciable reduction in the intensity of the peak around δ 3.1 (Figure 2c). As expected, this Na–PAN is colored intensely (Table I). Solution-polymerized PAN obtained with AN from DMF with alkali metal hydroxides like LiOH, NaOH, and KOH as initiators are also deeply colored and give ^1H NMR spectra similar to that of solution-polymerized Na–PAN. If coloration is responsible for the peak around δ 2.7, one would then expect this peak to be present in all colored PAN irrespective of its mode of coloration. ^1H NMR spectra of AIBN initiated PAN (AIBN–PAN), originally colorless but rendered colored by (a) heating at 100 °C in vacuo (1×10^{-2} mmHg) for 936 h, and (b) treatment with NaOH from DMF solution, substantiates this contention (Figure 3, Table II).

Heat-treated and alkali-degraded PAN as well as phenylmagnesium bromide or *n*-butyllithium initiated PAN and solution-polymerized Li–PAN or Na–PAN give, in addition to the three groups of peaks described so far, another group of peaks around δ 1.15 and 1.23. The latter peak has also been observed in free radical initiated PAN, though with very little intensity (Figure 1a), and in bulk-polymerized Li–PAN obtained at –33 °C (Figure 1b) and

be attributed to methyl protons in the branched structure (to be discussed later). All these PANs except Li–PAN have also been found to give another peak of variable low intensity around δ 8.31 which could be attributed to imide (–NH–) protons from D_2O exchange studies. The presence of –NH– groups in thermally degraded PAN has been advocated by Coleman et al.[15] and Rafalko[16] from FT-IR studies (the peak around δ 8.31 has not been shown in the figures).

It may be recalled at this stage that although Imai et al.[36] have reported ^1H NMR spectra of colored PAN obtained with organomagnesium initiators they have shown a break in the region δ 2.5–2.8 in the spectrum so that it is difficult to ascertain whether there is any observable peak around δ 2.7.

^{13}C NMR Studies. The ^{13}C NMR spectrum of typical PAN shows three groups of peaks centered around δ 27.0, 32.6, and 120.0 corresponding to the α-, β-, and nitrile carbon atom, respectively.[39] Data on the ^{13}C NMR spectra of the various PAN studied in the present investigation

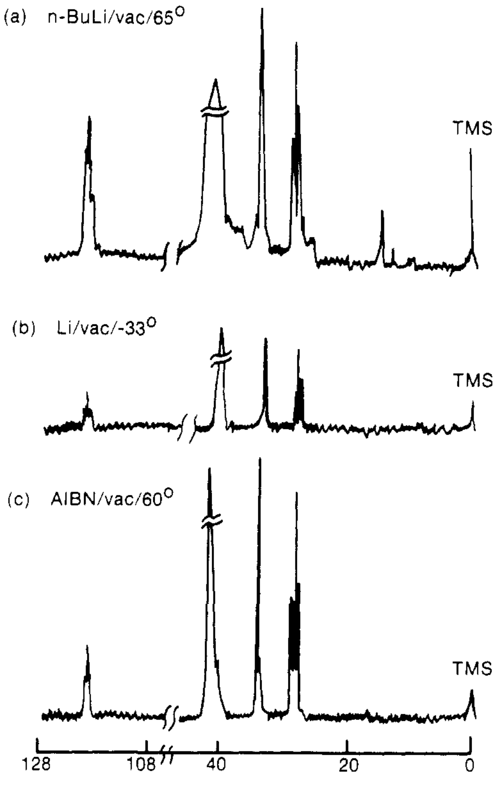


Figure 4. ^{13}C NMR spectra of PAN obtained with different initiators.

of peaks (Figure 4a). Similar is the case with Li–PAN obtained at −33 °C (Figure 4b). However, phenylmagnesium bromide initiated PAN obtained at 45 °C or *n*-butyllithium initiated PAN obtained at 65 °C has been found to give, in addition to these three groups of peaks, one peak around δ 14.2. This has been found, in agreement with earlier work,[44] to give a triplet in the ^{13}C NMR off-resonance spectrum, indicating it to be due to methylene carbon atoms—obviously different from the backbone β-methylene carbon atoms. Scheller et al.[44] have ascribed a peak occurring around δ 14.2 in alkali metal alkoxide initiated PAN to methylene carbon atoms in the branched structure. Na–PAN obtained at 65 through −33 °C (Figure 5, parts a and b) and Li–PAN obtained at 65 °C have also been found to give this peak. The peak around δ 14.2 has been found to be absent in heat-treated PAN, while it has been found to be present in alkali-degraded PAN (though with little intensity (Figure 6, parts a and b).

An examination of Figure 4a reveals that while the β-carbon peak in AIBN–PAN is a sharp singlet the α-carbon atom peak is a triplet showing thereby a triad tacticity of the polymer. However, in colored PAN the β-carbon peak has been split into a number of lines from which a triad tacticity could be identified, while from a number of finer peaks observed in the α-carbon atom peak a hexad tacticity of the polymer could be ascertained. The nitrile band has been found to split into a triplet in free radical initiated PAN as well as Li–PAN obtained at −33 °C (Figure 4, parts a and b), showing thereby a triad tacticity of the polymer while higher order placements could be observed in anionically obtained colored PAN.

Solution-polymerized Li–PAN or Na–PAN obtained from DMF (Figure 5c) or Me$_2$SO has been found to give a poor ^{13}C NMR spectrum. An examination of Figure 5c reveals that while intensity of the peaks around δ 27.0 and 32.6 has been drastically reduced in Na–PAN (solution) that of the peak around δ 14.2 has increased considerably.

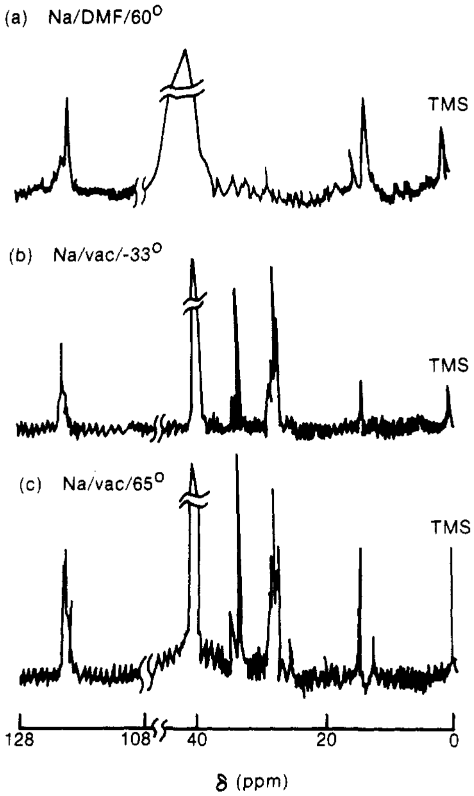


Figure 5. ^{13}C NMR spectra of sodium initiated PAN.

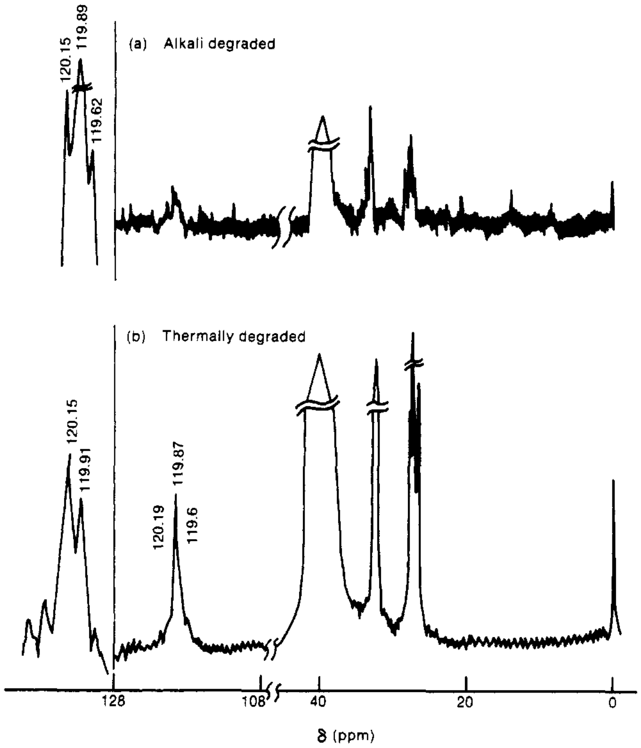


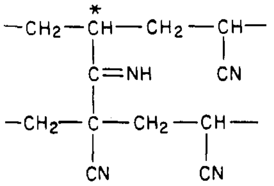
Figure 6. ^{13}C NMR spectra of (a) alkali-degraded PAN and (b) heat-treated PAN (left: original nitrile band expanded).

More significant, however, is the appearance of a very strong peak around δ 12.2 in this PAN. The peak around δ 12.2 has been found to give a triplet in the ^{13}C gated-coupled NMR spectrum, indicating it to be due to methylene carbon atoms. It is possible that most of the methylene and methine carbon atoms of the linear polymer have been converted into a highly branched structure under the prevailing polymerization conditions. Alkali-degraded PAN has been found to give ^{13}C NMR spectra similar to typical anionic colored PAN (Figure 6b). However, ^{13}C NMR spectra of heat-treated PAN is similar to that of the original PAN except that the nitrile band has undergone a significant change in its shape (i.e., sequence distribution).

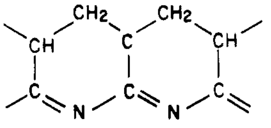
Stereoregularity of PAN samples studied in the present investigation has been determined according to Schafer,[39] who has attributed the three resonances observed in the nitrile band of typical PAN to isotactic, heterotactic, and syndiotactic placements in order of increasing field strength, and is presented in Table III. An examination of data presented in Table III reveals that Li–PAN obtained at 65 °C, the two Na–PANs, phenylmagnesium bromide initiated PAN obtained at 45 °C and *n*-butyllithium initiated PAN obtained at 65 °C, all of which are colored, have appreciable isotactic contribution (>40%) compared to free radical initiated PAN and Li–PAN obtained at −33 °C (<30%), all of which are colorless. Solution-polymerized Li–PAN and Na–PAN have been found to be highly isotactic (>50%) with appreciable reduction in their heterotacticity (<40%) or syndiotacticity (<20%). On heat treatment, heterotactic contribution (72.96%) has been found to increase quite significantly, mainly at the cost of its isotactic contribution, while the alkali-degraded PAN the isotactic contribution (41.31%) has been found to increase appreciably predominantly at the cost of its heterotactic contribution.

A comparison of the ^{1}H and ^{13}C NMR spectra of bulk-polymerized Li–PAN obtained at 65 °C to those of Li–PAN obtained at −33 °C reveals that the peak around δ 2.7 in the ^{1}H NMR spectrum is related to the peak around δ 14.2 in its ^{13}C NMR spectrum. This is also corroborated with ^{1}H and ^{13}C NMR spectra of bulk-polymerized Na–PAN (Figures 2 and 5). It has also been observed in the present investigation that the intensity of the peak around δ 2.7 in the ^{1}H NMR spectrum and that around δ 14.2 in the ^{13}C NMR spectrum run parallel to the intensity of coloration in these PANs. As already mentioned earlier, the peak around δ 14.2 has been attributed to methylene carbon atoms in the branched structure. Quite logically one could then assign the peak around δ 2.7 in the ^{1}H NMR spectrum of colored PAN to methylene protons.

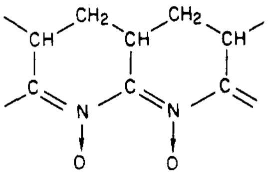
Coloration in PAN has been attributed to a number of plausible structures, viz. azomethine (I),[4] polyimine (II),[1,7,8] iminonitrone (III),[11,25] etc., type of structures.



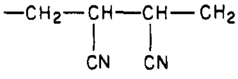
I



II

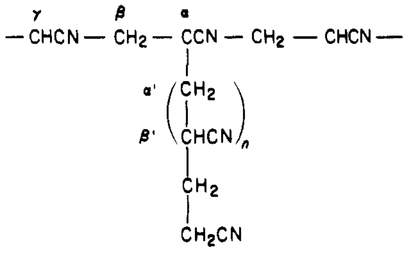


III



IV

So tentatively one could ascribe the peak around δ 2.7 observed in the ^{1}H NMR spectra of colored PAN to methylene and/or methine protons in structures I–III. The methine protons (marked with an asterisk in the structure), because of chain branching, get more shielded and as a result may move upfield. Similarly the methine protons in structures II and III may move upfield due to more shielding, while the methylene protons get deshielded and hence may move downfield—the two peaks thus shifted may appear as a single peak around δ 2.7. Structure I also accounts for the peak around δ 8.31 observed in a number of colored PAN (Table II). Structures II and III also may account for this peak if the structure ends up with –NH–. A tail-to-tail (or head-to-head) addition, unknown in normal free radical initiated PAN, giving rise to structure IV may also account for the peak around δ 2.7 in the ^{1}H NMR spectrum of colored PAN. However, none of these structures can account for the peaks in the region δ 12–16 observed in the ^{13}C NMR spectra of colored PANs. These peaks could perhaps be best represented by the branched structure V, put forward by Scheller et al.,[44] in which the α'-methylene carbon to the branched carbon (of the backbone) would appear most upfield due to maximum shielding from the nitrile group attached to the branching point carbon atom, β'-carbon to this branching point carbon would appear at a relatively lower field, and so on. The ^{13}C NMR spectrum of solution-polymerized Li–PAN has actually been found to give a number of peaks around δ 12.1, 14.2, to even 16 showing the presence of α', β', etc., carbon atoms with respect to the branching point carbon atom having appreciable intensity, so much so that the intensity of the original methine and methylene carbon peaks occurring around δ 27.0 and 32.6 has been drastically reduced. This means, in other words, there are more carbon atoms in the branched structure than the number of carbon atoms in the backbone.



V

$n = 0, 1, 2$

In conclusion it may be said that there are some common features in colored PAN irrespective of its mode of coloration; e.g., a prominent peak occurs around δ 2.7 together with less pronounced peaks around δ 1.15 and 8.31 in the ^{1}H NMR spectrum and one or more peaks appear in the region δ 12–16 in the ^{13}C NMR spectrum (except the heat-treated PAN). The intensity of all these peaks has been found to run parallel to the extent of coloration. Colorless PAN are predominantly random (50% or more) while colored PAN have appreciable isotactic contribution (40% or more).

Acknowledgment. We thank the authorities of the Sophisticated Instruments Centre, Indian Institute of Science, Bangalore, for recording all the NMR spectra. B.S. thanks Prof. C. L. Khetrapal of Sophisticated Instruments Centre for many helpful discussions. We also thank the reviewers, Dr. Jeanette Grasselli and Dr. J. Robert Mooney, for their helpful comments and suggestions.

Registry No. BuLi, 109-72-8; C_6H_5MgBr, 100-58-3; Li, 7439-93-2; Na, 7440-23-5; PAN, 25014-41-9; AIBN, 78-67-1; BPO, 94-36-0.

References and Notes

(1) LaCombe, E. M. *J. Polym. Sci.* **1957**, *24*, 152.
(2) Bamford, C. H.; Eastmond, G. C. *Encycl. Polym. Sci. Technol.* **1964**, *1*, 400.
(3) Sandler, S. R.; Karo, W. *Org. Chem.* **1974**, *29*, 326.

(4) Schurz, J. *J. Polym. Sci.* **1958**, *28*, 438.
(5) Kern, W.; Fernow, H. *Rubber Chem. Technol.* **1944**, *17*, 356.
(6) Houtz, R. *Text. Res. J.* **1950**, *20*, 786.
(7) Burlant, W. J.; Parsons, J. L. *J. Polym. Sci.* **1956**, *22*, 249.
(8) Grassie, N.; Hay, J. N.; McNeill, I. C. *J. Polym. Sci.* **1958**, *31*, 205.
(9) Grassie, N.; Hay, J. N. *J. Polym. Sci.* **1962**, *56*, 189.
(10) Monaham, A. R. *J. Polym. Sci., Part A-1* **1966**, *4*, 2391.
(11) Friedlander, H. N.; Peebles, L. H., Jr.; Brandrup, J.; Kirby, J. R. *Macromolecules* **1968**, *1*, 79.
(12) Dunn, P.; Ennis, B. C. *J. Appl. Polym. Sci.* **1970**, *11*, 1195.
(13) Grassie, N.; McGuchan, R. *Eur. Polym. J.* **1971**, *7*, 1091, 1357; **1972**, *8*, 257.
(14) Patron, L.; Mazzolini, C.; Morelti, A. *J. Polym. Sci., Part C* **1973**, *42*, 405.
(15) Coleman, M. M.; Petcavich, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 821.
(16) Rafalko, J. J. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1211.
(17) Chung, T. C.; Schlesinger, Y.; Elemad, S.; Macdiarmid, A. G.; Heeger, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1239.
(18) McCartney, J. R. *Mod. Plast.* **1953**, 118.
(19) Stubchen, H.; Schurz, J. *Monatsh. Chem.* **1958**, *89*, 234.
(20) Takata, T.; Hiroi, I.; Taniyama, M. *J. Polym. Sci., Part A* **1964**, *2*, 1567.
(21) Glazkovskii, Yu. V.; Mikhailov, P. V. *Vysokomol. Soedin, Ser. B* **1966**, *8*, 1673.
(22) Batty, N. S.; Guthrie, J. T. (a) *Polymer* **1978**, *19*, 1145; (b) *Makromol. Chem.* **1981**, *182*, 71.
(23) Endry, A. L. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2105.
(24) Batty, N. S.; Grandwell, A. J.; Guthrie, J. T.; Greig, D.; Hardy, N. D.; Jakeways, R.; Sahota, M. *Polymer* **1983**, *24*, 258.
(25) Peebles, L. H., Jr. *Encycl. Polym. Sci. Technol. Suppl.* **1976**, *1*, P1.
(26) Yamadera, R.; Murano, M. *J. Polym. Sci., Part B* **1965**, *3*, 821.
(27) Matsuzaki, K.; Uryu, T.; Ishigure, K.; Takeuchi, M.; *J. Polym. Sci., Part B* **1966**, *4*, 93.
(28) Matsuzki, K.; Uryu, T.; Okada, M.; Ishigure, K.; Ohki, T.; Takeuchi, M. *J. Polym. Sci., Part B* **1966**, *4*, 487.
(29) Bargon, J.; Hellwege, K. H.; Johnsen, U. *Kolloid Z.* **1966**, *212*, 51.
(30) Svegliado, G.; Talamini, G.; Vidotto, G. *J. Polym. Sci., Part A-1* **1967**, *5*, 2875.
(31) Murano, M.; Yamadera, R. *J. Polym. Sci., Part B* **1967**, *5*, 333.
(32) Yoshino, T.; Kenjo, H.; Kuno, K. *J. Polym. Sci., Part B* **1967**, *5*, 703.
(33) Murano, M. *Makromol. Chem.* **1968**, *112*, 281.
(34) Matsuzaki, K.; Uryu, T.; Okada, M.; Shiroki, H. *J. Polym. Sci., Part A-1* **1968**, *6*, 1475.
(35) Bracke, W.; Empeu, J.; Marvel, C. S. *Macromolecules* **1968**, *1*, 465.
(36) Imai, Y.; Minami, S.; Yoshiyara, T.; Joh, Y.; Sato, H. *J. Polym. Sci., Part B* **1970**, *8*, 281.
(37) Matsuzaki, K.; Okada, M.; Uryu, T. *J. Polym. Sci., Part A-1* **1971**, *9*, 1701.
(38) Matsuzaki, K.; Okada, M.; Goto, K. *J. Polym. Sci., Part A-1* **1972**, *10*, 823.
(39) Schaefer, J. *Macromolecules* **1971**, *4*, 105.
(40) Inoue, Y.; Nichioka, A. *Polym. J. (Tokyo)* **1972**, *3*, 149.
(41) Nishioka, A.; Ando, I.; Inoue, Y. *Kobunshi Kagaku* **1973**, *30*, 139.
(42) Balard, H.; Fritz, H.; Meybeck, J. *Makromol. Chem.* **1977**, *178*, 2393.
(43) Turska, E.; Grobelny, J.; Dworak, A.; Adamowicz, H. *Acta Polym.* **1981**, *32*, 114.
(44) Scheller, D.; Krippner, W.; Grossman, G.; Berger, W. *Acta Polym.* **1982**, *33*, 632.
(45) Bajaj, P.; Padmanaban, M. ; Gandhi, R. P. *Polymer* **1985**, *26*, 391.

Spectroscopic and Calorimetric Studies on the Protonation of Polymeric Amino Acids

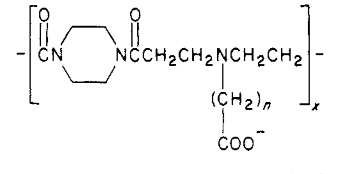
R. Barbucci,[*,†] **M. Casolaro,**[†] **P. Ferruti,**[‡] **and M. Nocentini**[†]

Dipartimento di Chimica, Università di Siena, Piano dei Mantellini 44, 53100 Siena, Italy, and Dipartimento di Ingegneria Meccanica, Università di Brescia, V.le Europa 39, 25060 Brescia, Italy. *Received December 27, 1985*

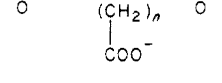
ABSTRACT: The protonation of some poly(amido amines) has been studied in aqueous solution by FTIR spectrophotometry and by calorimetry. On the basis of the stretching bands of both the ionized and the un-ionized carboxyl groups, the structures of all four polymeric amino acids in their different protonation states are determined. Calorimetric studies show that the enthalpies of protonation do not change with pH and follow a trend similar to that observed in simple amino acids of comparable structure. An anomalously high value of $|\Delta H_2°|$ observed for the polymer obtained by the polyaddition of β-alanine to diacryloylpiperazine has been found and attributed to the formation of a very highly symmetrical structure when the carboxyl groups are in the un-ionized form.

Introduction

In previous papers we have reported the synthesis, the protonation, and Cu^{2+} ion complexing behavior of a series of polymeric amino acids with a poly(amido amine) backbone and the corresponding nonmacromolecular models, having the following structure:



PAAA$_n$ (n = 1, 2, 4, 5)



MAAA$_n$ (n = 1, 2)

These studies are performed by potentiometric, viscosimetric, and spectrophotometric techniques.[1] To better elucidate the mechanism of protonation of these polymers, we have now carried out spectroscopic and calorimetric studies. The spectroscopic studies have been performed by FTIR techniques in water.

Experimental Section

Materials. The syntheses of polymers $PAAA_1$, $PAAA_2$, $PAAA_4$, and $PAAA_5$ have been previously described.[1] The corresponding nonmacromolecular models $MAAA_1$ and $MAAA_2$ were synthesized in a similar way as previously reported.[2]

A CO_2-free NaOH solution was prepared, stored, and standardized as described elsewhere.[3] Stock solutions of 0.1 M NaCl were prepared from sodium chloride (Suprapur Merck) and used without further purification as the ionic medium for calorimetric measurements.

FTIR Spectra. Transmission infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer M1500 with a nitrogen purge. Typically 250 scans at a resolution of 3.2 cm^{-1} were averaged and the spectra were stored on a microfloppy disk. The frequency scale of the instrument was internally calibrated by

---

[†] Università di Siena.
[‡] Università di Brescia.