# Thermal and Rheological Behavior of Acrylonitrile–Carboxylic Acid Copolymers and Their Metal Salt Complexes

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**ABSTRACT:** The influence of acrylic, methacrylic, and itaconic acid comonomers in the nitrile oligomerization of acrylonitrile copolymers has been studied by DSC and DSC-FTIR in air and nitrogen atmospheres. Addition of metal salts in poly(acrylonitrile–acrylic acid) copolymer, PA on thermal and rheological behavior has also been reported. Incorporation of $CuSO_4$, $FeSO_4$, $ZnSO_4$, and $Al_2(SO_4)_3$ (1 to 5 wt %) salt in the polymer solution affects its solubility in DMF. The complexes of PA with zinc sulphate, took a longer time to dissolve in DMF, whereas the complexes with $Fe(SO_4)$ and $Al_2(SO_4)_3$ are almost insoluble in DMF, perhaps due to intermolecular crosslinking. Addition of these metal salts to the PA solution also affects its Brookfield viscosity. The viscosity of 10 wt % polymer solution increases from 400 centipoise (Cps) to 1090 Cps for complex with 5% $FeSO_4$ (on the weight of dope solids) and 690 Cps for $Al_2(SO_4)_3$ and 906 cps for $ZnSO_4$ complex. However, for $CuSO_4$ salt complex this value is 770 Cps. FTIR spectra shows the participation of COOH and CN group in the complex formation, which is responsible for enhanced Brookfield viscosity. Thermal behavior of the polymer–metal salt complex showed that these salts also affect the exothermic reaction. The initiation of cyclization reaction takes place at a lower temperature compared to neat acrylonitrile–acrylic acid copolymer. However, the heat liberated per unit time in $N_2$ atmosphere in case of neat polymer is 6.3 $Jg^{-1}$ $min^{-1}$, which reduces to 5.5 $Jg^{-1}$ $min^{-1}$ in the case of the PA/Al complex, confirming the role of $Al_2(SO_4)_3$ in retarding the rate of cyclization reaction. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 567–582, 1999

**Key words:** thermal behavior; rheological behavior; acrylonitrile–carboxylic acid copolymers; metal salt complex

## INTRODUCTION

Ion exchange fibers based on poly acrylonitrile (PAN) have generated great interest in solving a number of practical problems in ion-exchange technology. To introduce ionogenic groups into PAN, it is possible to use the transesterification of nitrile groups to carboxylic groups by alkaline and acid hydrolysis or with water[1,2] at 180–200°C

under reduced pressure (15 atm. 180°C). Acidic reagents[3] such as acetic acid, benzene sulphonic acid, at 85°C, 75% sulphuric acid of 5°C, and at room temperature to 60°C, and alkaline reagents[5–9] such as sodium carbonate, sodium hydroxide, and potassium hydroxide at room temperature to 85°C and sodium metasilicate[10] have been used for the hydrolysis of nitrile groups in PAN.

Bajaj and coworkers[8,9,11,12] have reported the kinetics and structural investigations of the saponified acrylonitrile terpolymer having methyl acrylate or vinyl acetate and sodium methallyl sulphonate. The study revealed that the rate of saponification is greater for the terpolymer than for the homopolymer due to loose packing of the

molecular chains in the terpolymer. Geller et al.[7] found that during alkaline hydrolysis of AN–methylacrylate–itaconic acid terpolymer fibers, the nitrile groups that are sufficiently remote from the carboxylic acid units are saponified more quickly.

Metallized electrically conducting fibers have been produced by chemical nickelling of freshly spun Nitron fibers.[13,14] The fiber was withdrawn from the manufacturing stream after final washing, and was subjected to sorptive chemical metallization. The use of sodium formaldehyde sulfoxylate as the reducing agent in metallization leads to the reduction of $Ni^{+2}$ to $Ni^{O}$ with the formation of nickel sulphide *in situ* in the fiber. Two percent by weight of nickel in the fiber reduced its specific resistance by six to seven orders of magnitude.

In another study, freshly spun PAN gel fibers containing 92% acrylonitrile, 6.3% methyl acrylate, and 1.7% itaconic acid were treated with alkali metal salts for 2 s at room temperature. From IR spectra of the treated fibers, it was established that alkali metal cations (Li, Na,K) form a complex with the COOH groups present in the acrylic fibers.[15,16]

Use of calcium salts for producing antistatic and hygroscopic acrylic fibers has been suggested.[17] In this study, the freshly spun PAN fibers were treated with calcium salts (1 to 3%) after plasticized stretching and washing, for 60 s at 50°C. Calcium chloride causes a greater effect than calcium nitrate on moisture sorption properties of acrylic fibers.

Introduction of Ca(II) into polyacrylonitrile fiber based on the acrylonitrile/methyl acrylate/itaconic acid terpolymer led to a loss of its solubility in dimethylformamide, even upon boiling.[18] The IR spectrum of the acrylic fiber containing calcium, showed a reduction in 2240 and 1735 $cm^{-1}$ absorption band intensity, with a simultaneous appearance of a new absorption band at 2365 $cm^{-1}$. The displacement in the stretching frequency due to carboxylate ion (—COO$^-$) from 1590 $cm^{-1}$ to a higher wave number at 1640 $cm^{-1}$ may be due to the complex formation.

In another study, Platova et al.[19] reported the effect of lithium chloride, calcium chloride, or aluminum chloride on the wettability and hygroscopicity of Nitron fibers. Influence of $CdSO_4$ and ethylenediamine on the deformability and thermal stability of acrylic terpolymer fiber containing 92% (by wt) AN, 6.3% MA, and 1.7% itaconic acid has been demonstrated by Abdurakhmanova et al.[20] An increase in $T_g$ up to 100% has been observed in fibers treated with $CdSO_4$, along with high values of deformation. However, the process of cyclization in the acrylic fiber treated with $CdSO_4$ takes place more slowly, while treatment with a mixture of $CdSO_4$ and ethylene diamine solutions causes the nonuniformity in the development of structure and twisting of the fiber.

The sorption of cations of silver, copper, and mercury by as-spun acrylic fibers[21] has also been reported. The introduction of metal cations produced appreciable changes in the mobility of the acrylonitrile copolymer as reflected from the thermomechanical curves. Cations of copper and silver increased the $T_g$ by 10–15°C of the metallated acrylic fibers, but $Hg^{2+}$ did not produce any appreciable change.

Metal chlorides such as lithium chloride, magnesium chloride, zinc chloride, and calcium chloride are also known to influence the rheological behavior of acrylic dope and its spinning performance.[22,23] It was found that the dope viscosity decreases with an increase in lithium chloride concentration. This dope could be stored at a lower temperature for a longer time without gelling, and could be spun easily with a higher polymer content (25–32% in the dope) into filaments without any deterioration in the physico-mechanical properties.

The effect of aluminum and other metals on gelation in the spinning solutions for the production of polyacrylonitrile fiber, nitron-S, has been investigated by Burd et al.[24] It was shown that gelation in industrial spinning solutions is caused by the aluminum–iron electric pair contained in the filter press. The aluminum ions formed crosslinks the acrylonitrile copolymers leading to gelation.

Copper-catalyzed gelation of dilute polyacrylonitrile solutions has been investigated by Xue and Dong,[25] and a gelation mechanism has been proposed on the basis that metallic copper catalyses the hydrolysis of nitrile groups, and the partially neutralized acid tightly coils the chain, leading to precipitation of polyacrylonitrile.

Microbicidal acrylic fibers[26,27] have been produced by using dope additives like 0.1–10% Ag, $H_y A_z M_2 (PO_4)_3$, where A = alkali metal; M = Zr, Ti, Sn; x,y,z < 1; x+y+z = 1; Ag = 1–7% in acrylonitrile–methylacrylate–Na-2-acrylamido-2-methylpropane sulphonate terpolymer in DMF.

The introduction of certain inorganic salts, viz, $AgNO_3$, $HgNO_3$, Cr $(OCOCH_3)_3$, $K_2Cr_2O_7$, Pb $(OCOCH_3)_2$, etc., into the fibers make them suit-

**Table I  Characterization of Acrylonitrile-Carboxylic Acid Copolymers**

| S. No. | Copolymer | Code | Vinyl Acid Content mol % | Intrinsic Viscosity dL g$^{-1}$ |
|--------|-----------|------|--------------------------|---------------------------------|
| 1. | P (AN-AA) | PA | 3.1 | 1.3 |
| 2. | P (AN-MAA) | PM | 2.6 | 1.35 |
| 3. | P (AN-IA) | PI | 2.2 | 1.24 |

able as bactericidal and antimicrobial fibers for air sterilization, thermostable fibers for bag filters, catalyst for carbon fiber production, radiation-protective fibers, etc.[28]

Electrically conductive polyacrylonitrile fibers have also been produced through surface modification with nitrogen, copper, or sulphur-containing compounds and reductors.[29] The effect of inorganic salts on the thermal oxidative stabilization and the carbonization of acrylic precursor (AN-IA-MA) fibers has also been reported.[30] It has been demonstrated that NaCl, $CuCl_2$, $CaCl_2$, $MnCl_2$, $AlCl_3$, and $Na_2SiO_4$ increase the total gas evolution during the oxidative degradation stage. All these salts increase the volume and the surface area of the carbonized fibers and decrease the size of micro and mesopores.

Treatment of acrylic fibers with metal salts help in thermo-oxidative stabilization either by reducing the activation energy or by improving the structure. Treatment with CuCl and $COCl_2$ are of particular interest, as they affect the structure morphology of the acrylic fiber, besides helping in the stabilization reaction.[31,32] The effects of metal ion on the thermal behavior of acrylonitrile polymers were also studied by Bajaj et al.[33]

From the foregoing literature, it is evident that the metal salts used for the modification of acrylic fiber change the structure and thermal behavior of the modified acrylonitrile copolymer fibers. However, not much work on the rheology of metallized acrylonitrile copolymers spinning dope has been reported. It was, therefore, considered of interest to study the effect of some metal salts on the rheological and thermal behavior of poly(acrylonitrile-acrylic acid). Structural investigations of the acrylonitrile carboxylic acid copolymers and their metal salt complexes were carried out using micro-FTIR interfaced with DSC.

## EXPERIMENTAL

### Materials

Three copolymers of acrylonitrile–carboxylic acids, i.e., acrylic methacrylic and itaconic acid,

were prepared by solution polymerization in DMF. The details of polymerization are given elsewhere.[31] The intrinsic viscosity [η] and the chemical composition are given in Table I.

### Metallation of Acrylonitrile–Acrylic Acid Copolymers (PA)

Polymer dope with a known solid content (15 wt %) and 1% oxalic acid (on the weight of the polymer in the dope) was taken for rheological and metallation studies. The required quantity of $Al_2(SO_4)_3$, $ZnSO_4$, $FeSO_4$, and $CuSO_4$ salts (5 wt % on the basis of dope solids) was dissolved in 2 mL of water in a separate test tube. An adequate amount of DMF was then added to the aqueous salt solutions and mixed with the polymer dope. The total solid content of the dope was reduced to 10%. The addition of a metal salt solution to the polymer dope was done with continuous stirring and at a slow rate to ensure the homogeneity of the solution. This polymer–salt complex dope was used for Brookfield viscosity measurements.

The polymer–metal salt (1–5 wt % salt conc.) complex solution was made into a thin film on a glass plate, washed with water, dried, and washed again in warm water to remove the unreacted metal salt adhered to the film, and finally washed again with acetone and dried in the vacuum oven. The polymer metal complex film thus obtained was used for DSC, DSC-FTIR and for solubility studies. The codes used for the polymer metal salt complexes are given below:

| Copolymer and [η] | Metal Salt | Code | Metal Content in the Film (wt %) |
|-------------------|------------|------|----------------------------------|
| P (AN-AA) (AA = 3.1 | $Al_2(SO_4)_3$ · 18H$_2$O | PA/Al | 0.6 |
| mol %) | $ZnSO_4$ · 7H$_2$O | PA/Zn | 0.3 |
| [η] = 1.3 | $FeSO_4$ · 7H$_2$O | PA/Fe | 0.09 |
| dL g$^{-1}$ | $CuSO_4$ · 5H$_2$O | PA/Cu | 0.2 |

**Table II   Brookfield Viscosity of PM Polymer Solutions at 100 rpm**

| Dope Temp. °C | Brookfield Viscosity (Cpoise) | | | | |
| --- | --- | --- | --- | --- | --- |
| | Solid Content, wt % | | | | |
| | 25 | 22 | 20 | 18 | 15 |
| 30 | 8400 | 5800 | 4260 | 3000 | 2000 |
| 40 | 7300 | 5100 | 3800 | 1600 | 1800 |
| 50 | 6600 | 4500 | 3300 | 2000 | 1600 |
| 60 | 5800 | 4000 | 3000 | 1800 | 1400 |
| 70 | 5300 | 3800 | 2800 | 1500 | 1300 |
| 80 | 4900 | 3200 | 2400 | 1300 | 1100 |

1% oxalic acid was added in the dope (on the basis of polymer content).

## Brookfield Viscosity

Brookfield viscosity measurements were carried out on a Brookfield RVTD Digital viscometer with a thermosol attachment. This Brookfield viscometer is of the rotational variety, and measures the torque required to rotate the spindle in the fluid. The spindle (29 BS) is driven by a synchronous motor through a calibrated spring, and the deflection of the spring is indicated by a digital display. Brookfield viscosity was used to determine the effect of shear rate given by rpm of the spindle and the temperature (at a constant shear rate) from 30 to 90°C ($\pm1$°C) on the rheological properties of the PA metal complexes. Effect of solids content on the Brookfield viscosity of PA, PM, and PI was also studied.

## Differential Scanning Calorimetry (DSC)

### Dynamic Mode

The DSC of acrylonitrile–acrylic acid copolymer–metal complexes was carried out on Perkin-Elmer

Delta-7 series up to 400°C in air and nitrogen atmosphere at a heating rate of 5°C/min. A sample weight of 4–5 mg in the form of finely powdered polymer was used.

### Isothermal Mode

Acrylonitrile–acrylic acid copolymer and its complex with metal salts were also heat treated isothermally at 210 to 240°C in a DSC cell. Mettler FP-84 HT DSC was used for these studies, along with a central processor mettler FP-90, in air for 60 min at a flow rate of 2.5 L/min.

## DSC-FTIR

Chemical structural changes occurring during thermal treatments of PA, PM, and PI along with the PA copolymer metal salt complexes were investigated using a DSC-FTIR (Jasco Micro FTIR 200) coupled with a Mettler FP-84 HT thermal analyser microscopy cell. Polymer complexes were sandwiched between the KBr disc and

**Table III   Brookfield Viscosity vs. Temp. of PI Polymer (+1% Oxalic Acid) Solutions at 100 rpm**

| Dope Temp °C | Brookfield Viscosity (Cpoise) | | | | |
| --- | --- | --- | --- | --- | --- |
| | Solid Content, wt % | | | | |
| | 25 | 22 | 20 | 18 | 15 |
| 30 | 4100 | 3050 | 2000 | 1300 | 920 |
| 40 | 3600 | 2700 | 1800 | 1000 | 810 |
| 50 | 3100 | 2200 | 1500 | 900 | 720 |
| 60 | 2800 | 1800 | 1250 | 820 | 640 |
| 70 | 2300 | 1600 | 1100 | 740 | 500 |
| 80 | 2000 | 1500 | 900 | 600 | 460 |

**Table IV   Effect of Metallation on Brookfield Viscosity of PA (10% in DMF + 5% Metal Salt Complexes at 100 rpm**

| Dope Temp °C | Brookfield Viscosity (Cpoise) | | | | |
|---|---|---|---|---|---|
| | PA | (PA/Fe) | (PA/Al) | (PA/Zn) | (PA/Cu) |
| 30 | 750 | 1400 | 1300 | 1170 | 1220 |
| 40 | 620 | 1280 | 1100 | 1060 | 1080 |
| 50 | 500 | 1190 | 990 | 980 | 880 |
| 60 | 400 | 1090 | 915 | 780 | 770 |
| 70 | 300 | 970 | 800 | 740 | 580 |
| 80 | 260 | 860 | 670 | 680 | 480 |

5% on the basis of PA content in the dope.

mounted on DSC cell interfaced with micro-FTIR. The samples were heated at 10°C/min up to 350°C.

## RESULTS AND DISCUSSION

### Metallation of Acrylonitrile–Acrylic Acid Copolymers (PA)

The solubility behavior of these complexes in DMF was studied. The metal complex formed with $ZnSO_4$ (PA/Zn) and $CuSO_4$ (PA/Cu) took a longer time to dissolve in DMF compared to neat polymer (PA), whereas the complex formed with ferrous and aluminium sulphate made it almost insoluble in DMF. This shows that the addition of these metal salts to the copolymer solution form some complex either through nitrile (C≡N) and/or carboxyl (COOH) groups that affect the solubility.

Insolubility of Fe and Cu transition metal complexes with the PA copolymer in DMF may be due to the crosslinking network formed through coordination. With the addition of $FeSO_4$ to the polymer dope in DMF, the color of the dope also changed. At a lower concentration of the metal salt, it is not noticeable, but at high concentration (>3–5%), the color is quite distinguishable, and it turns more bluish. This color change was also observed with the $CuSO_4$ complex, where the dope solution turned light blue. The intensity of the color, however, depended on increasing the concentration of the metal salt in the polymer solution.

### Rheological Behavior

#### Brookfield Viscosity of Acrylonitrile–Carboxylic Acid Copolymer Solution in DMF

The viscosity of the dope solution of acrylonitrile–vinyl acid copolymers, i.e., PA, PI, and PM, has been measured with varying solid contents in DMF. The change in the Brookfield viscosity of PA, PM, and PI copolymer solutions with different solid contents at 30–80°C is given in Tables II, III, and IV. The data reveals that the viscosity of the polymer dope depends on the temperature as well as dope solids (Fig. 1).

As the temperature increases, there is a significant fall in the dope viscosity (Tables II–IV). For example, at 30°C PA with 25% solid content, the Brookfield viscosity was 6400 cps, whereas at 80°C this value reduced to 3800 Cps. Also, in PM, as the temperature increases, the Brookfield viscosity drops. At 30°C Brookfield viscosity of 25% dope is 8400 cps, which reduced to 4900 cps at 80°C. A similar observation was made for PI copolymer. The dope viscosity is 4100 cps at 30°C, which drops to 2000 cps with increasing the temperature to 80°C. The drop in the viscosity at



**Figure 1**   Effect of temperature on the Brookfield viscosity of the PA copolymer solution with different solid contents at 100 rpm.

**Figure 2** Change in Brookfield viscosity vs. temperature for PA and its complex (PA/Al) dope at different concentrations.

higher temperatures is due to the reduction in the solute–solvent and solute–solute interaction, which reduces the resistance to flow. Further, about a 50% drop in viscosity of PI dope at 80°C in comparison to a 39 to 41% fall in PA and PM may be attributed to weaker nitrile–nitrile dipolar interactions due to the presence of bulkier carboxylic acid groups (—COOH) of itaconic acid in PI.

It can be seen from Figure 1 that viscosity increases almost monotonously with the increase in the solid content. In PA, with 15% solid content of the Brookfield viscosity at 50°C is 910 cps, which increased to 5050 cps at 25% solid content of the dope. Similar behavior was also observed with other copolymers. In PM, the Brookfield viscosity at 50°C for polymer dope with 15% solids was 1600 cps, which increased to 6600 cps when the solid content increased to 25%. In PA, this value for 15 wt dope solids was 720 cps (at 50°C), which increased to 3100 Cps with 25 wt % solids. Comparing these three copolymers, PM shows the highest Brookfield viscosity at the same solid content of the dope and temperature followed by PA. Theoretically, for the same molecular weight of the acrylonitrile–carboxylic acid copolymer, PM and PI should show maximum viscosity for the same solid content having bulkier side substituents on the basis of hydrodynamic volume.

However, the viscosity values obtained in the present study demonstrate the influence of both the molecular weight and molecular packing (intermolecular forces) due to the presence of bulky side substituents.

## Effect of Metal Salts on Brookfield Viscosity

The metallation of acrylonitrile–acrylic acid copolymer (PA) showed interesting rheological behavior. Addition of the metal salts to the polymer dope increases its viscosity and restricts the flow behavior of the dope (Table IV).

The Brookfield viscosity of PA with 10% solid content at 30°C is 750 cps; however, in the metal complexes, this value increases. In the PA/Zn complex (5 wt % of the salt), the Brookfield viscosity at 30°C is 1170 cps, which reduced to 680 cps with an increase in temperature to 80°C. In the PA/A1 (5 wt % salt) complex, the viscosity at 30°C is 1300 Cps, while in the PA/Fe complex at 30°C, it is 1400 Cps. The change in Brookfield viscosity of PA and PA/A1 (5% salt) as a function of temperature is shown in Figure 2.

The viscosity of the metal complex increases as the content of metal salts in the polymer solution increases from 1 to 5 wt % (Fig. 3). From the above observations it can be concluded that these metal salts participate in replacement of $H^+$ ion of the COOH group and/or form bonds with nitrile $C\equiv N$ groups to achieve some kind of crosslinking.

Another fact is that the coordination number of metal cations is different, due to their electronic configuration: Zn $(d^{10}s^2)$, Cu $(d^{10}s^1)$, Fe $(d^6s^2)$, Al $(3s^23p^1)$. Iron $(Fe^{++})$ and aluminum $(Al^{+++})$ have coordination number 6, whereas it is 4 in case of copper $(Cu^{++})$ and zinc $(Zn^{++})$. This means that $Fe^{++}$ and $Al^{+++}$ cations can form



**Figure 3** Effect of metal salt content on the Brookfield viscosity of the polymer–metal salt complex system at 60°C.

**Table V   DSC Data of Acrylonitrile–Acrylic Acid Copolymer (PA) With Its Metal Complexes at 5°C/min**

| Copolymer Code | $T_i$ (°C) | $T_f$ (°C) | $T_{pk1}$ (°C) | $T_{pk2}$ (°C) | $\Delta H$ Jg$^{-1}$ | $\Delta H/\Delta t$ Jg$^{-1}$ min$^{-1}$ |
|---|---|---|---|---|---|---|
| In N$_2$ atmosphere | | | | | | |
| PA | 263 | 291 | 279 | — | 178 | 6.3 |
| PA/Al | 260 | 290 | 273 | — | 173 | 5.5 |
| PA/Fe | 258 | 287 | 275 | — | 176 | 5.8 |
| PA/Zn | 259 | 286 | 282 | — | 160 | 5.9 |
| PA/Cu | 257 | 289 | 270 | — | 161 | 5.0 |
| In Air | | | | | | |
| PA | 216 | 344 | 273 | 314 | 3445 | 26.9 |
| PA/Al | 222 | 380 | 282 | 328 | 4721 | 29.9 |
| PA/Fe | 213 | 336 | 284 | 310 | 3018 | 24.5 |
| PA/Zn | 214 | 341 | 280 | 313 | 3251 | 25.6 |
| PA/Cu | 210 | 343 | 285 | 312 | 3371 | 25.3 |

Rate of heating = 5°C; Total scan = 50–400°C; $T_i$ = initiation temperature of exothermic reaction; $T_f$ = final temperature of exothermic reaction; $T_{pk}$ = peak temperature of exothermic reaction.

chelate compounds with six groups from the same or different polymer chains. The COOH and nitrile groups could be from the same chain or different polymer chains.

The coordination complexes formed through groups of the same chain would result in intramolecular crosslinking, whereas if the coordination takes place through groups from different chains, i.e., intermolecular crosslinking would cause an exponential rise in the viscosity. Similar observation was made by Bhatia,[31] where the effect of aluminum sulphate on the saponified acrylonitrile terpolymer was investigated. Aluminum compounds are unusual because they have a dimeric structure.

### Differential Scanning Calorimetry

#### *Dynamic Mode: DSC in Nitrogen Atmosphere*

DSC curves of the AN–AA copolymer (PA) and its metal complexes showed a sharp exotherm in nitrogen atmosphere. In PA, onset of exothermic reactions, $T_i$, appears at 263°C with $T_{pk}$ at 279°C. In polymer–metal complexes, the initiation of cyclization reaction $T_i$ shifts to a lower temperature, viz; 257°C for the PA/Cu complex, 258°C for the PA/Fe, and 260°C for the PA/A1 complex (Table V). However, the shift in the peak maximum ($T_{pk}$) is quite large. In the PA/A1, the $T_{pk}$ is 273°C, while in the PA/Cu complex it is 270°C. This indicates that the introduction of these metal salts into the PA copolymer influences the initiation of nitrile oligomerization.

The total heat of reaction is 178 Jg$^{-1}$ in PA, which reduces in the PA–metal salt complexes due to a complex formation.

The total heat produced per unit time ($\Delta H/(t)$ is (6.3 Jg$^{-1}$ min$^{-1}$) for PA, but it is reduced to 5.5 Jg$^{-1}$ min$^{-1}$ for PA/A1 and further reduced to 5.0,



**Figure 4**   DSC scan of the PA copolymer and its complex with metal salts recorded in air at 5°C/min.

**Figure 5** (a) Heat-flow profile of the PA at different temperatures in air (isothermal mode). (b) Heat-flow profile of the PA–Fe complex at different temperatures in air (isothermal mode). (c) Heat-flow profile of the PA–Al complex at different temperatures in air (isothermal mode).

5.8, and 5.9 $Jg^{-1}$ $min^{-1}$ for PA/Cu, PA/Fe, and PA/Zn, respectively. On the basis of $T_i$ values, this indicates that the cyclization reaction is no doubt initiated at a lower temperature, but the propagation of cyclization reaction is slow due to intermolecular or intramolecular crosslinking of COOH and nitrile groups due to metal complex formation. From this data, it may be inferred that in the PA/Cu complex the degree of nitrile oligomerization is least or it will take a longer time for the cyclization reaction to produce ladder polymer compared to Zn, Al, and Fe complexes.

### DSC in Air Atmosphere

The DSC exotherm of the acrylonitrile–acrylic acid copolymer (PA) and its metal complexes showed two distinct peaks. The primary peak ($T_{pk1}$) and the secondary peak ($T_{pk2}$), which, in some cases appeared as a shoulder (Fig. 4). In PA, the exothermic reaction ($T_i$) begins at 216°C, but it shifts to a lower temperature in PA/Fe, PA/Zn,

and PA/Cu complexes (Table V). This shows that the initiation of cyclization has been affected by the incorporation of these metal salts in the neat polymer. However, in PA/A1, the $T_i$ begins at 222°C, indicating that the exothermic reaction has been delayed in the complex, perhaps due to the crosslinking reaction.

The primary peak temperature $T_{pk1}$ in the PA copolymer is at 273°C. However, it appears at a higher temperature for metal complexes. In PA/Al, $T_{pk1}$ is at 282 and 285°C for the PA/Cu complex system.

The secondary peak ($T_{pk2}$) is a result of oxidation reaction during the heat treatment of the acrylic copolymer. In PA, $T_{pk2}$ appears at 314°C. In the metal complex systems it appeared at 310°C for the A1/Fe and 313°C for the PA/Zn complex. However, in the PA/A1 complex the second peak temperature ($T_{pk2}$) appears at a much higher temperature, i.e., 328°C. This further supports the fact that the thermo-oxidative reaction

**Table VI   DSC Data (Isothermal Mode) of Acrylonitrile–Acrylic Acid Copolymer (PA) and Its Complex with Metal Salts**

| DSC Cell Temp. (°C) | Exotherm | PA | PA/Al | PA/Fe | PA/Zn | PA/Cu |
|---|---|---|---|---|---|---|
| 210 | Exotherm time (min) | 19.8 | 239 | 4.6 | 17.2 | 14.4 |
|  | $\Delta H$ (Jg$^{-1}$) | 41.5 | 50.3 | 11.5 | 39.9 | 46.4 |
|  | $\Delta H/\Delta t$ (Jg$^{-1}$ min$^{-1}$) | 2.09 | 2.1 | 2.5 | 2.3 | 3.2 |
| 220 | Exotherm time (min) | 23.7 | 18.6 | 6.2 | 16.9 | 14.1 |
|  | $\Delta H$ (Jg$^{-1}$) | 17.8 | 68.8 | 18 | 91.5 | 78.5 |
|  | $\Delta H/\Delta t$ (Jg$^{-1}$ min$^{-1}$) | 7.5 | 3.7 | 2.9 | 5.4 | 5.6 |
| 230 | Exotherm time (min) | 20.7 | 19 | 3.1 | 13 | 13 |
|  | $\Delta H$ (Jg$^{-1}$) | 212 | 130 | 16 | 240 | 115 |
|  | $\Delta H/\Delta t$ (Jg$^{-1}$ min$^{-1}$) | 10.2 | 6.8 | 5.2 | 18.5 | 8.8 |
| 240 | Exotherm time (min) | 22.95 | 16.0 | 6.9 | 13.8 | 15.1 |
|  | $\Delta H$ (Jg$^{-1}$) | 453 | 150 | 107 | 249 | 134 |
|  | $\Delta H/\Delta t$ (Jg$^{-1}$ min$^{-1}$) | 19.8 | 9.4 | 15.5 | 18.1 | 8.9 |

involving the PA/A1 complex is significantly delayed due to the intermolecular and intramolecular crosslinking through COOH and nitrile groups, as discussed earlier.

The total heat liberated in air per unit time was 26.9 Jg$^{-1}$ min$^{-1}$ for PA, while in PA/A1, it is 29.9 Jg$^{-1}$ min$^{-1}$. The value of $\Delta H/\Delta t$ was, however, lower for PA/Fe (24.5 Jg$^{-1}$ min$^{-1}$), PA/Cu (25.3 Jg$^{-1}$ min$^{-1}$), and PA/Zn (25.6 Jg$^{-1}$ min$^{-1}$). The initiation of the exothermic reaction has been accelerated with the incorporation of metal salts; however, the propagation appears to be slow.

### DSC (Isothermal Mode)

DSC of the neat acrylonitrile–acrylic acid copolymer (PA) and its complexes with metal salts recorded in air atmosphere are shown in Figure 5. The heat flow behavior as a function of time shows the presence of a broad peak, which is due to the propagation reaction, and the initiation of cyclization seems to be instantaneous and fast.

A comparison of heat flow behavior of PA at 210 and 240°C indicates that the initiation of cyclization takes place after 0.85 min at 210°C, while it takes only 0.53 min at 240°C (Table VI). The maxima of the propagation reaction, however, reached earlier at an elevated temperature, i.e., 1.4 min at 240°C. This suggests that the reaction proceeds faster at elevated temperatures. The total heat flow, also increased significantly from 41.5 Jg$^{-1}$ to 453 Jg$^{-1}$ for 210 to 240°C heating temperatures, respectively. This demonstrates that the

rate and extent of nitrile cyclization increased significantly as the heating temperature in the DSC cell was raised from 210 to 240°C.

The DSC exotherm of the metal salt complex showed different behavior compared to neat polymer. In PA/Al, the reaction is delayed as shown in dynamic DSC. For example, at 240°C the initiation takes place after 1.17 min compared to 0.53 min of the neat PA. The heat produced per unit time was 9.4 Jg$^{-1}$ min$^{-1}$ for PA/Al compared to 19.8 Jg$^{-1}$ min for PA. This indicates that the exothermic reaction rate is retarded to a greater extent in the PA/Al complex.

On the contrary, the initiation of cyclization reaction is accelerated in the PA/Fe, PA/Cu, and PA/Zn complex systems. The onset of exothermic reaction at 240°C begins within 0.32, 0.43, and 0.53 min for PA/Fe, PA/Cu, and PA/Zn, respectively. The time taken to complete the reaction is also less for these metal complexes compared to neat polymers (PA). $\Delta H/\Delta t$ also reduces for these complexes, viz., it is 15.5, 18.1, and 8.9 Jg$^{-1}$ min$^{-1}$ for PA/Fe, PA/Zn, and PA/Cu, respectively. This demonstrates that the initiation of exothermic reaction is fast, and has been promoted in the case of PA/Fe, PA/Zn, and PA/Cu; however, the propagation is slow, and overall cyclization reaction is retarded due to complexation with these metal salts; thus, $\Delta H$ has reduced from 453 Jg$^{-1}$ in the PA to 107 Jg$^{-1}$ in the PA/Fe complex. The reason may be that the COOH group used in the complex formation may not be available for the initiation of cyclization reactions, and also, it

**Figure 6** FTIR spectra of PA in the range of 600–3600 cm$^{-1}$ recorded between 180 and 340°C.

is quite likely that the mechanism of cyclization may be ionic only.

### DSC-FTIR Studies

#### Effect of Carboxylic Acid Comonomers on the Nitrile Oligomerization

DSC-FTIR was used to understand the structural changes taking place during thermal treatment of acrylonitrile–carboxylic acid copolymers. The spectra of these copolymers were recorded at different temperatures while heating in a DSC cell at 10°C/min in a KBr disc are given in Figures 6–8.

These spectra are overlaid one over the other to show the changes occurring with an increase in temperature in the DSC cell. At 50°C the major absorption bands characteristic of the acrylonitrile unit in the PAN homopolymer are: 2940 cm$^{-1}$ region due to C—H stretching, 2243 cm$^{-1}$ region due to C≡N stretching, 1455 cm$^{-1}$ due to CH$_2$ bending, and 1250 cm$^{-1}$ due to the twisting deformation of C–H. In acrylonitrile–carboxylic acid copolymers the characteristic band due to C=O stretching appears at 1726 cm$^{-1}$ for PI and PM and at 1722 cm$^{-1}$ for PA.

Upon heating the PAN homopolymer, there is a decrease in the nitrile absorption band at 2243 cm$^{-1}$ and in the methylene absorption band at 2940 cm$^{-1}$, 2860 cm$^{-1}$, and 1460 cm$^{-1}$ due to asymmetric vibration of CH$_2$ groups. The band at 2940 cm$^{-1}$ merges with 2860 cm$^1$ at 268°C. In PAN, on heating some new bands appear, 3260 cm$^{-1}$ at 288°C and 1600 cm$^{-1}$ at 268°C, 1400 cm$^{-1}$ and 1060 cm$^{-1}$ at 287°C, 1275 cm$^{-1}$ at 277°C. From the above spectral changes, it may be seen that the nitrile oligomerization in the homopolymer takes place after 275°C.

In the acrylonitrile–acrylic acid copolymer, PA, the temperature at which these absorbance bands changed in intensity was different. The band at 2243 cm$^{-1}$ due to C≡N starts diminishing at 230°C, and the band at 2926 cm$^{-1}$ due to CH$_2$ stretching starts diminishing at 215°C (Fig. 9a). A new band appears at 1597 cm$^{-1}$ around 220°C, whose intensity increases upon further heating and reaches its maximum at about 265°C, after which it falls around 300°C. A band at 3250 cm$^{-1}$ and at 2320 cm$^{-1}$ appeared around 271°C as a shoulder. However, at 340°C the intensity of both these bands increased.

In the acrylonitrile–methacrylic acid copolymer, PM, upon heating the absorption band at 2243 cm$^{-1}$, starts diminishing at 200°C, and the maximum change in absorbance of the band takes place around 295°C. However, the band at 2926 cm$^{-1}$ starts diminishing at 235°C, which levels off around 300°C. A new band around 1600 cm$^{-1}$ has

**Figure 7**   FTIR spectra of PM in the range of 600–3600 cm$^{-1}$ recorded between 180 and 340°C.

been observed. At 215°C, this band starts appearing, and its intensity increases with increasing the temperature. It reaches its maximum at around 270°C (Fig. 9b).The band at 1453 cm$^{-1}$ also disappeared at 340°C. At 244°C the band due

to C=O at 1726 cm$^{-1}$ has disappeared. Appearance of some new bands has also been noted. A new band at 3250 cm$^{-1}$ region appears at 244°C, and as the temperature increases, the intensity of this band also increases. A new weak band due to



**Figure 8**   FTIR spectra of PI in the range of 600–3600 cm$^{-1}$ recorded between 180 and 340°C.

**Figure 9** (a) Change in the intensity of absorbance bands 2926, 2243, and 1597 cm$^{-1}$ as a function of temperature for PA copolymer. (b) Change in the intensity of absorbance bands 2926, 2243, and 1600 cm$^{-1}$ as a function of temperature for PM copolymer. (c) Change in the intensity of absorbance bands 2926, 2241, and 1586 cm$^{-1}$ as a function of temperature for the PI copolymer.

C≡N at 2180 cm$^{-1}$ has also been observed at 340°C.

In the acrylonitrile–itaconic acid copolymer, PI, the nitrile band at 2241 cm$^{-1}$ starts diminishing at 180°C upto 290°C. The band at 2926 cm$^{-1}$ also starts diminishing around 180°C. A band at 1586 cm$^{-1}$ has appeared around 180°C, which

reaches its maximum intensity at 260°C (Fig. 9c). A new band near nitrile region appears at 2180 cm$^{-1}$. The band at 1726 cm$^{-1}$ is not very intense, and at 244°C it almost disappeared. The absorption band at 3250 cm$^{-1}$ absent in the other two copolymers at 180°C, is present in PI. However, its intensity increases upon heating, and at 340°C, two bands at 3250 and 3320 cm$^{-1}$ appear due to √OH and √NH groups, as noted in the PM spectrum.

From this data, it may be concluded that carboxylic acids participate in the cyclization reaction of polyacrylonitrile and lower the onset of exothermic reaction. However, among these three acids itaconic acid initiates this reaction at a much lower temperature. A similar observation was made from dynamic DSC and isothermal studies as well.

To compare the role of these carboxylic acid comonomers in initiating the cyclization reaction and to find the sequence of occurence these reactions, the change in the intensity of bands at 2926 cm$^{-1}$ due to CH$_2$ group stretching and at the 2243 cm$^{-1}$ region due to the C=N group, which participate in the dehydrogenation and cyclization reactions, respectively, were followed as a function of the temperature. From the absorbance ratios of C≡N and CH$_2$ (Table VII), it may be seen that the rate of THE nitrile group participation in the cyclization is maximum in PM, while dehydrogenation reaction appears to be maximum for PA in the temperature range of 230 to 290°C. This again confirms that itaconic acid no doubt initiates the exothermic reaction, and the dehydrogenation as well as cyclization reaction begin around 180°C, but the overall rate of cyclization and dehydrogenation is lowest. Hence, PI copolymers would require a longer time for producing the ladder polymer, which is an intermediate for the production of carbon fibers.

## Deconvulation of IR Bands in the 1500–1800 cm$^{-1}$ Region

To trace the sequence of chemical reactions and elucidate the thermal stabilization mechanism, the major changes occurring in 1500–1800 cm$^{-1}$ region were resolved using computer software, and the peak areas were measured after deconvolution from DSC-FTIR spectra taken at 10°C/min, as reported by Shimada et al.[34]

Three to five distinct IR bands are observable in the carbonyl and √$_{C=C}$ region after resolution (Fig. 10). To compare the relative rates of thermal

**Table VII** **IR Absorbance Ratios of Nitrile and Methylene Groups With Respect to Temperature**

| Sample Code | Temperature Range (°C) | Absorbance Ratio of $\sqrt{}$C≡N | Temperature Range (°C) | Absorbance Ratio of $\sqrt{}$CH$_2$ |
|---|---|---|---|---|
| PA | 230–290 | (290/230°C) 0.15 | 215–295 | (295°/215°C) 0.21 |
| PM | 200–295 | 295/200°C 0.05 | 235–300 | (300 –225°C) 0.25 |
| PI | 180–280 | (280/180) 0.24 | 180–280 | (280/180°C) 0.36 |
| PA/Zn | 195–272 | (272/195°C) 0.39 | 220–300 | (308/220°C) 0.51 |
| PA/Cu | 186–285 | (285/186°C) 0.28 | 240–290 | (290/248) 0.49 |
| PA/Al | 200–285 | (285/200°C) 0.29 | 240–290 | 290/240°C 0.58 |

degradation of three copolymers, PA, PI, and PM, peak areas at 180 and 271°C were calculated (Table VIII). The band attributable to carboxylic group, $\sqrt{}_{C=O}$ between 1724–1740 cm$^{-1}$ almost disappeared at 271°C, while 11.3% carboxylic group was still left. The extent of carboxylic acid participation in the initiation of cyclization reaction could be expressed as under: IA > MAA > AA.

On close examination, a weak band at 1785 cm$^{-1}$ is discernible in PI's spectra at 180°C, which can be attributed to the formation of cyclic anhydride from itaconic acid.

The prominent absorbance band observed in the 1696–1720 cm$^{-1}$ region in PI and PM at 180°C due to the carbonyl of the COOH group



**Figure 10** Deconvolution of the FTIR band between 1500–1800 cm$^{-1}$ of the PI copolymer recorded at 180°C in a DSC cell.

overlapped with free ketones in the form of hydronaphthyridine is absent in PA, but on subsequent heating a strong band appears around 271°C (56.5% area in PA). On the contrary, the band in the same region disappears at 270°C in PM.

The experimental samples were sandwiched in the KBr disc while subjected to DSC-FTIR studies in the air stream. The oxygen pickup in the form of the free ketone as the hydronaphthyridine ring is maximum in PA at 271°C, but its disappearance in PM and the drop in its optical density in PI clearly illustrates the following: (a) acrylic acid component in PA follows a different path of thermal stabilization during heating; (b) itaconic acid and methacrylic acid copolymers pick up oxygen even at 180°C and accelerate the dehydrogenation reaction. That is why the absorbance band generated due to hydronaphthyridene rings diminishes in PI or disappears in PM at 270°C.

An increase in the peak area for the 1644–1690 cm$^{-1}$ absorbance band in PI and PM (Table VIII) due to the generation of acridone type structures further supports the role of itaconic acid in accelerating the dehydrogenation reaction to the maximum.

From the peak area of absorbance bands in the 1570–1595 cm$^{-1}$ region, due to the development of >C=C<, C=C—C=N and (C=C) + (NH) mixed mode at 271°C, one may conclude that the dehydrogenation and cyclization reactions occur almost simultaneously in PI at a much lower temperature compared to PM and PA.

**Table VIII   Deconvolution Data of IR Bands in 1500–1800 cm$^{-1}$ Region of PA, PM, and PI Copolymers**

| | PA DSC Cell Temperature | | PM DSC Cell Temperature | | PI DSC Cell Temperature | |
| --- | --- | --- | --- | --- | --- | --- |
| Wave Number (cm$^{-1}$) | 180°C | 271°C | 180°C | 271°C | 180°C | 271°C |
| | | | Area   % | | | |
| 1785–1746 acid anhydride | | Absent | | | 2.3 | Disappeared |
| 1724–1745 C=O of COOH | 44 | 11.3 | 28.6 | 23 | 15.1 | Disappeared |
| 1696–1720 C=O of hydronaphthyridine | Absent | 56.5 | 16.5 | Disappeared | 41.8 | 14.9 |
| 1644–1690 C=O as in acridone | 24.2 | Disappeared | 18.7 | 27.6 | 81 | 2.1 |
| 1610–1628 (C=C) + (C=O) mixed modes, C=C—C=N | 31.8 | 26.6 | 30.8 | 48.3 | 26.8 | Disappeared |
| 1570–1590 (C=C) + (C=)) (NH) + —C=C—C=N— | Absent | 5.6 | 5.4 | 21.8 | 5.9 | 64.0 |

## FTIR Spectra of the Metal Salt Complexes of the PA Copolymer

Metallation of the PA polymer solution with zinc, aluminum, copper, and ferrous sulphates can be confirmed from their IR spectra (Figs. 11–13). The band at 1585 cm$^{-1}$ due to the carboxylate group (COO$^-$) disappears because of metal carboxylate formation. The participation of the nitrile group in the complex formation through its lone pair is also confirmed with the appearance of a new band around 2365 cm$^{-1}$ (C≡N → M).

DSC-FTIR of acrylonitrile–acrylic acid (PA) after metallation with various salts shows interesting differences. Due to metallation (COO)$_2$M (M = Zn, Cu, Fe), the initiation of nitrile oligomerization shifts to a lower temperature, but the rate of disappearance of the carboxylic group has reduced significantly.



**Figure 11** FTIR spectra (600–3800 cm$^{-1}$) of the PA/Al complex at different temperatures in the DSC cell.



**Figure 12** Change in intensity of absorbance bands at 2940, 2242, 1736, and 1601 cm$^{-1}$ of the PA/Cu complex upon heating the DSC cell interfaced with FTIR.

**Figure 13**  Change in intensity of absorbance bands at 2940, 2242, 1736, and 1601 $cm^{-1}$ of the PA/Zn complex upon heating the DSC cell interfaced with FTIR.

In the PA/Cu complex (Fig. 12), the initiation of the nitrile group cyclization shifts to a much lower temperature (186°C) than neat polymer (230°C). However, the disappearance of the nitrile group follows a two-step reaction unlike PA, the rate of the second step being higher. Among the three metal complexes, the degree of nitrile oligomerization seems to be the highest in PA/Cu (C≡N 285/186°C) as shown in Table VIII.

*PA/Cu > PA/Al > PA/Zn*

While the extent of dehydrogenation reaction (290/240°C) is also found to be maximum in the PA/Cu complex. The lower the absorbance ratio of (290/240°C), the higher will be the degree of dehydrogenation.

*PA/Cu > PA/Zn > PA/Al*

Although the dehydrogenation reaction starts early in the PA/Zn complex (Fig. 13), the overall extent of dehydrogenation in all the metal complexes is much lower compared to the neat PA polymer. In addition, the intensity of 1601 $cm^{-1}$ absorbance band increases significantly between 200 to 265°C in the PA/Cu complex. In the PA/Al complex, the absorbance ratio of 1601 $cm^{-1}$ due to C=C—C=C and —C=C—C=N— increases steadily but at a higher temperature.

From these structural changes, it may be concluded that aluminum sulphate forms a stable complex with PA through nitrile as well as the COOH group, which is responsible for the delay in the dehydrogenation reaction and the overall ladder polymer formation.

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