

# Thermal Behavior of Acrylonitrile Carboxylic Acid Copolymers

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**ABSTRACT:** Polyacrylonitrile (PAN) and copolymer of acrylonitrile–vinyl acids prepared by solution polymerization technique have been characterized by Differential Scanning Calorimetry (DSC) (under dynamic as well as isothermal conditions), thermogravimetric analysis (TGA), and online DSC-FTIR spectroscopy. The DSC of copolymers was carried out at 5°C/min in nitrogen and air. In nitrogen atmosphere the DSC exotherm show a very sharp peak, whereas, in air atmosphere DSC exotherm is broad, and starts at a much lower temperature compared to what is observed in nitrogen atmosphere. The initiation temperature of PAN homopolymer is higher than that for the copolymers. For instance, the initiation temperature of PAN in air is 244°C, whereas, the onset of exothermic reaction is in the

range of 172 to 218°C for acrylonitrile–vinyl acid copolymers. As the vinyl acid content increases the  $\Delta H$  value reduces. The  $\Delta H$  value of PAN in air was 7025 J/g, whereas, for P(AN-AA) with 5.51 mol % of acid it was 3798 J/g. As the content of acrylic acid comonomer is increased to 17.51 mol % the value of  $\Delta H$  decreases further to 1636 J/g. The same trend was observed with MAA and IA as well. DSC-FTIR studies depict various chemical changes taking place during heat treatment of these copolymers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 685–698, 2003

**Key words:** thermal properties; activation energy; differential scanning calorimetry (DSC)

## INTRODUCTION

Thermal behavior of acrylonitrile homo- and copolymers has always been a subject of great interest, because polyacrylonitrile and its copolymers are used as precursors for the production of high-strength carbon fibers.<sup>1</sup> The demand for high-quality carbon fibers in composite materials has intensified the interest in the thermal characterization of acrylic polymers particularly under programmed conditions. The oligomerization of nitrile groups, an important step in the manufacture of carbon fibers from polyacrylonitrile, is influenced by the method of polymerization,<sup>2–4</sup> nature of comonomers,<sup>5–16</sup> additives,<sup>17</sup> as well as preheat treatment.<sup>18–21</sup>

Various authors<sup>9,11,13,22,23</sup> have reported the influence of itaconic, acrylic, and methacrylic acids, methyl methacrylate, acrylamide, vinyl acetate, vinyl chloride, etc., on the nitrile oligomerization.

Grassie and McGuchan<sup>22</sup> reported that 20% acrylate or methylacrylate content in polyacrylonitrile copolymer exhibits a diluent effect without inhibiting the reaction, while comonomers with styrene type structures behave differently; showing a marked inhibiting

effect on the nitrile oligomerization. Ferguson et al.<sup>14</sup> showed the role of acrylic acid comonomer as accelerator in cyclization, while N-vinyl pyrrolidone acts as an inhibitor.

Grassie and McGuchan<sup>11</sup> also showed the strong initiating effect of acrylic, methacrylic, and itaconic acid and acrylamide on the exothermic nitrile group oligomerization. As the acid content increases, the exotherm becomes less intense and broader with lower initiation and peak temperature. The methacrylic and itaconic acid copolymers show more complex and broad exotherms than the AN-AA copolymer. In N<sub>2</sub> atmosphere, the initiation temperature for these copolymers was found to be:

$$Ti = \begin{matrix} \text{AN-AA} > \text{AN-MAA} > \text{AN-IA} \\ 220^\circ\text{C} & 200^\circ\text{C} & 190^\circ\text{C} \end{matrix}$$

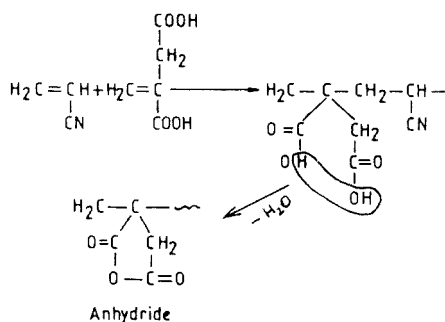
The effect of itaconic acid as a comonomer and additive on the exothermic reaction of acrylonitrile copolymers has been studied by Tsai et al.<sup>5</sup> As the itaconic acid content increases from 0.5 to 3.5 mol % in the copolymer, the exothermic peak becomes complex with several distinct maxima. Further, the initiation of nitrile oligomerization was also confirmed with itaconic acid as an additive. The rate of cyclization, however, would depend on the sequence distribution of the comonomer in the acrylonitrile copolymers.

Klimenko et al.<sup>24</sup> have also studied the effect of itaconic acid (IA) in acrylonitrile–itaconic acid co-

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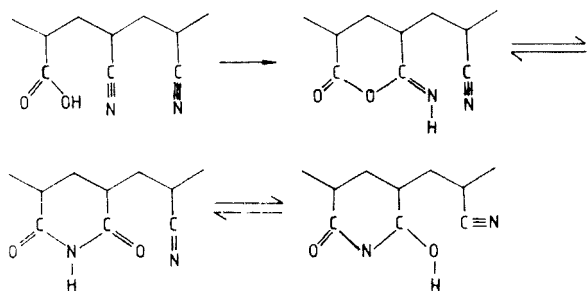
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polymer and AN–methacrylate–itaconic acid terpolymer on their thermal-oxidative degradation. Depending on the method of polymerization, itaconic acid in the AN copolymer/terpolymer can exist in various forms, i.e., dibasic acid, ionized, or monobasic acid, anhydride bridges, etc., which would influence the rate of thermo-oxidative cyclization and the composition of polyconjugated structures:



IR absorptions at 1850 and 1780  $\text{cm}^{-1}$  suggest the formation of intramolecular anhydride formation.<sup>11</sup> In another study, it is reported that the onset of exotherm shifts to a lower temperature as the content of itaconic acid is increased from 1.2 to 6.4 wt % in the (AN–MA–IA) terpolymer.<sup>25</sup>

Pyrolysis of acrylonitrile–methacrylic acid (MAA) copolymers having 2 to 10 mol % of MAA and their sodium salts have been studied by Guyot et al.<sup>13</sup> under inert atmosphere at various heating rates using thermogravimetric analysis coupled with gas liquid chromatography, thermal volatilization analysis, and DSC. According to them, nitrile oligomerization, which is not directly related to any loss in weight, can be initiated through a molecular mechanism by the carboxylic group of the acid:



After the first step, an imide structure is formed by isomerization. Molecular propagation needs this isomerization, which explains why it is slower than the radical propagation in pure polyacrylonitrile.<sup>11</sup> The slower propagation explains the occurrence of the exotherm over a wider temperature range.

The neutralized acid copolymers show behavior intermediate between those of the AN–MAA copolymers and pure PAN.<sup>13</sup> Coleman and Sivy<sup>9</sup> have used

Fourier transform IR spectroscopy to understand the mechanism of degradation of P(AN–MAA 96:4 wt %) at 130°C under a reduced pressure of  $5 \times 10^{-2}$  Torr. It was demonstrated that inclusion of methacrylic acid considerably enhanced the rate of degradation. It was found that on an average 3 to 4 nitrile groups to one methacrylic acid group get involved in the initial stages of degradation. Further, the distribution of atactic placements in the copolymer chain is a factor limiting the degree of cyclization of the available nitrile groups.

In addition to the effect of comonomers, the method of polymerization also influences the thermal behavior of acrylonitrile polymers.<sup>6,7,26</sup> For example, PAN produced by solution polymerization is shown to have lower  $T_{pk}$  of the exotherm compared to the polymer prepared by suspension or bulk polymerization. This is because of the difference in tacticity, molecular defects, molecular weight, and dispersity of the polymers produced by these methods. Increase in isotacticity tends to shorten the induction period in the thermal treatment of PAN.<sup>23,27</sup>

A number of researchers have studied the kinetics of heat flow behavior of acrylonitrile copolymers and terpolymers and proposed kinetic models. On the basis of heat flow profile for PAN and Beslon fiber (AN : MA 98 : 2 wt %) in nitrogen at 265°C Collins et al.<sup>28</sup> have developed a kinetic model that included two rate processes: a consecutive first-order process with an exothermic second step and an autoaccelerated process.

Fitzer and Muller,<sup>29</sup> Dale et al.,<sup>30</sup> and Dunham and Edie<sup>31</sup> have proposed mathematical modes for thermo-oxidative stabilization of acrylic fibers. The Kissinger method<sup>32</sup> has been used by a number of researchers to estimate the kinetics of the principal stabilization reaction from differential scanning calorimetry.

Fitzer and Muller<sup>29</sup> showed that the first of the two DSC peaks observed in Courtauld's SAF precursor (AN/MA/IA : 93/6/1 wt %) in an air atmosphere is due both to the cyclization and dehydrogenation reactions. Thus, the first peak can be used to obtain estimates of the kinetic constants for both of these reactions. The second peak was assigned to oxidation reaction. However, in a nitrogen atmosphere, a single DSC peak for Courtauld's SAF resulting from the cyclization reaction was observed. From the enthalpy data, heats of cyclization and dehydrogenation reactions were calculated.

$$\Delta H_{\text{cyclization}} = \Delta H_{\text{N}_2}$$

$$\Delta H_{\text{dehydrogenation}} = \Delta H_{\text{air (primary peak)}} - \Delta H_{\text{N}_2}$$

Kakida<sup>33</sup> has also studied the role of comonomers in the stabilization reaction of PAN through DSC and

FTIR. Heat flow profiles for some AN copolymers, P(AN-MAA), P(AN/MAA/acrylamide), and P(AN-Am) at 240°C in air. From the DSC curves, it may be stated that the comonomers accelerate the second reaction which appeared on a DSC chart at longer time region as the broad exothermic peak. Quantitative analysis of the IR spectra of partially oxidized samples has been used to determine the kinetics of stabilization. The decrease in the strong nitrile and methylene absorption bands was correlated with the extent of cyclization and dehydrogenation, respectively. Appearance of a shoulder at 2180 cm<sup>-1</sup> due to nitrile group conjugated with C=C groups and weak bands at 1665 and 1680 cm<sup>-1</sup> pertaining to —C=C—C=N and —C=N—C=N— confirms the cyclization reaction through nitrile groups.<sup>34</sup>

Mathur et al.<sup>35</sup> have shown an additional exothermic peak in air at about 350°C along with the prominent exothermic peak at 270°C for Courtelle precursor, which has been attributed to intermolecular crosslinking and aromatization of the structure. Effect of heating rate on the melting behavior of acrylonitrile copolymers has been recently reported.<sup>36</sup> Thermal and rheologic behavior of acrylonitrile-carboxylic acid copolymers and its metal salt complexes has been investigated.<sup>37</sup>

The present work deals with the effect of carboxylic acids, viz., acrylic, methacrylic, and itaconic acid on the thermal behavior of acrylonitrile copolymers, specifically on the oligomerization of nitrile groups and thermal stability of the copolymers in nitrogen and air atmosphere.

## EXPERIMENTAL

### Materials

Polyacrylonitrile (PAN) and copolymers of acrylonitrile with carboxylic acids, i.e., acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) were prepared by solution polymerization technique in DMF using AIBN as initiator. The details of the copolymerization have been reported in the previous article.<sup>38</sup> The composition and the intrinsic viscosity along with the coding of the copolymers used for thermal studies are given in Table I.

### Thermal analysis: differential scanning calorimetry (DSC)

#### Dynamic mode

A Perkin-Elmer delta series thermal analyzer was used for differential scanning calorimetry (DSC) in dynamic mode. The samples were scanned on DSC-7 module of this thermal analyzer at a flow rate of 2.5 L/min, and a heating rate of 5°C/min under nitrogen and 5 to 20°C in air atmosphere from ambient temper-

**TABLE I**  
Composition of PAN and Acrylonitrile-Carboxylic Acid Copolymers

Copolymer	Code	Comonomer Content mol %	Intrinsic Viscosity dL/g
PAN	P <sub>0</sub>	—	0.72
P(AN-AA)	PA	3.1	1.3
	PA <sub>1</sub>	5.51	1.10
	PA <sub>2</sub>	7.12	1.20
	PA <sub>3</sub>	8.52	1.24
	PA <sub>4</sub>	17.51	1.25
P(AN-MAA)	PM	2.6	1.35
	PM <sub>1</sub>	3.08	1.20
	PM <sub>2</sub>	4.57	1.17
	PM <sub>3</sub>	8.22	1.19
	PM <sub>4</sub>	10.15	1.21
	PM <sub>5</sub>	14.61	1.19
P(AN-IA)	PI	2.2	1.24
	PI <sub>1</sub>	3.58	1.05
	PI <sub>2</sub>	4.35	1.07
	PI <sub>3</sub>	5.87	1.00
	PI <sub>4</sub>	6.07	1.15
	PI <sub>5</sub>	8.81	0.95

ature to 400°C. The oxygen free nitrogen was obtained by passing the nitrogen gas over heated copper turnings. A sample weight of 4–5 mg in the form of fine powder was used to ensure good thermal contact. The sample was sealed, with a perforated lid to ensure good exposure to environment (air or nitrogen).

#### Isothermal mode

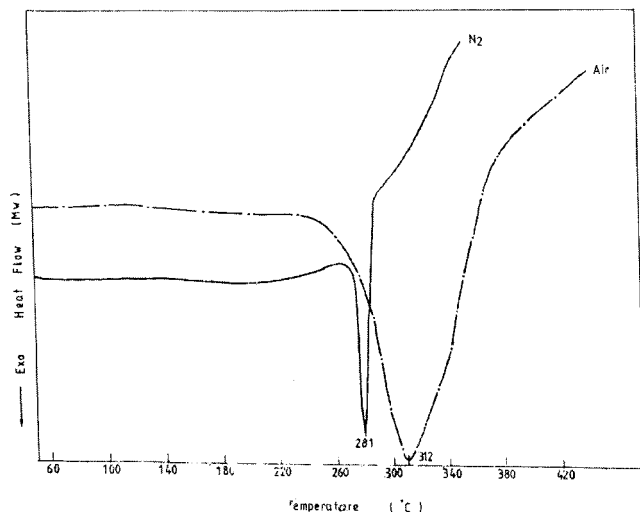
Mettler FP-84 HT DSC was used for isothermal studies at different temperatures ranging from 210 to 240°C along with central processor Settler PF-90. The studies were conducted in air for 60 min at a flow rate of 2.5 L/min.

### DSC-FTIR

To investigate the structural changes occurring during heating, the polymer samples PA, PM, and PI were subjected to heat treatment at a constant temperature, 230°C in air atmosphere in a DSC cell. IR spectra were taken at different time intervals, i.e., 15, 30, 45, 60, and 120 min. These investigations were carried on a DSC-FTIR system. It comprises a Jasco Micro FTIR-200 with an interferometer, microscope, and work station interfaced with a Mettler FP-84 HT thermal analyzer microscopy cell. This has a program that is used to measure an infrared absorption spectrum and caloric temperature data at the same time.

### Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Perkin-Elmer Delta series TGA-7 instrument in air and



**Figure 1** DSC curves of the PAN homopolymer (Po) in air and nitrogen atmosphere at 5°C/min.

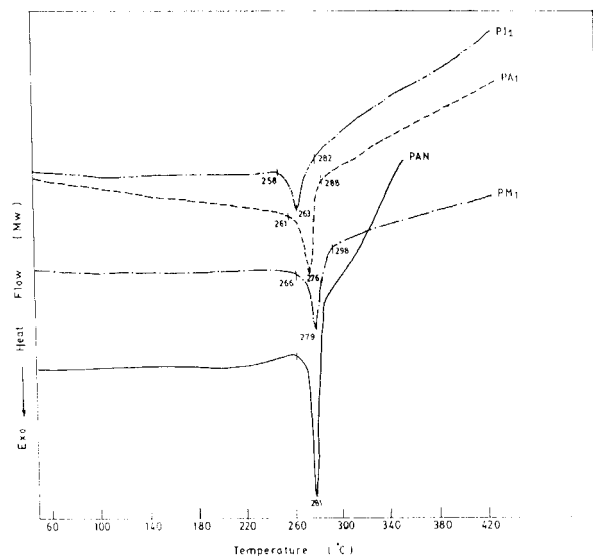
nitrogen from 50 to 600°C at a heating rate of 5°C/min. To establish the relationship between the weight loss and the temperature, TG and DTG curves were obtained. A sample size of 3–4 mg in the form of fine powder was used.

## RESULTS AND DISCUSSION

### Differential scanning calorimetry (dynamic mode)

#### DSC in nitrogen atmosphere

The DSC traces (Figs. 1 and 2) show that the initiation temperature ( $T_i$ ) of the exothermic transition due to cyclic oligomerization in polyacrylonitrile homopolymer in nitrogen atmosphere starts at 265°C with a



**Figure 2** DSC curves of the PAN homopolymer and acrylonitrile-carboxylic acids copolymer in nitrogen atmosphere at 5°C/min.

**TABLE II**  
DSC Data of PAN (Po) and Acrylonitrile-Carboxylic Acid Copolymers in N<sub>2</sub> Atmosphere at 5°C/min

Sample	$T_i$ (°C)	$T_f$ (°C)	$T_f - T_i$ (°C)	$T_{pk}$ (°C)	$\Delta H$ Jg <sup>-1</sup>	$\Delta H/\Delta t$ Jg <sup>-1</sup> min <sup>-1</sup>
PA <sub>0</sub>	265	290	25	281	511	102.0
PA <sub>3</sub>	261	295	34	274	152	22.3
PM <sub>3</sub>	263	303	42	281	77	9.2
PI <sub>5</sub>	222	252	30	239	52	8.7

peak maximum ( $T_{pk}$ ) at 281°C, while in acrylonitrile-carboxylic acid copolymers (Table II), the onset of exothermic reaction starts at a lower temperature, for example, in PA<sub>3</sub> the  $T_i$  is 261°C while for PI<sub>5</sub> it is 222°C. Among the three copolymers, on the basis of  $T_i$  values, it seems itaconic acid accelerates the cyclization reaction the most. However, the lowest  $\Delta H$  value, 52 Jg<sup>-1</sup>, indicates that the degree of cyclization and the heat produced per unit time is the least in the case of PI<sub>5</sub>. Efficiency of itaconic acid in initiating the nitrile group oligomerization has also been reported by Grassie et al.<sup>11</sup> The broad exotherms and lower  $T_i$  values in acrylonitrile-carboxylic acid copolymers suggest a basically different initiation mechanism and relatively much slower propagation.

Guyot et al.<sup>13</sup> have also studied the pyrolysis of homo polyacrylonitrile and AN-MAA copolymers in nitrogen atmosphere at 10°C/min. They reported  $\Delta H$  values for PAN as 114 calg<sup>-1</sup> (477.3 Jg<sup>-1</sup>) and AN-MAA copolymer having 10 mol % MAA content as 82.0 calg<sup>-1</sup> (217.7 Jg<sup>-1</sup>).

#### DSC studies in air atmosphere

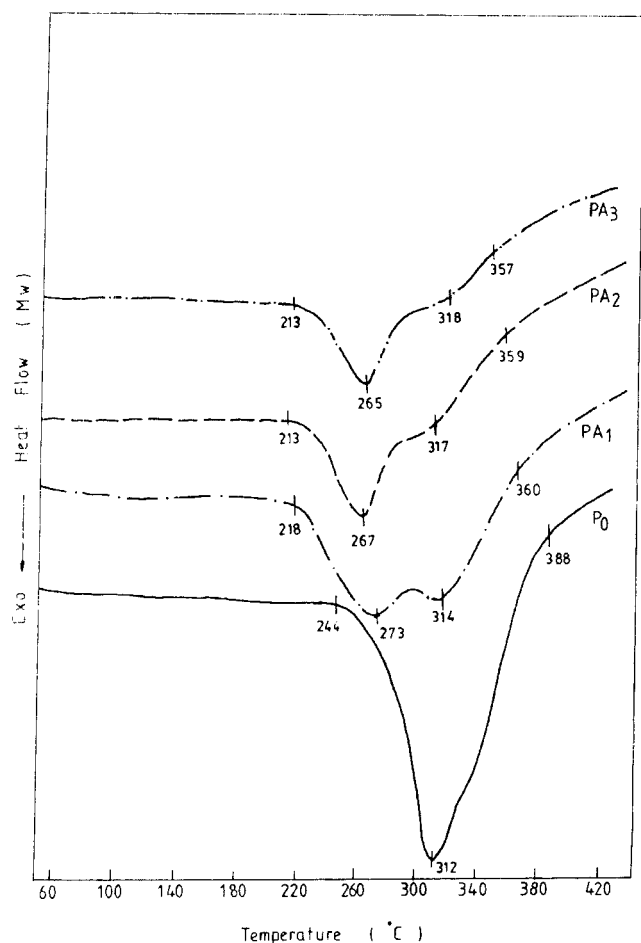
The DSC exotherm of acrylonitrile-carboxylic acid copolymers exhibit a doublet with superposition of two

**TABLE III**  
DSC Data of PAN and Copolymers of AN-Carboxylic Acids Recorded Under Air at 5°C/min

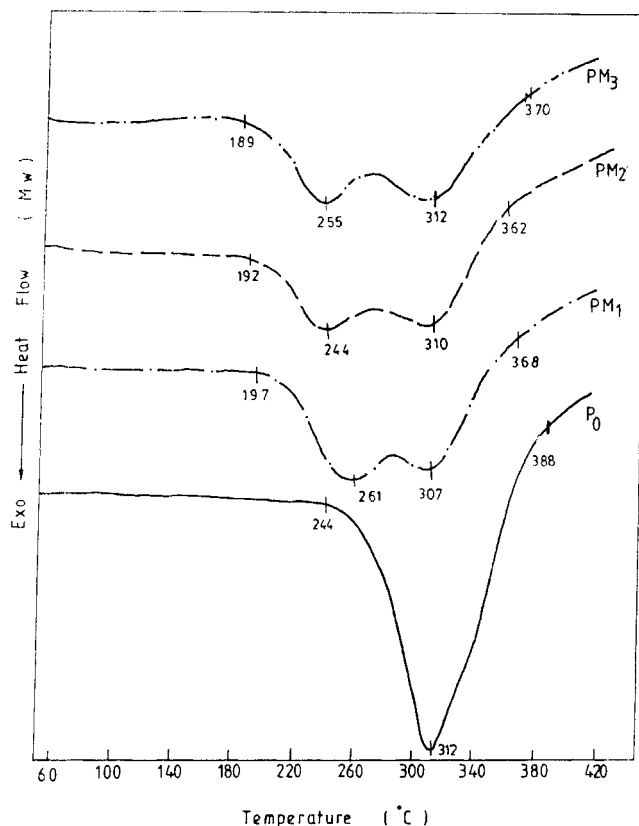
Sample Code	$T_i$ (°C)	$T_f$ (°C)	$T_i - T_f$ (°C)	$T_{pk1}$ (°C)	$T_{pk2}$ (°C)	$\Delta H$ Jg <sup>-1</sup>
P <sub>o</sub>	244	388	144	312	—	7025
PA <sub>1</sub>	218	360	142	273	314	3798
PA <sub>2</sub>	213	359	146	267	317	1993
PA <sub>3</sub>	213	357	144	265	318	1683
PA <sub>4</sub>	215	358	143	259	321	1636
PM <sub>1</sub>	197	368	171	261	—	3448
PM <sub>2</sub>	192	362	170	244	307	2953
PM <sub>3</sub>	189	370	177	255	310	3033
PM <sub>4</sub>	185	368	175	253	312	2832
PM <sub>5</sub>	182	356	174	250	314	2534
PI <sub>1</sub>	181	371	190	251	314	2772
PI <sub>2</sub>	177	366	189	245	327	2301
PI <sub>3</sub>	181	363	182	249	316	2084
PI <sub>4</sub>	174	360	186	249	310	1831
PI <sub>5</sub>	172	361	189	250	—	1510

or three peaks (Table III). In PAN homopolymer the doublet is visible but is not distinct (Figs. 3 to 5). In this case, the onset of exotherm has shifted to lower temperature (244°C) compared to the exotherm recorded in nitrogen atmosphere ( $T_i = 265^\circ\text{C}$ ), but overall enthalpy of exothermic reaction is quite high.

Incorporation of acidic comonomers further reduces the onset temperature of exothermic reaction in air. At approximately the same mol % of carboxylic acid in acrylonitrile copolymers, it is observed that for  $\text{PA}_3$ , P(AN-AA) sample the  $T_i$  is  $213^\circ\text{C}$ , for  $\text{PM}_3$   $189^\circ\text{C}$ , and for  $\text{PI}_5$   $172^\circ\text{C}$ . With an increase in the acid content, the exotherm becomes less intense and broader;  $\Delta T = (T_f - T_i)$  with lower initiation temperature for all the polymers; with maximum differences in PI series. In P(AN-AA) and P(AN-MAA) copolymers, two distinct peak maxima can be seen but in P(AN-IA) copolymers, the second peak seen on the higher temperature side of the primary peak as a shoulder. The differential nature of the exotherm observed in acrylonitrile-itaconic acid copolymers may be attributed to the complex multiple reactions occurring during heat treatment.



**Figure 3** DSC curves of the PAN homopolymer ( $\text{P}_0$ ) and acrylic-itaconic acid copolymer in air atmosphere at  $5^\circ\text{C}/\text{min}$ .  $\text{PA}_1$  (5.51 mol %),  $\text{PA}_2$  (7.12 mol %),  $\text{PA}_3$  (8.52 mol %).



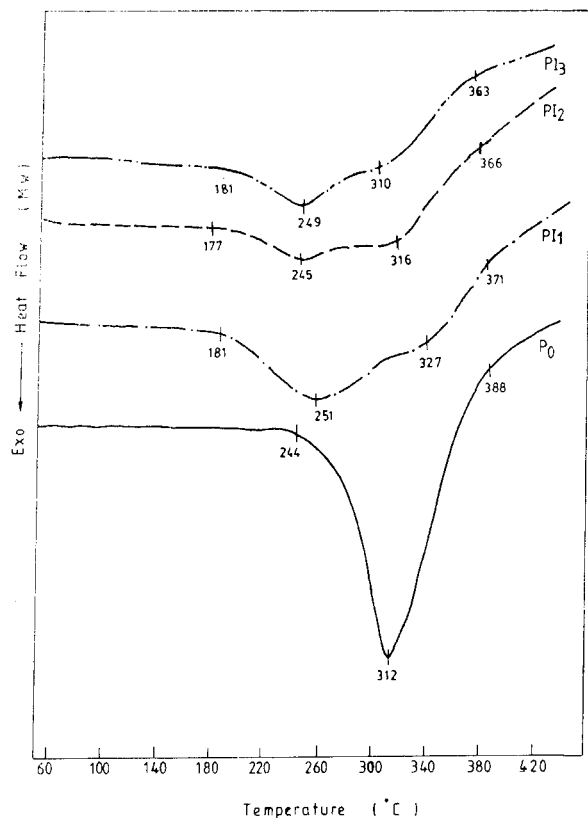
**Figure 4** DSC curves of the PAN homopolymer ( $\text{P}_0$ ) and acrylonitrile-methacrylic acid copolymer in air atmosphere at  $5^\circ\text{C}/\text{min}$ .  $\text{PM}_1$  (3.08 mol %),  $\text{PM}_2$  (4.57 mol %),  $\text{PM}_3$  (8.22 mol %).

In P(AN-AA) copolymers, as the acid content increases from 5.5 to 17.51 mol %  $T_i$  and  $T_{pk1}$  shift to lower temperature, for instance  $T_{pk1}$  shifts from  $273$  to  $259^\circ\text{C}$ .  $\Delta H$  also reduces to less than half from  $3798 \text{ Jg}^{-1}$  ( $\text{PA}_1$ ) to  $1636 \text{ Jg}^{-1}$  ( $\text{PA}_4$ ).

In the case of methacrylic acid copolymers P(AN-MAA), a similar trend was observed. In  $\text{PM}_1$  with 3.08 mol % of methacrylic acid, the exotherm starts ( $T_i$ ) at  $197^\circ\text{C}$  and is completed at  $368^\circ\text{C}$  ( $T_f$ ), while in  $\text{PM}_5$  with 14.61 mol % of methacrylic acid content, this shifts to  $182$  and  $356^\circ\text{C}$ , respectively. The peak temperature ( $T_{pk1}$ ) also reduces from  $261^\circ\text{C}$  ( $\text{PM}_1$ ) to  $250^\circ\text{C}$  ( $\text{PM}_5$ ). In the case of acrylonitrile-itaconic acid copolymers, particularly at high acid content ( $\text{PI}_5$  8.8 mol %), the exotherm becomes very broad and less intense.

From the above discussion, it follows that the copolymers of acrylonitrile-itaconic acid have the ability to initiate the exothermic reaction at a much lower temperature compared to acrylonitrile-methacrylic and acrylonitrile-acrylic acid copolymers.

The presence of two carboxylic groups in itaconic acid obviously increases the probability of these groups to initiate the exothermic reaction leading to nitrile cyclization, depending on which one of these carboxylic groups are in the vicinity of the nitrile



**Figure 5** DSC curves of the PAN homopolymer ( $P_0$ ) and acrylonitrile-itaconic acid copolymer in air atmosphere at  $5^\circ\text{C}/\text{min}$ .  $PI_1$  (3.58 mol %),  $PI_2$  (4.35 mol %),  $PI_3$  (5.87 mol %).

group. Sequence length distribution of carboxylic acids would also influence the cyclization reaction. At high itaconic acid content, however, the rate of cyclization is reduced significantly.

As mentioned earlier, the exotherm of acrylonitrile-carboxylic acid copolymers, in air, is broad, which shows a primary peak and a secondary peak in the form of a shoulder. In PAN homopolymer, the exotherm temperature  $T_{pk1}$  appears at  $312^\circ\text{C}$ , because the initiation of cyclization reaction follows free radical mechanism the exotherm peak appears at a higher temperature. However, in acrylonitrile-carboxylic acid copolymers the initiation of cyclization reaction follows an ionic mechanism as reported by Grassie,<sup>36</sup> Fitzer,<sup>29</sup> and Guyot.<sup>13</sup> This affects the cyclization reaction with initiation starting at a lower temperature. The distribution of carboxylic units in the chain also affects the  $T_i$  of exothermic reaction. It is evident from these data that carboxylic acid comonomers effect the ( $T_{pk1}$ ) and bring it to a lower temperature; however, the position of second peak ( $T_{pk2}$ ) does not change much.

In acrylonitrile-acrylic acid copolymers P(AN-AA), the second peak appears in the temperature range of  $314$  to  $321^\circ\text{C}$ , for P(AN-MAA) copolymers in the range of  $307$ – $314^\circ\text{C}$  and for P(AN-IA) copolymers in

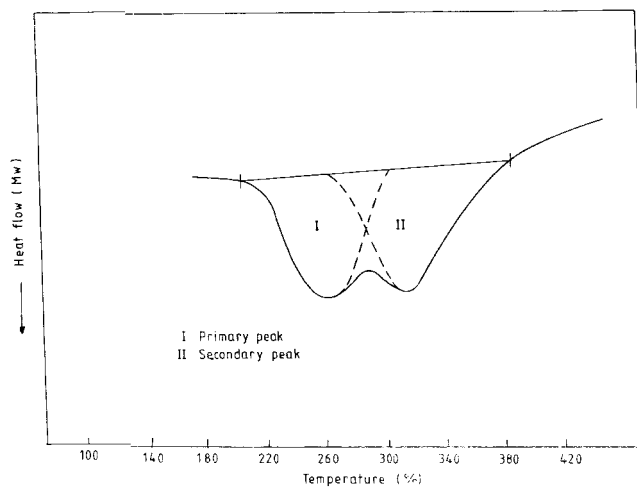
the range of  $310$ – $327^\circ\text{C}$ . Interestingly at very high levels of itaconic acid it is not very easily identifiable. This second peak has been assigned to oxidation reaction and may be associated with the longer sequences of AN units in the polymer chain.

The changes in the shape of these exotherms from that of PAN homopolymer suggest that the function of these carboxylic acid units is more complex than merely initiating the reaction; otherwise, these would have simply shifted the sharp exotherm to a lower temperature. The broad exotherm in case of copolymers and small  $\Delta H$  values, therefore, suggest different reaction mechanism and relatively much slower propagation for producing ladder polymers.

According to Fitzer and Muller,<sup>29</sup> the large primary peak in air atmosphere is a result of both cyclization and dehydrogenation reaction. The total heat of exothermic reaction,  $\Delta H$  in air atmosphere decreases with incorporation of carboxylic acid in polyacrylonitrile. However, the  $\Delta H$  of exotherm in air is higher than that of nitrogen atmosphere due to additional oxidation reactions, irrespective of the comonomer content.

The  $\Delta H$  of PAN homopolymer in air is  $7025 \text{ Jg}^{-1}$ , and that for  $PA_3$  is  $1683 \text{ Jg}^{-1}$ ,  $PM_3$  is  $3033 \text{ Jg}^{-1}$ , and  $PI_5$  is  $1510 \text{ Jg}^{-1}$ .

In PAN-homopolymer, the  $\Delta H/\Delta t$  in air is  $268.1 \text{ Jg}^{-1} \text{ min}^{-1}$ , indicating that the heat liberation per unit time is high. With the incorporation of carboxylic acids the rate of heat liberation is considerably reduced. For instance, in case of acrylonitrile-acrylic acid copolymer ( $PA_3$ ),  $\Delta H/\Delta t$  in air is  $58 \text{ Jg}^{-1} \text{ min}^{-1}$ , while for  $PM_3$  it is  $85.7 \text{ Jg}^{-1}$  and for  $PI_5$ ,  $39.9 \text{ Jg}^{-1} \text{ min}^{-1}$ . This shows that in acrylonitrile-itaconic ( $PI_5$ ) the exothermic reaction takes a much longer time to be completed with lower heat liberation per unit time. This is advantageous in the production of carbon fibers, as a higher rate of heat evolution during thermo-oxidative



**Figure 6** Resolution of DSC curve of the acrylonitrile-methacrylic acid copolymer.

TABLE IV  
Heat Produced in Different Exothermic Reactions

Sample Code	Acid Content mol %	Total $\Delta H$ in Air $\text{J g}^{-1}$	Heat of Reaction $\text{J g}^{-1}$ ( $\text{KJ mol}^{-1}$ )		
			Cyclization $\Delta H_1$	Dehydrogenation $\Delta H_2$	Oxidation $\Delta H_3$
PA <sub>3</sub>	8.52	1683	152 (8.05)	453 (24.0)	1078 (57.1)
PM <sub>3</sub>	8.22	3033	77 (4.1)	1166 (61.8)	1790 (94.9)
PI <sub>5</sub>	8.81	1510	52 (2.8)	622 (33)	836 (44.3)

stabilization would lead to burning out the core, resulting into a poor quality of the carbon fibers.

The heat of reaction was also calculated using DSC data assigning cyclization and dehydrogenation reactions to the first peak and the oxidation reaction to the second peak/shoulder. For the calculations, the exotherm was carefully resolved as per the method used by Dunham and Edie using a computer-based peak fitting program.<sup>31</sup> The typical resolved exotherm is shown in Figure 6, where the resolved constituent peaks are labeled as peak 1 and peak 2. The heat of these two exothermic reactions can be calculated using the following equations:

$$\Delta H_{\text{cyclization}} = \Delta H_{\text{N}_2}$$

$$\Delta H_{\text{dehydrogenation}} = \Delta H_{\text{air}} - \Delta H_{\text{N}_2} \quad (\text{primary peak})$$

where the subscript indicates the atmosphere used during the DSC test. The heats of reactions were computed from the peak areas (Table IV). The heat of oxidation reaction  $\Delta H_3$  is more in all the three copolymers followed by the heat of reaction of dehydrogenation  $\Delta H_2$ .

### Effect of heating rate

When copolymers of acrylonitrile-carboxylic acid are thermally characterized by DSC at different rates of heating in air, a significant change in the thermal behavior is observed. The peak temperature ( $T_{pk1}$ ) is shifted to a higher temperature as the heating rate is increased. Kissinger<sup>23</sup> has proposed a method by which the activation energy can be calculated using the DSC data.

Based on a series of DSC curves obtained at different heating rates (2, 5, 10, and 20°C), the activation energy ( $E$ ) of acrylonitrile-carboxylic acid copolymers has been computed using the Kissinger method. The Arrhenius activation energy,  $E$  was calculated from the temperature at which the peaks reach their maxima ( $T_{pk1}$ ) by

$$-\frac{E}{R} = \frac{d \ln(\phi/T_{pk1}^2)}{d(1/T_{pk1})}$$

where  $R$  is the gas constant, and  $\phi$  is the heating rate.

The right-hand side of this equation is the slope of a plot of heating rate divided by the square of the peak temperature viz. the reciprocal of the peak temperature. The activation energy is obtained from the slope of plot between  $\ln(\phi/T_{pk1}^2)$  vs.  $1/T_{pk1}$  (Fig. 7). This analysis is valid only for first-order reactions, because the slope of  $E/R$  is constant only for first-order reactions. The Arrhenius preexponential factor  $A_0$  has been calculated from the activation energy using following equation:

$$A_0 = \frac{E}{RT_{pk1}^2} e^{-E/RT}$$

Fitzer and Müller<sup>29</sup> have shown that the first of the two DSC peaks observed when acrylic copolymers are heat treated in air atmosphere can be used for estimating the kinetic constants for both the cyclization and dehydrogenation reactions. The activation energy and frequency factor for the primary exotherms thus obtained are shown in Table V.

The value of activation energy is 184.8  $\text{kJ mol}^{-1}$  for acrylonitrile-acrylic acid (PA), compared to that of acrylonitrile-methacrylic acid (PM), 123.3  $\text{kJ mol}^{-1}$ . The activation energy of acrylonitrile-itaconic acid (PI) was the lowest, i.e., 109.1  $\text{kJ mol}^{-1}$ . This indicates that the exothermic reaction has been strongly influenced by the presence of these carboxylic acids, and among them, itaconic acid seems to be the most effective in lowering the initiation temperature of exothermic reaction and reducing the rate of reaction.

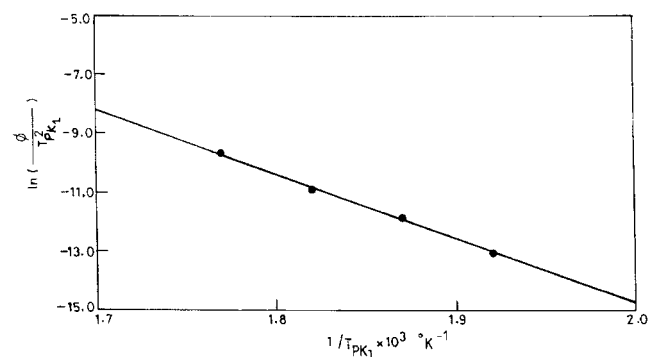


Figure 7 Kissinger analysis of DSC peak temperature results for polyacrylonitrile-acrylic acid, PA.

TABLE V  
Peak Temperatures of Primary Exotherm at Different Heating Rates and Activation Energy for Acrylonitrile–Carboxylic Acid Copolymers

Copolymer Composition	Code	Rate of Heating °C	Peak Temperature °K $T_{pk_1}$	$E_a$ Kcalmol <sup>-1</sup> (KJmol <sup>-1</sup> )	$A_0$ S <sup>-1</sup>
P(AN-AA) AA = 3.1 (mol %)	PA	2	535	44.2 (184.8)	$2.94 \times 10^{17}$
		5	550		
		10	—		
		20	566		
P(AN-MAA) MAA = 2.6 (mol %)	PM	2	522.5	29.5 (123.3)	$3.93 \times 10^{11}$
		5	534		
		10	550		
		20	589		
P(AN-IA) IA = 2.2 (mol %)	PI	2	522	26.1 (109.1)	$8.21 \times 10^9$
		5	543		
		10	554		
		20	577		

Activation energy and Arrhenius frequency factor values of acrylonitrile copolymers reported by various researchers are listed in Table VI.

#### DSC (isothermal mode)

The heat flow behavior of copolymers of acrylonitrile–carboxylic acids in isothermal conditions in air atmosphere is presented in Figures 8–10. The test was conducted in the DSC cell at temperatures ranging from 210 to 240°C for 1 h.

The DSC scans showed a distinct peak due to exothermic reaction. The initiation of the cyclization reaction is instantaneous with liberation of heat followed by another broad peak due to the propagation reaction. Incorporation of carboxylic acid accelerates the secondary reaction.<sup>33</sup> The isothermal temperature has significant effect on the initiation time of the reaction as well as the time required for the propagation reaction to reach its maximum. In the case of PA<sub>1</sub> at 210°C, the reaction starts after 0.85 min and the secondary reaction reaches its maximum after 6.2 min with total heat liberated 126 Jg<sup>-1</sup>. However, in this copolymer at 240°C the exotherm starts earlier, 0.53 min, and reaches its maximum in a shorter time, i.e., 1.3 min. The total heat liberated, however, is increased to 260 Jg<sup>-1</sup>, indicating that increasing the isothermal temper-

ature accelerates the reaction with liberation of larger amount of heat over a shorter span of time (Table VII). Comparing the thermal behavior of these carboxylic acid copolymers, at 230°C, in PA the reaction starts at 0.96 min, and it reaches its maximum after 2.2 min, with total heat liberation of 249 Jg<sup>-1</sup>. In PM<sub>2</sub>, however, the first reaction is instantaneous, and starts after 0.4 min, which reaches its maximum after 0.5 min with  $\Delta H$  of 193 Jg<sup>-1</sup>. PI<sub>3</sub> showed a different behavior, i.e., the initiation of cyclization reaction is fast, and takes 0.18 min. However, it reaches its maxima after 0.21 min, but showed a sharp shoulder as well. Similar observation was made by Collins for Beslon fibers.<sup>28</sup>

The value of  $\Delta H/\Delta t$ , i.e., the heat liberated per unit time is highest for PM<sub>2</sub> (8.6 Jg<sup>-1</sup> min<sup>-1</sup>) followed by PA<sub>3</sub> (6.25 Jg<sup>-1</sup> min<sup>-1</sup>) and PI<sub>5</sub> (2.3 Jg<sup>-1</sup> min<sup>-1</sup>). This indicates itaconic acid that accelerates the cyclization reaction, but the role of propagation is slow as the total heat liberated per unit time is lowest.

#### DSC-FTIR

Structural transformations during heating of acrylonitrile–carboxylic acid copolymers at 230°C

To investigate the structural transformations taking place during heat treatment of acrylic copolymers,

TABLE VI  
Activation Energy Values Reported in the Literature

Polymer	Type of Reaction	$E_a$ kcalmol <sup>-1</sup>	$A^\circ$ s <sup>-1</sup>	Ref.
PAN	Cyclization in N <sub>2</sub>	301	$2 \times 10^{11}$	29
AN:MA (95:5)	Stabilization in air	26.6	$1.5 \times 10^{10}$	29
AN:MA (95:5)	Cyclization in N <sub>2</sub>	25.5	$1.3 \times 10^{10}$	29
AN:MA:IA (93:6:1)	Cyclization	25.8	$1.22 \times 10^8$	31
AN:MA:IA (93:6:1)	Dehydrogenation in air	25.8	$1.22 \times 10^8$	31
AN:MA:IA (93:6:1)	Oxidation	30	$1.3 \times 10^9$	31
AN:MA:IA (93:6:1)	Stabilization in air	34.4	—	35
AN:MA:IA (93:6:1)	Oxidation in air	53.2	$1.3 \times 10^9$	39



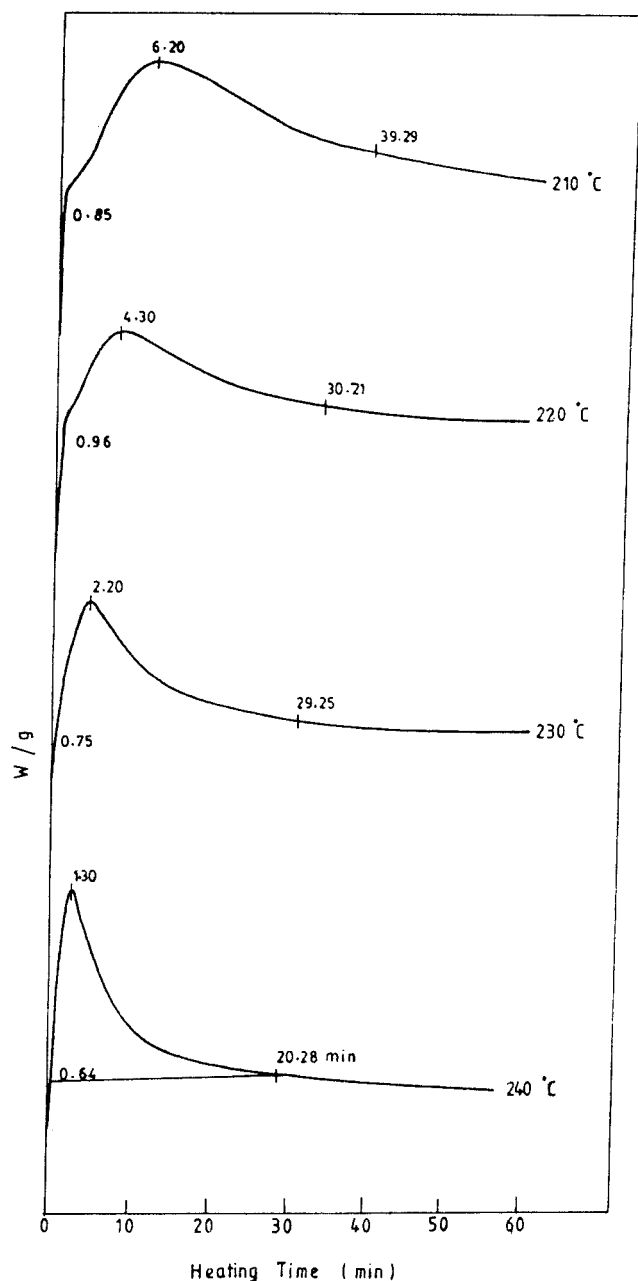


Figure 8 DSC curves (isothermal mode) of the acrylonitrile acrylic acid copolymer (PA<sub>1</sub>) at different temperatures.

samples were heated in a DSC cell at 230°C for 15 to 120 min. The extent of cyclization or dehydrogenation in these samples was found through FTIR spectra of samples taken at different time intervals (Figs. 11 and 12). The spectra showed distinctive peaks at 2926 cm<sup>-1</sup> due to the methylene (CH<sub>2</sub>) group and 2243 cm<sup>-1</sup> due to the nitrile (C≡N) group.

Infrared spectra can be used to follow the decrease in the strong nitrile and methylene absorption bands that participate in the cyclization and dehydrogenation reactions respectively (Table VIII).

Quantitative analysis of the FTIR spectra of partially oxidized samples has been used to determine the ki-

netics of stabilization. The cyclization reaction is usually treated as first order in the nitrile group concentration, C<sub>C≡N</sub>, with allowance made for the unreacted nitrile groups remaining after 120 min of heating at 230°C, C<sub>C≡N</sub><sup>∞</sup>. Thus, the driving force for the reaction is C≡N—C≡N because the nitrile groups are dilute, absorbance is assumed to be proportional to concentration (Beer's Law), leading to the integrated form of the rate equation.

$$-\ln \frac{A - A^\infty}{A^0 - A^\infty} = kt.$$

where,  $A$  is the nitrile absorbance at time  $t$ ,  $A^0$  is the initial nitrile absorbance;  $A^\infty$  is the final complete con-

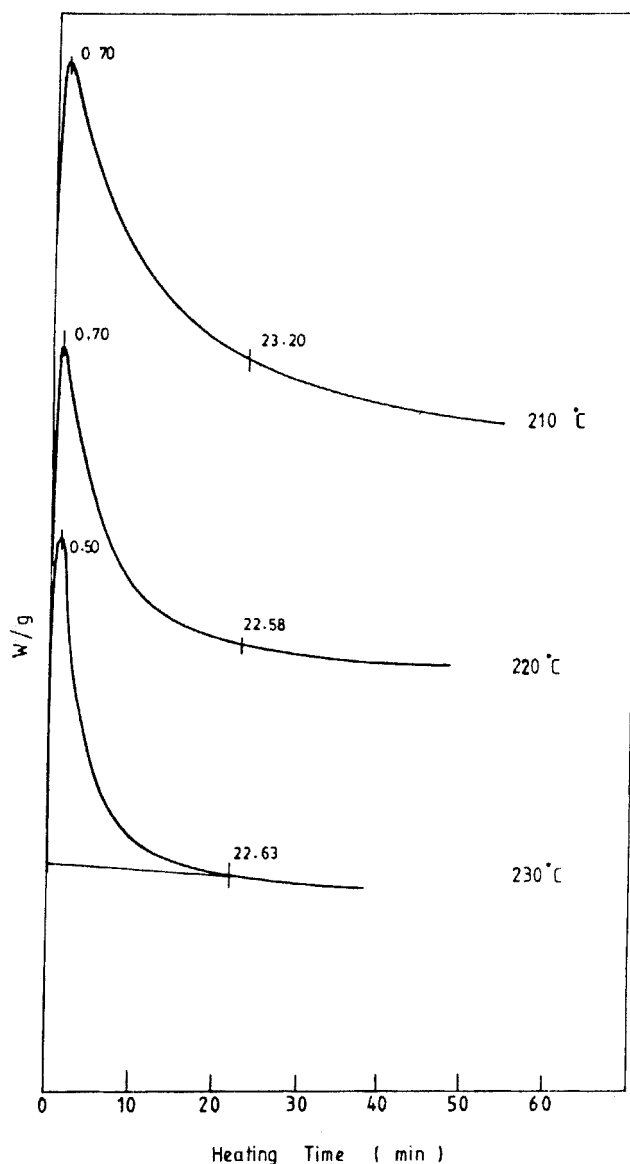
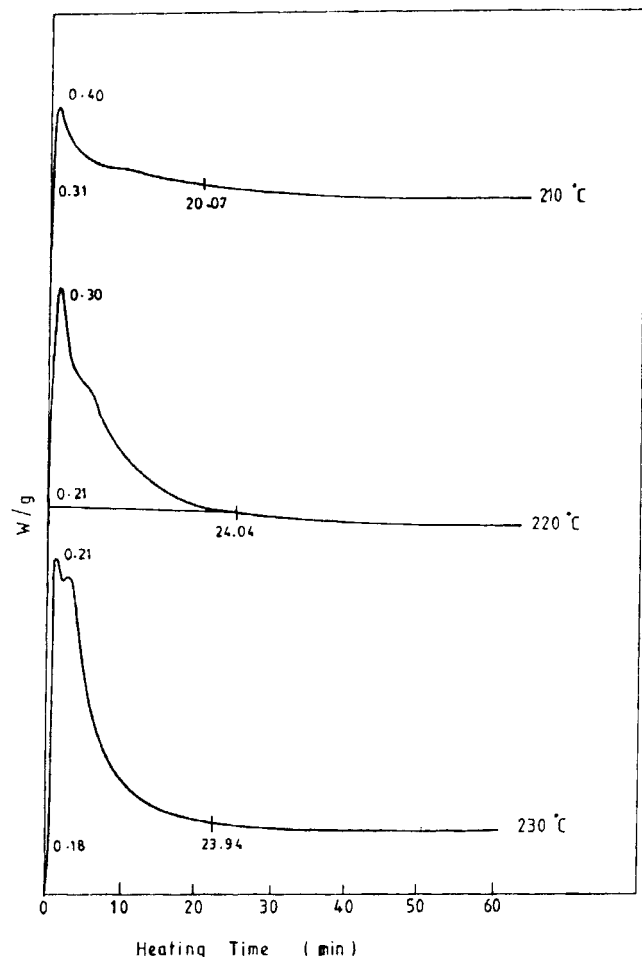


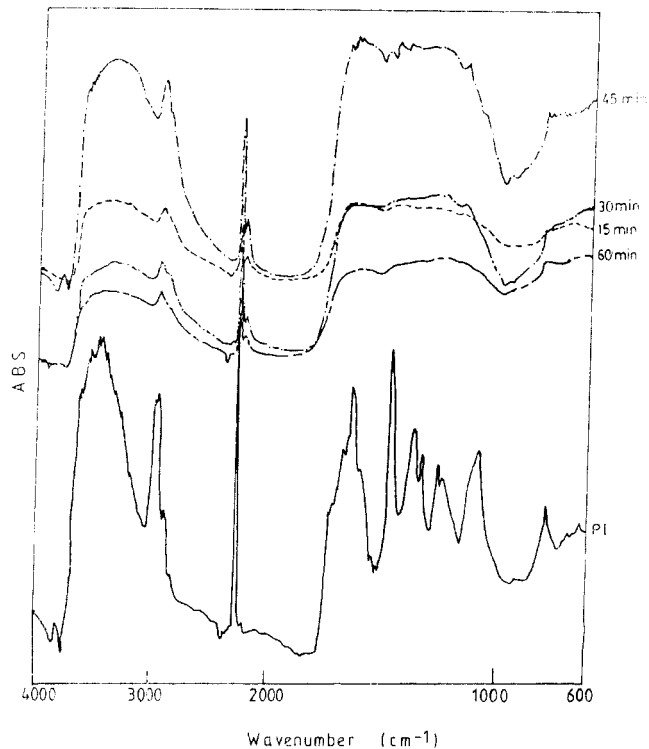
Figure 9 DSC curves (isothermal mode) of acrylonitrile methacrylic acid copolymer (PM<sub>2</sub>) at different temperatures.



**Figure 10** DSC curves (isothermal mode) of the acrylonitrile itaconic acid copolymer (PI<sub>3</sub>) at different temperatures.

version nitrile absorbance,  $t$  is the time, and  $k$  is the reaction rate constant at the temperature of heat treatment in the DSC cell.

The rate constant can be found from a plot of the left-hand side of this equation vs. time. These rate



**Figure 11** FTIR spectra of the PI copolymer heated at 230 °C for different time durations in air.

constants depend on the heating temperature according to the standard Arrhenius relationship.

$$K = K_0 e^{-E/RT}$$

The rate constant calculated from the change in the band intensity at 2243  $\text{cm}^{-1}$  due to  $\gamma\text{C}\equiv\text{N}$  for PI is 0.04195  $\text{min}^{-1}$ , whereas it is 0.0195  $\text{min}^{-1}$  and 0.0198  $\text{min}^{-1}$  for PA and PM copolymers, respectively, indicating that the reaction in PI copolymer is faster as itaconic acid IA accelerates the cyclization reaction (Fig. 13). Similarly, the rate constant calculated from

**TABLE VII**  
DSC Data of Acrylonitrile-Carboxylic Acid Copolymers Run under Isothermal Mode

Heat Treatment Temp. (°C)	DSC Data	PA <sub>1</sub> (4.51 mol %)	PM <sub>2</sub> (4.61 mol %)	PI <sub>3</sub> (5.87 mol %)
210	Exotherm Time (min)	39.3	23.2	17.6
	$\Delta H$ ( $\text{Jg}^{-1}$ )	126	117	27.7
	$\Delta H/\Delta t$ ( $\text{Jg}^{-1} \text{min}^{-1}$ )	3.2	5.0	1.5
220	Exotherm Time (min)	40.2	22.6	30.3
	$\Delta H$ ( $\text{Jg}^{-1}$ )	218	179	57.6
	$\Delta H/\Delta t$ ( $\text{Jg}^{-1} \text{min}^{-1}$ )	5.4	7.9	1.8
230	Exotherm Time (min)	39.9	22.6	27.1
	$\Delta H$ ( $\text{Jg}^{-1}$ )	249	193	61.7
	$\Delta H/\Delta t$ ( $\text{Jg}^{-1} \text{min}^{-1}$ )	6.2	8.6	2.2
240	Exotherm Time (min)	40.2	30.0	21.8
	$\Delta H$ ( $\text{Jg}^{-1}$ )	260	221	94.3
	$\Delta H/\Delta t$ ( $\text{Jg}^{-1} \text{min}^{-1}$ )	6.5	7.4	4.3

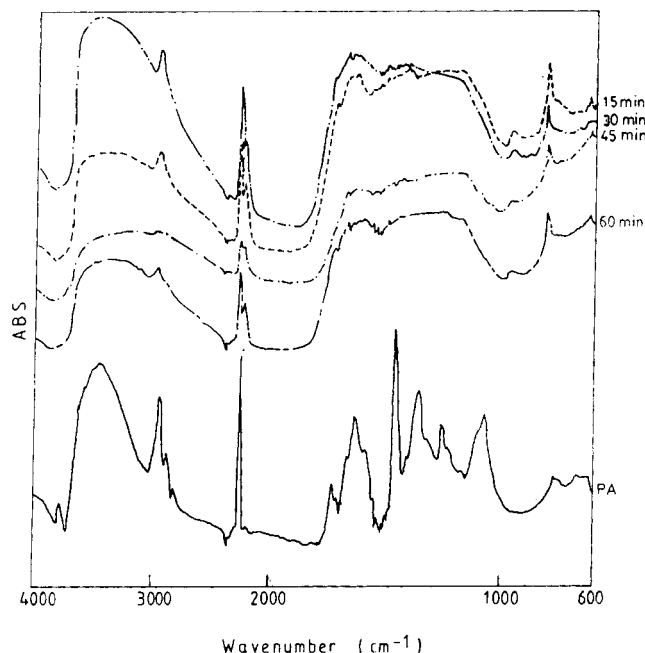


Figure 12 FTIR spectra of PA copolymer heated at 230°C for different time durations in air.

the disappearance of 2926  $\text{cm}^{-1}$  band due to  $\text{CH}_2$ , leading to dehydrogenation reaction. From Figure 14 it can be seen that the rate constant for the dehydrogenation is 0.027, 0.033, and 0.058  $\text{min}^{-1}$  for PA, PM, and PI, respectively, suggesting that the dehydrogenation is also the quickest in the case of PI and slowest

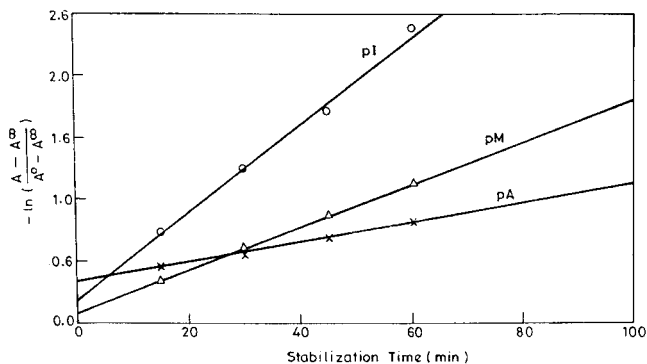


Figure 13 Determining the first-order rate constants for nitrile consumption at 230°C.

in PA. In other words, itaconic acid facilitates both the dehydrogenation and cyclization reactions. Assuming the concentration of oxygen is approximately constant, then the first order consumption of methylene groups concentration,  $\text{CH}_2$  in the polymer is given by

$$\frac{dC_{\text{CH}_2}}{dt} = k' C_{\text{CH}_2}$$

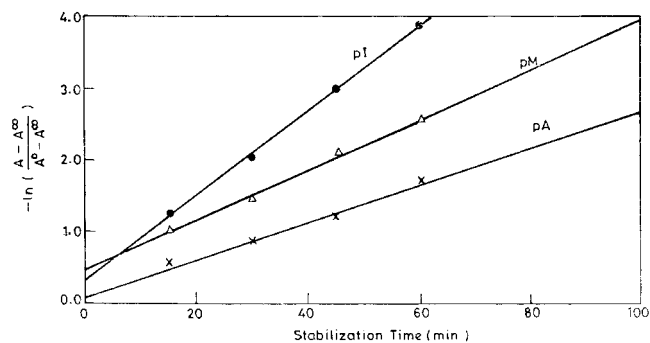
and the above modified equation after integration can be written as:

$$-\ln \frac{C_{\text{CH}_2} - C_{\text{CH}_2}^{\infty}}{C_{\text{CH}_2}^0 - C_{\text{CH}_2}^{\infty}} = k't$$

TABLE VIII  
FTIR Data of AN-Carboxylic Acid Copolymer Heated at 230°C in Air

Polymer Code	Peak Height 2926 $\text{cm}^{-1}$	Peak Height 2243 $\text{cm}^{-1}$	Peak Ratio $A_t/A_0$	
			2926 $\text{cm}^{-1}$	2243 $\text{cm}^{-1}$
PA <sub>0</sub>	0.172	0.363	—	—
PA <sub>15</sub>	0.063	0.282	2.73	1.29
PA <sub>30</sub>	0.053	0.202	3.25	1.79
PA <sub>45</sub>	0.049	0.171	3.51	2.13
PA <sub>60</sub>	0.035	0.126	4.9	2.89
PM <sub>0</sub>	0.135	0.188	—	—
PM <sub>15</sub>	0.101	0.180	1.34	1.04
PM <sub>30</sub>	0.052	0.135	2.59	1.39
PM <sub>45</sub>	0.035	0.116	3.86	1.26
PM <sub>60</sub>	0.030	0.110	4.5	1.71
PM <sub>120</sub>	0.024	0.080	5.6	2.35
PI <sub>0</sub>	0.365	0.689	—	—
PI <sub>15</sub>	0.072	0.353	5.07	1.954
PI <sub>30</sub>	0.052	0.267	7.02	2.58
PI <sub>45</sub>	0.042	0.213	8.69	3.24
PI <sub>60</sub>	0.038	0.184	9.61	3.74
PI <sub>120</sub>	0.028	0.102	13.04	6.54

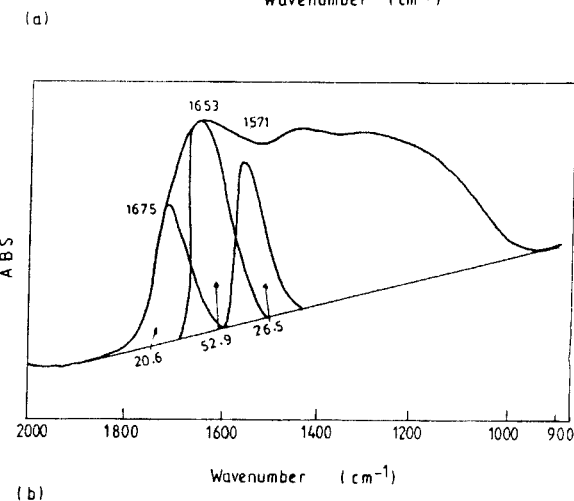
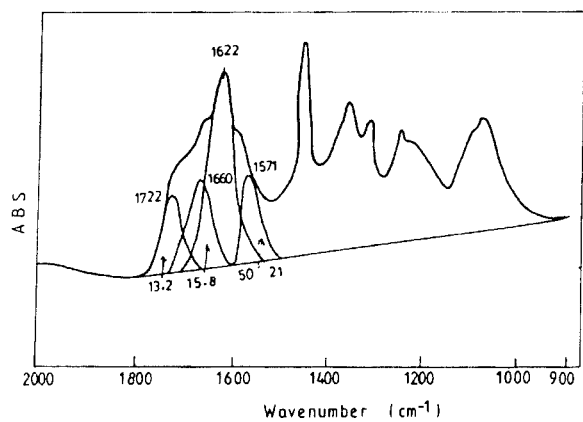
PA<sub>0</sub> = Before heating, A<sub>t</sub> = After heating at time, t,  
 15 = Heated at 230°C for 15 min,  
 30 = Heated at 230°C for 30 min,  
 45 = Heated at 230°C for 45 min,  
 60 = Heated at 230°C for 60 min,  
 120 = Heated at 230°C for 120 min.



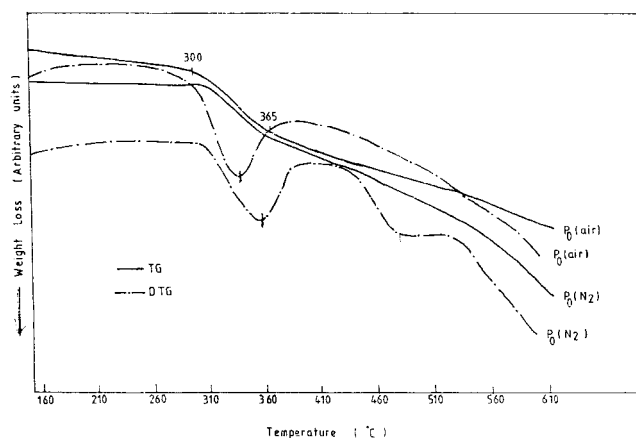
**Figure 14** Determining the first-order rate constants for methylene consumption at 230°C.

where  $C_{\text{CH}_2}$  is the concentration of  $\text{CH}_2$  at time  $t$ ;  $C_{\text{CH}_2}^0$  is the concentration of the  $\text{CH}_2$  groups of untreated polymer, i.e., at time  $t = 0$ ;  $C_{\text{CH}_2}^\infty$  is the concentration of  $\text{CH}_2$  groups after heat treatment at 230°C for 120 min;  $k'$  is the rate constant of the disappearance of methylene groups during the heat treatment in air at 230°C.

For quantitative analysis of structural changes occurring during heating, the IR spectra were deconvoluted



**Figure 15** Deconvolution of FTIR spectra in the range 1550–1745  $\text{cm}^{-1}$  region (a) PI before heating (b) after heating at 230°C for 15 min in air.

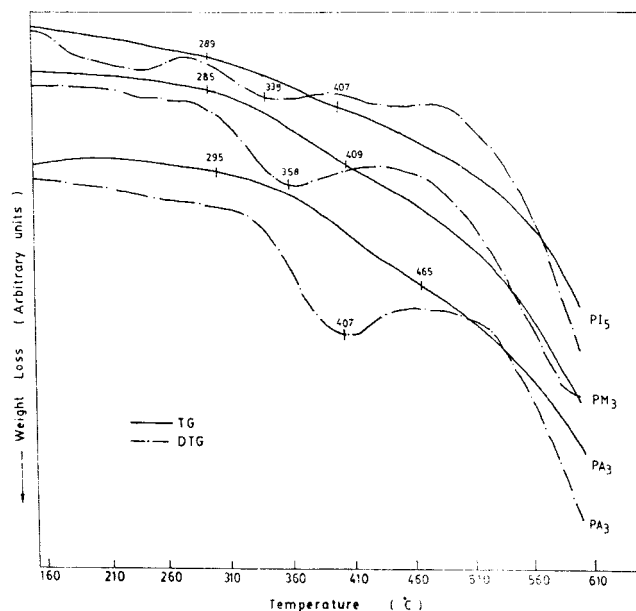


**Figure 16** TG and DTG curves of PAN homopolymer ( $P_0$ ) in air and nitrogen at 5°C/min.

luted in the 1800–1550  $\text{cm}^{-1}$  region. The peak area for the 1660–1745  $\text{cm}^{-1}$  region due to the  $\text{C}=\text{O}$  and the 1571–1600  $\text{cm}^{-1}$  region due to the  $\text{C}=\text{C}$  were considered for comparison (Fig. 15).

The PA copolymer has two distinct peaks in the 1660–1745  $\text{cm}^{-1}$  region, with its maxima at 1730 and 1620  $\text{cm}^{-1}$ . It is interesting to note that the area of the 1730  $\text{cm}^{-1}$  absorbance band due to  $\text{C}=\text{O}$  increases from 17.6 to 42.3% after heating at 230°C for 15 min in air. Although in PM, the  $\text{C}=\text{O}$  band area has increased from 51 to 58% only, in the case of PI it has increased from 29 to 73%, about 2.5-fold.

This indicates that among the three acid comonomers, itaconic acid is more effective in picking up the oxygen during heating in the form of ketone and hydroxyl groups, which facilitate the dehydrogena-



**Figure 17** TG and DTG curves of acrylonitrile-carboxylic acid copolymers ( $P_0$ ) in air and nitrogen at 5°C/min.

**TABLE IX**  
**Thermogravimetric Analysis of Acrylonitrile–Carboxylic Acid Copolymers in Air, 5°C/min**

Copolymer Code	$T_i$ (°C)	$D_{max}$ (°C)	Weight Loss % at $D_{max}$	Weight Loss % at 600° C
PA <sub>3</sub>	295	407	18.3	63
PM <sub>3</sub>	285	358	14.4	73
PI <sub>5</sub>	289	339	10.7	81

tion and exothermic reactions compared to acrylic and methacrylic acid. However, it has been demonstrated that oxygen acts in two opposite ways during stabilization: on one hand it initiates the formation of activated centers for cyclization, while on the other hand it retards the reactions by increasing the activation energy. Even then the stabilization in an oxidizing medium is preferred because it results in the formation of some oxygen-containing groups in the backbone of a ladder polymer. These groups subsequently help in fusion of the ladder chains during carbonization.

#### Thermogravimetric analysis (TGA)

The thermogravimetric curves of PAN and acrylonitrile–carboxylic acids reveals that the incorporation of carboxylic acid comonomers brings interesting changes. The TG curves corresponding to weight loss apparently occurring in three steps indicating different types of reactions taking place. The first step up to 250°C, in which the weight loss is not substantial, is followed by a second step between 250–350°C in which weight loss is very rapid. This temperature zone corresponds to the DSC exotherms, the last step above 350°C in which the loss in weight is quite steady.

The TG curves of the PAN homopolymer (P<sub>0</sub>) in air atmosphere does not show any substantial weight loss in the first zone (Fig. 16), while in the second zone starting from 300 to 365°C the weight loss is fast and rapid. The maximum weight loss ( $D_{max}$ ) in this zone is 20%. The final zone shows a steady and slow weight loss up to 600°C. The weight loss at 600°C was 50.8%.

In acrylonitrile–carboxylic acid copolymers, P(AN–AA) PA<sub>3</sub> showed a steady region up to 295°C without much weight loss (Fig. 17). In the second step, ranging between 265 to 465°C, the weight loss is fast. At 407°C  $D_{max}$  the weight loss is 18.3%. A similar observation has been made for PM<sub>3</sub>. The weight loss associated with the first step was not substantial, i.e., up to 285°C, whereas in the second zone ranging from 285 to 409°C, the weight loss is quite high and becomes steady with gradual weight loss in the third zone, i.e., above 409°C.

According to Grassie and McGuchan<sup>11</sup> and Guyot et al.,<sup>13</sup> the products involved in the initial degradation

of P(AN–MAA) copolymers are HCN and NH<sub>3</sub>. Recently, Schield<sup>36</sup> has reported the formation of polymethacrylic anhydride as the major product in the degradation of polymethacrylic acid in nitrogen around 210°C. On-line TGA/FTIR was used to show that the formation of poly methacrylic anhydride at elevated temperatures (250–300°C) results with the formation of H<sub>2</sub>O as the major product along with CO<sub>2</sub> due to decarboxylation reaction. The fast weight loss in second zone in PM<sub>3</sub> may be attributed to the evolution of H<sub>2</sub>O and CO<sub>2</sub> along with other products of degradation like HCN and NH<sub>3</sub>. The weight loss above these temperatures is due to thermo-oxidative degradation and chain scission.

TG curves of PI<sub>5</sub> showed slightly different behavior. In this copolymer, the TG curve showed no weight loss up to 170°C followed by a second zone from 170–289°C in which the weight loss is high. Anhydride formation also takes place in the region due to intramolecular dehydration of two carboxylic acid groups of the itaconic acid. Another zone ranging from 289 to 407°C has been observed in which the weight loss is high but is not fast and finally a steady weight loss upto 600°C.

Comparing these three copolymers, which had almost equal comonomer content, it is observed that the weight loss at 600°C for PM<sub>3</sub> is more than PA<sub>3</sub> and PI<sub>5</sub> (Table IX).

The TG curves of these copolymers in N<sub>2</sub> showed slightly different behavior, i.e., the total weight loss at 600°C in these copolymers in air was less than that of N<sub>2</sub> atmosphere (Table X). This is because in air atmosphere oxidation reaction (oxygen pickup) takes place, which improves the weight retention at the exotherm. This is in agreement with Grassie and McGuchan,<sup>11</sup> who suggested that the pyrolysis in air results in less weight loss than in nitrogen atmosphere because of oxidation reaction. The oxygen uptake no doubt com-

**TABLE X**  
**Thermogravimetric Analysis of Acrylonitrile–Acrylic Acid with Different Comonomer Content in Air and Nitrogen at 5°C/min**

Copolymer (AA mol %)	Temperature (°C)	Weight Loss %	
		Air	N <sub>2</sub>
PPA <sub>1</sub> (5.51)	300	2.5	3
	400	12	16
	600	56	78
PA <sub>2</sub> (7.12)	300	3	5.5
	400	14	23
	600	66	85
PA <sub>3</sub> (8.52)	300	4	6.8
	400	18	20.5
	600	68	86
PPA <sub>4</sub> (17.51)	300	9.5	8
	400	21	25
	600	73	89

pensates in part for the weight loss. However, as the content of acidic comonomer is increased the total weight loss in air is increased. The weight loss at 600°C in PA<sub>1</sub> with 5.51 mol % of comonomer content was 56%, whereas in PA<sub>4</sub> with 17.5 mol % of comonomer the weight loss was found to be 73%.

## References

1. Sen, K.; Bahrami, S. H.; Bajaj, P. *JMS-Rev Macromol Chem-Phys* 1996, C36.
2. Minagawa, M. *J Polym Sci Polym Chem Ed* 1980, 18, 2307.
3. Glazkovski, Yu. V.; Mikhailov, P. V. *Vysokomol. Soedin* 1966, 8, 1673.
4. Grassie, N.; McGuchan, R. *Eur Polym J* 1971, 7, 1091.
5. Tsai, J. S.; Lin, C. H. *J Mater Sci Lett* 1990, 9, 869.
6. Minagawa, M.; Iwamatsu, T. *J Polym Sci Polym Chem Ed* 1980, 18, 481.
7. Grassie, N.; McGuchan, R. *Ibid* 1971, 7, 1357.
8. Grassie, N.; McGuchan, R. *Ibid* 1973, 9, 113.
9. Coleman, M. M.; Sivy, G. T. *Carbon* 1981, 19, 123 and 127.
10. Grassie, N.; McGuchan, R. *Eur Polym J* 1973, 9, 507.
11. Grassie, N.; McGuchan, R. *Eur Polym J* 1972, 8, 257.
12. Grassie, N.; Heaney, A. *Eur Polym J* 1974, 10, 415.
13. Guyot, A.; Bert, M.; Hamoudi, A.; McNeil, I.; Grassie, N. *Eur Polym J* 1978, 14, 107.
14. Ferguson, J.; Debanath Ray, N. *Fibre Sci Technol* 1980, 13, 167.
15. Bajaj, P.; Padmanaban, M. *Eur Polym J* 1984, 20, 513.
16. Gupta, D. C.; Agrawal, J. P. *J Appl Polym Sci* 1989, 38, 265.
17. Grassie, N.; McGuchan, R. *Eur Polym J* 1971, 7, 1503.
18. Bahl, O. P.; Mathur, R. B.; Dhami, T. L. *Mater Sci Eng* 1985, 73, 105.
19. Ko, T. K.; Huang, L. C. *J Mater Sci* 1992, 27, 2429.
20. Mathur, R. B.; Mittal, J.; Bahl, O. P. *J Appl Polym Sci* 1993, 49, 469.
21. Mathur, R. B.; Mittal, J.; Bahl, O. P.; Sandle, N. K. *Carbon* 1994, 32, 71.
22. Grassie, N.; McGuchan, R. *Eur Polym J* 1972, 8, 865.
23. Coleman, M. M.; Sivy, G. T.; Painter, P. C.; Snyder, R. W.; Gordon, B., III. *Carbon* 1983, 21, 255.
24. Klimenko, I. B.; Platonova, N. V.; Tarakanov, B. M.; Maiburov, S. P. *Khim Volokna* 1993, 6, 20.
25. Mitsubishi Rayon Co., Ltd. *Jpn Kokai Tokkyo Koho JP 04254,921* (1992); *Chem Abstr* 1993, 118, 1104705.
26. Thompson, E. V. *Polym Lett* 1966, 4, 361.
27. Geiderikh, M. V.; Din, D. S.; Davydov, B. E.; Kappcheva, G. P. *Polym Sci USSR* 1973, 15, 1391.
28. Collins, G. L.; Thomas, N. W.; Williams, G. E. *Fibre Sci Technol* 1984, 20, 37.
29. Fitzer, E.; Müller, D. J. *Carbon* 1975, 13, 63.
30. Grove, D. A., III; Abhiraman, A. S. *Carbon* 1992, 30, 435.
31. Dunham, M. G.; Edie, D. D. *Carbon* 1992, 30, 435.
32. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
33. Kakida, H. *Polym Preprints (Eng Ed)* 1992, 41, 28 w12.
34. Koshelev, I. V.; Sokolovskii, V. N.; Kotorlenko, L. A.; Plygan, E. P.; Sergeev, V. P. *Fibre Chem* 1993, 25, 342.
35. Mathur, R. B.; Bahl, O. P.; Matta, V. K.; Nagpal, K. C. *Carbon* 1988, 26, 3.
36. Gupta, A. K.; Paliwal, D. K.; Bajaj, P. *J Appl Polym Sci* 1998, 70, 2703.
37. Bajaj, P.; Bahrami, S. H.; Sen, K.; Sreekumar, T. V. *J Appl Polym Sci* 1999, 74, 567.
38. Bajaj, P.; Sen, K.; Bahrami, S. H. *J Appl Polym Sci* 1996, 59, 1539.
39. Heine, M. Ph.D. Dissertation, University of Karlsruhe Germany (1988).