Thermal behaviour of acrylonitrile copolymers having methacrylic and itaconic acid comonomers

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Abstract

The effect of comonomers, methacrylic (MAA 3–6 mol%) and itaconic acid (IA 2–3 mol%) on the glass transition temperature, T_g, hydration melting and thermo-oxidative stabilization of acrylonitrile copolymers has been studied by differential scanning calorimetry (DSC). While, two T_g's were observed, near 70 and 140°C, for PAN homopolymer, copolymers showed another baseline shift below 70°C. The melting point, T_m, of PAN and copolymer, P(AN/IA) containing 3.2 mol% of IA, has been reduced to 186 and 158°C, respectively, in high-pressure DSC. The copolymers showed two distinct melting peaks in the first heating cycle, but the melt on subsequent cooling exhibited a single exotherm due to crystallization. The melting point of IA copolymer (158°C) was found to be lower than that of MAA copolymer (164°C) and PAN homopolymer (186°C). T_m further decreases with increase in the comonomer content. In the second heating cycle, observed T_m is higher than that noted in the first heating run, indicating some amount of physical transformations. The enthalpy of fusion, ΔH_f decreases with the incorporation of comonomers, e.g. it is maximum for PAN homopolymer (57.8 J g^{-1}) and minimum for P(AN/IA) copolymer (26 J g^{-1}) having 3.2 mol% of IA content. The lower entropy of fusion (ΔS_f) of copolymers indicates that they are less mobile in the molten state. DSC of copolymers run in air atmosphere, at a heating rate of 10°C min^{-1}, shows a broader exotherm compared to homopolymer. But, the broadening of exotherm seems to be more in P(AN/IA) polymers than P(AN/MAA) and the onset of cyclization shifts to a lower temperature as compared to PAN. The activation energy of nitrile cyclization, E_a, for PAN is found to be 30 kcal mol^{-1}. For copolymer P(AN/IA), IA = 3.2 mol%, E_a is 18 kcal mol^{-1}. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PAN; Acrylonitrile vinyl acid copolymers; High-pressure DSC

1. Introduction

Acidic comonomers such as acrylic acid (AA), methacrylic acid (MAA) and itaconic acid (IA) provide supplemental dye sites, modify the fibre morphology, increase the hydrophilicity and facilitate the cyclization of nitrile groups during thermo-oxidative stabilization of acrylic fibres prior to carbonization [1–6].

The effect of comonomers on the thermal behaviour of PAN and its copolymers has been the subject of several investigators [7–16]. Thermal behaviour of acrylonitrile copolymers is highly dependent on the method of polymerization, chemical nature of comonomer and its content. Properties like glass transition temperature (T_g), melting (T_m) and crystallization (T_c) is affected by the change in crystallinity and perfection. Gupta and coworkers [8–10] investigated the

effect of 2-hydroxy ethyl methacrylate, methacrylonitrile and methyl acrylate on crystallinity and crystalline perfection using X-ray and dielectric measurements.

The determination of T_g using differential scanning calorimetry (DSC) has been difficult due to the strong exothermic reaction, minor transitions like T_g cannot be seen. A step-like change at 100°C and an endothermic peak at 155°C has been observed by Gupta and Chand [8]. Bajaj and Padmanabhan [12] reported two endothermic transitions at 102 and 156°C for PAN, which is reduced to 96 and 136°C, respectively, for AN copolymer containing 6.1 mol% of 3-chloro, 2-hydroxypropyl acrylate. Bashir [13] also reported, two glass transitions using DSC, which could not be recognized, mainly because of the enthalpy relaxation masking the true nature of the transition. Two glass transitions in unoriented PAN while a single T_g at ~100°C in oriented fibres has been observed.

As PAN undergoes nitrile cyclization at a temperature between 180 and 220°C, followed by degradation at a higher temperature, melting is not observed under normal set of conditions. However, if the heating rate is sufficiently high

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$(80–160°C \, min^{-1})$, some melting would occur, at about 320–370°C, before the polymer degrades [15,17,18]. Melting endotherm of PAN has been observed at higher heating rates as well as in the presence of small quantities of water. The strong nitrile dipolar interactions are believed to be the prime reason for high melting point of PAN [19]. Water breaks down the strong nitrile dipolar interactions, leading to a reduction in T_m. Based on the above principle, melt spinning of PAN based polymers was tried [20].

Frushour [21] studied the effect of vinyl acetate (VA) comonomer on the melting of PAN copolymers. He observed a significant reduction in T_m with increase in comonomer content. Incorporation of 11% VA reduced the T_m to 142°C in the presence of water, using one part of polymer to two parts of water. Further, reduction in T_m with increase in water content was also observed. However, a water content above 0.2 weight fraction did not change the T_m. Min et al. [22] have also demonstrated the influence of various diluents such as dimethyl formamide (DMF), water, polyethylene glycol (PEG), polyvinyl alcohol (PVA) and polyacrylic acid (PAA) on the melting behaviour of PAN. Incorporation of water under autogenous pressure sharply lowered the T_m, but levelled off (153°C) above critical water content of 23 wt%. However, addition of DMF into the hydrated PAN further lowered the T_m to 140°C, even above the critical water content. while, addition of PAA, PEG and PVA to hydrated PAN slightly raised the T_m.

Grassie and McGuchan [7,23] studied the effect of AA, MAA and IA on the cyclization reaction using DTA, DSC and TGA techniques. The introduction of small amount of acid comonomers (2–4 mol%) lowered the initiation of cyclization in air atmosphere from 275°C for PAN to 200°C for P(AN/IA) copolymer containing ≃2 mol% of IA. Authors suggested that the mechanism of nitrile cyclization perhaps changes from radical to ionic mechanism due to the incorporation of vinyl acid in P(AN/IA), which is responsible for the shift to lower side in the onset temperature of nitrile group cyclization. Thus, homopolymer showed a single prominent exothermic peak (315–325°C), while copolymers exhibited a shoulder at a lower temperature (260–265°C). Tsai et al. [24] studied the effect of IA as a comonomer as well as an additive on the initiation of nitrile cyclization reaction. It was shown that the incorporation of IA during copolymerization is more efficient in reducing the onset of cyclization temperature than IA used as an additive. Coleman [25] investigated the chemical transformations of P(AN/MAA), P(AN/VA) and P(AN/Acrylamide) copolymers having 4 wt% of MAA during isothermal heating at 200°C using FTIR. The rate of degradation was observed to be markedly dependent on the chemical nature of the comonomers and it was found to increase in the order: PAN < PAN/VA < PAN/AM ≅ PAN/MAA.

The present study deals with the affect of vinyl acid comonomers (MAA and IA) on glass transition, melting, crystallization and thermo-oxidative degradation of PAN copolymers using DSC and TGA.

2. Experimental

2.1. Synthesis and characterization

PAN and its copolymers with MAA and IA were synthesized by solvent–water suspension polymerization using α,α'-azobisisobutyronitrile (AIBN) as initiator. The details of polymerization conditions are described elsewhere [26]. The comonomer content was determined using elemental analysis, NMR, FTIR and acidimetric titration. Intrinsic viscosity of the samples was measured at 25°C in *N,N*-dimethyl formamide (Table 1).

2.2. Measurements

DSC and TGA studies were carried out on DSC-7 and TGA-7 module of a Perkin–Elmer Delta series thermal

Table 1
Characterization of acrylonitrile/ MAA or IA copolymers (MAA = methacrylic acid; IA = itaconic acid)

| Polymer code	Conversion (%)	Copolymer composition (mol%)		$[\eta]$ (dl g^{-1})	Crystallinity (%)	Isotacticity (%)	Sequence distribution of CN tacticities		
		AN	MAA/IA				n_o	n_m	n_r
P(AN/MAA)									
P_0	80	100	–	1.76	51	30	2.17	2.25	1.92
P_1	74	96.8	3.2	2.80	46	32	2.20	2.42	2.62
P_2	49	96.3	3.7	2.50	43	31	2.22	2.29	1.88
P_3	24	94.9	5.1	1.36	41	30	2.15	2.28	1.98
P_4	22	93.9	6.1	0.69	42	31	2.17	2.35	2.00
P(AN/IA)									
P_5	60	98.0	2.0	2.90	43	31	2.17	2.35	2.00
P_6	35	97.7	2.3	2.67	49	33	2.2	2.54	2.12
P_7	22	97.4	2.6	1.45	40	31	2.17	2.29	1.92
P_8	18	96.8	3.2	0.67	41	30	2.17	2.25	1.92
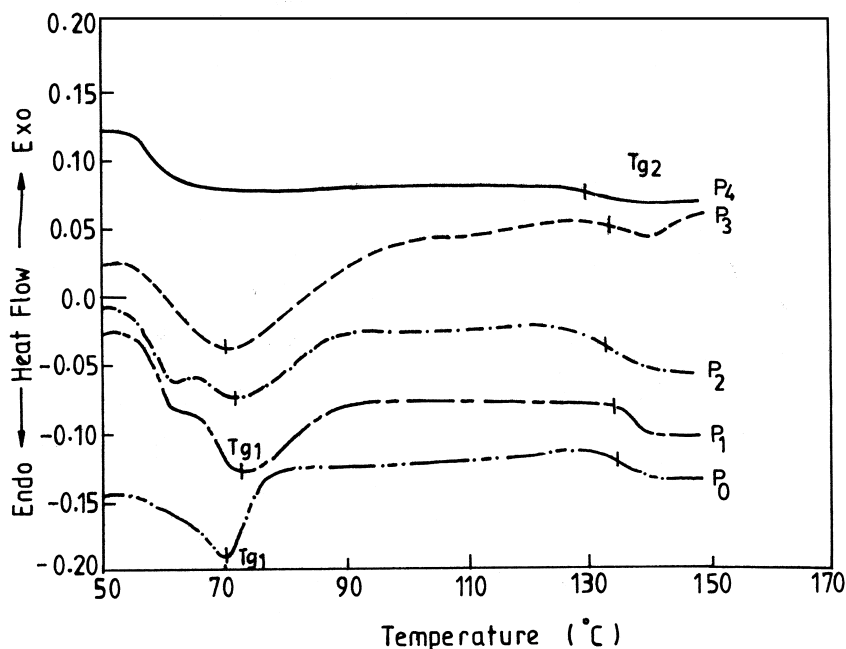
Fig. 1. Glass transition temperature of acrylonitrile homo and copolymers. Rate of heating 10°C min^{-1}.

analyser. DSC studies were carried out at heating rates ranging between 2 and 20°C in air and nitrogen atmosphere and TGA at 10°C in air. In order to find out the glass transition temperature, the 40–150°C region in DSC thermogram is expanded along the heat flow axis so as to get a distinct shift in the baseline after making base line correction.

Activation energy E_a, for the nitrile cyclization was calculated using following equation by Kissinger's method [27]. The peak maximum (T_{pk}, K) at different heating rates was recorded.

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

where, R is the universal gas constant, ϕ is the heating rate and T is the temperature in Kelvin scale. The value of $1/T_{pk}$ is plotted against ln ϕ/T_{pk}^2 and the slope is equated to E/R.

2.3. High-pressure DSC

For melting and crystallization studies, 5 mg of the polymer samples, wetted by 7.5 μl of distilled water, were taken in a specially designed gold-plated pressure sample pan capable of withstanding the vapour pressure of water up to 200°C. The sealed pan was left for 12 h, and then DSC thermogram was taken at a heating rate of 5°C min^{-1}. Precautions were taken to avoid any escape of water vapour during the heating process above 100°C. In order to avoid the boiling peak of water, the system was held at 100°C for 1 min before scanning the melting endotherm of these polymers.

3. Results and discussions

3.1. Glass transition temperature

Fig. 1 shows the DSC curves of acrylonitrile homo and copolymers from 50 to 150°C. In case of P_0, acrylonitrile homopolymer, there is an endothermic transition with a peak at about 70°C (T_{g1}) followed by a baseline shift at about 135°C (T_{g2}). The copolymers, P_1 (MAA = 3.2 mol%)

Table 2
Glass transition temperature of acrylonitrile polymers through DSC

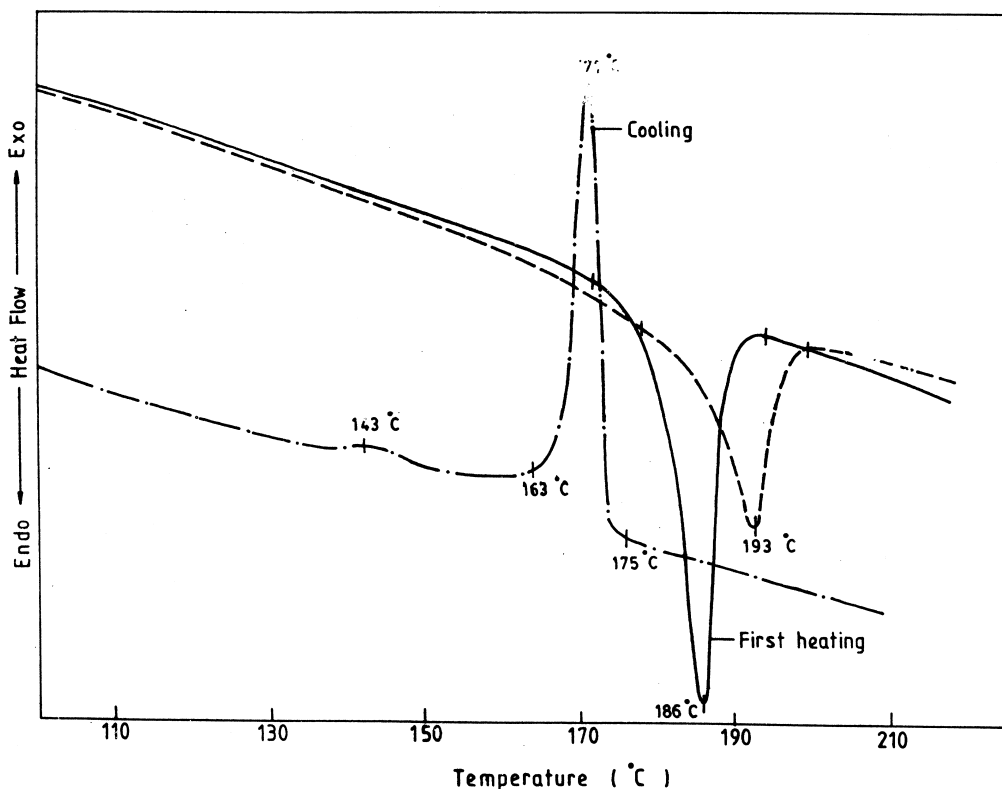| Polymer code	MAA composition (mol%)	[η] Intrinsic viscosity (dl g^{-1})	Crystallinity (χ_c)	T_{g1} (°C)	T_{g2} (°C)
P_0	0	1.76	51	70.3	135
P_1	3.2	2.80	46	71.8	134
P_2	3.7	2.50	43	70.5	133
P_3	5.1	1.36	41	70	134
P_4	6.1	0.69	42	58	130

Fig. 2. High-pressure DSC thermograms of PAN homopolymer under autogenous water vapour pressure. Heating rate 5°C min^{-1}.

and P$_2$ (MAA = 3.7 mol%) showed one more shoulder-like baseline shift below 70°C. P$_3$ (MAA = 5.1 mol%) shows a single broad endothermic peak at 70°C and T_{g2} at 134°C. P$_4$ (MAA = 6.1 mol%) shows two baseline shifts, one at 58°C and the other at 130°C (Table 2). Bajaj [12] and Bashir [13] also considered the endotherm near 70°C as the glass transition temperature, although the classical DSC profile of glass transition is a step-like or sigmoidal change in the base line. T_{g1} has been attributed to the onset of backbone mobility and T_{g2} to intermolecular bonding associated with the nitrile groups.

There is no significant change in T_{g2}, due to the chemical composition of the polymer until P$_3$ (133–135°C) which contains 5.1 mol% MAA; while P$_4$ shows a lowering in the temperature, and T_{g2} occurs at 130°C (Table 2). Howard [28] also observed that T_g of acrylonitrile–vinyl acetate (AN/VA) copolymers remained constant until VA level exceeded to 27 wt%, and then began to decrease.

T_{g1} of PAN homopolymer (70–73°C) is at a lower temperature compared to P$_1$, although the crystallinity (lateral order) of homopolymer is higher. The reason may be that at lower concentration of MAA comonomer (2–4 mol%) there may be some amount of nitrile–carboxylic intra- and intermolecular interactions. Another reason for a slightly higher T_g for copolymer may be the presence of a

third transition, the shoulder near 60°C, which might take some amount of energy creating a temperature lag. The T_{g2} reduces from P$_1$ to P$_4$ during which both crystallinity and molecular weight reduce (Table 2).

3.2. Melting behaviour of hydrated PAN under autogenous vapour pressure of water

The high-pressure DSC thermogram of PAN homopolymer shows a sharp melting at 186°C (Fig. 2), under autogenous water vapour pressure. The reduction in T_m is due to the weakening of strong nitrile–nitrile dipolar interactions in the presence of steam under high pressure. It may be noted that the amorphous region would be easily hydrated compared to ordered region and there has to be a reduction in T_m as reported by Frushour [18], Atureliya and Bashir [29] and Min et al. [22]. During the heating process in the presence of water vapour at high pressure the amorphous region will be first hydrated. At this stage, water having small molecular weight and size can easily penetrate the two-dimensional pracrystalline PAN leading to the breakage of nitrile–nitrile interaction which is actually the binding force. The weakening of C≡N interactions takes place when the nitrile dipoles are surrounded by the dipoles of water molecules (hydration) leading to C≡N water hydrogen bonding as under.
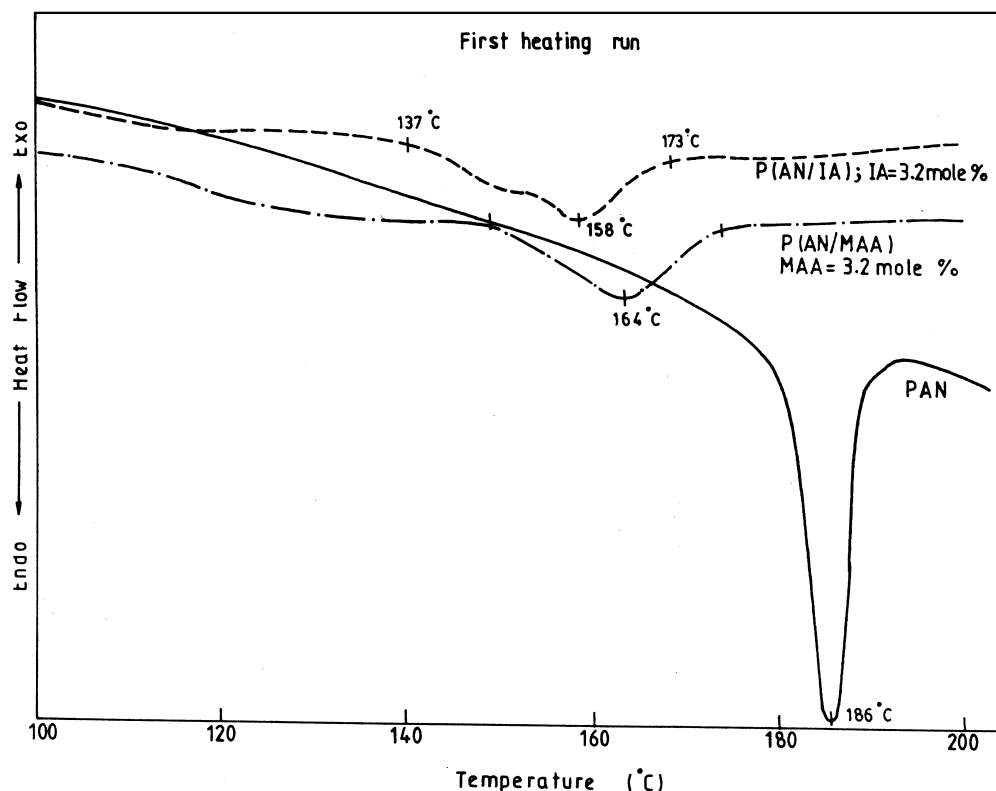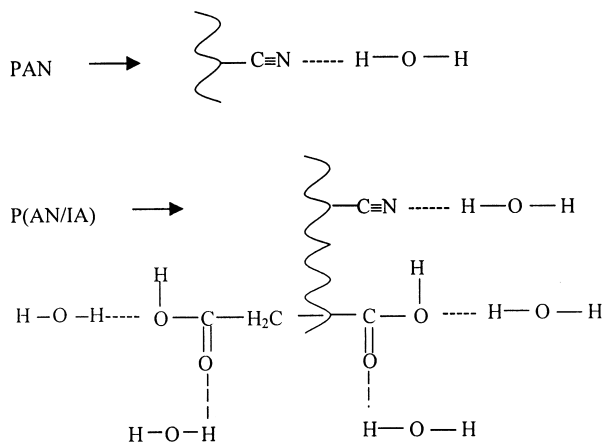
Fig. 3. Effect of acid comonomers on the melting behaviour of acrylonitrile copolymers.

Atureliya and Bashir [29] has proposed the co-crystallization of PAN with propylene carbonate (PC) during the melt spinning of PAN in the presence of PC. However, no evidences for crystal containing water have been obtained. In the cooling cycle, the molten PAN showed a strong crystallization exotherm at 171°C along with a weak shoulder at 143°C. Frushour [18] and Gupta et al. [15] also made similar observations. This has been attributed to the formation of some unknown structure on cooling of the polymer melt. When the polymer is remelted (second heating run), the T_m is shifted to a higher temperature, 193°C. This may be because of the reduction in water

vapour pressure, as some of the water molecules still entrapped in the melt during the hydration process of nitrile groups will not evaporate. The melting process is accompanied by the conversion of fine polymer powder into viscous liquid droplets which combines to form a polymer lump on solidification [15]. There is a substantial reduction in the surface area during this process. The reduction in surface area will also contribute to the increase in T_m. Olive and Olive [30] have also demonstrated the plasticization effect of water both under normal pressure and high temperature and high pressure. According to them a single phase was formed when the polymer was heated under pressure in the presence of water. The stretching frequency of the polymer CN groups at 2234 cm^{-1} disappeared; instead a new band at 2050 cm^{-1} was observed. Presumably, some kind of reversible hydration of CN group might have taken place under the experimental conditions of high temperature and pressure.

3.3. P(AN/MAA) and P(AN/IA) copolymers

A comparison of the DSC thermograms of P(AN/MAA) and P(AN/IA) copolymers having 3.2 mol% of VA comonomers (Fig. 3) shows a single broad melting endotherm in P(AN/MAA) copolymer in the temperature range of 149–173°C with a peak at 164°C which shifts to a lower temperature range, 141–169°C with a
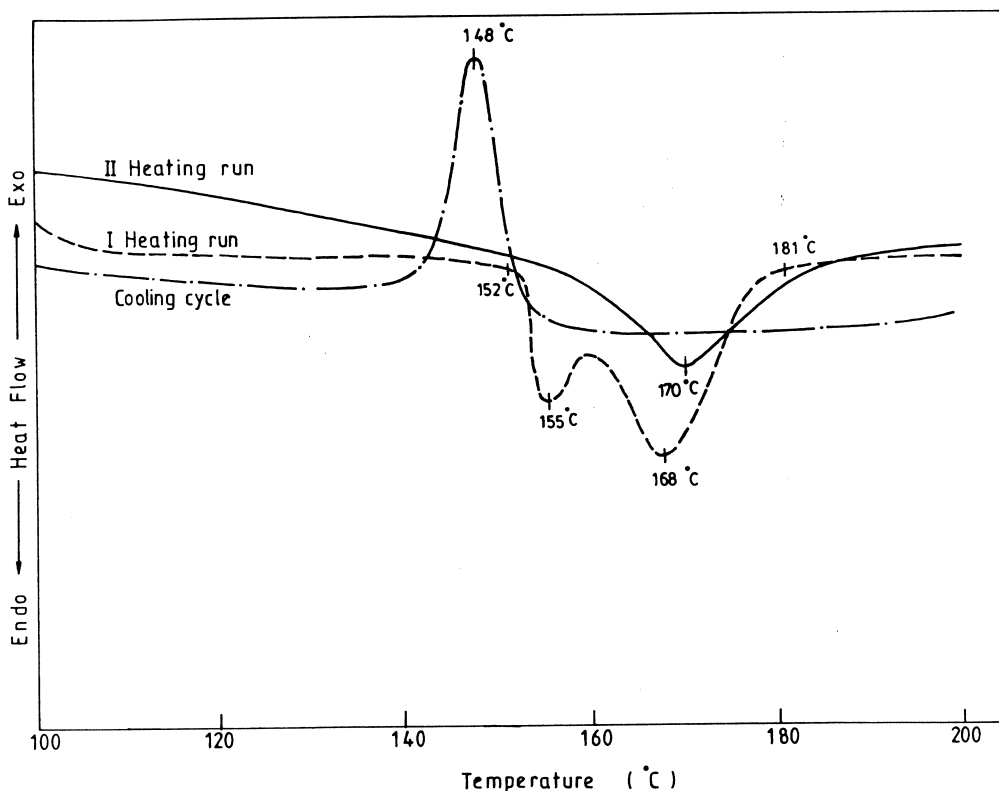
Fig. 4. High-pressure DSC scans of P(AN/IA) copolymer containing 2.3 mol% IA under autogenous water vapour pressure. Heating rate 5°C min^{-1}.

peak at 158°C in the case of P(AN/IA). The latter also shows a shoulder at 149°C. However in P(AN/IA) copolymer containing 2.3 mol% IA, (Fig. 4), the scans obtained in high-pressure DSC show two sharp melting endotherms at 155 and 168°C.

Generally, polyacrylonitrile is considered as a single-phase laterally ordered structure, one should expect a single melting endotherm. So, the formation of two distinct T_m in acrylonitrile random copolymer containing only 2.3 mol% IA is difficult to explain. The high-pressure hydration melting of PAN copolymers, P(AN/IA), showing two distinct T_m may presumably be due to the different degree of hydration because of the polar carboxylic groups (hydrophilic) present in random P(AN/IA) copolymer. Thus, the region with –A–A–A–A–A–A– sequence rich in acrylonitrile units will be less hydrated, and is expected to melt at a higher temperature as compared to those with –A–A–I–A–A–I–A–A– sequences which will be hydrated more due to the hydrophilic IA moiety, and melt at a lower temperature.

On cooling of the melt, only one crystallization exotherm is observed, as the hydrated carboxylic acid region would be difficult to crystallize. Had there been two different types of crystal formation, two crystallization exotherms would have been observed in the cooling cycle. This can be further substantiated through the second heating run of the same copolymer where only a single T_m is observed and that too at a higher temperature: It could be noticed that copolymer,

P(AN/IA) with IA = 2.3 mol%, reduced the T_m to 167.6 from 186°C (homopolymer).

The single endotherm for P(AN/MAA) may be because of the hydrophobic nature of MAA compared to IA, consequently leading to lower degree of hydration. The lower T_m for P(AN/IA) copolymers can be explained on the basis of Flory theory [19], according to this model the efficacy of a particular comonomer to depress the melting point is to a first approximation proportional to the molar volume of the comonomer. It could be noted that molar volume of IA comonomer would be higher due to the bulky side groups compared to MAA.
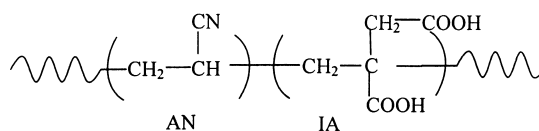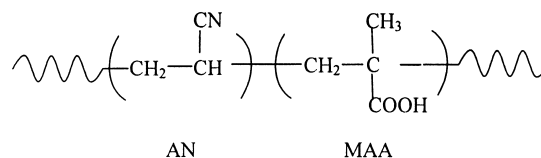
Thus, it is expected that the lateral order may be higher for MAA copolymers compared to IA copolymers. This

Table 3
High-pressure DSC data of acrylonitrile polymers

Heating cycle						Cooling cycle					
Polymer code/ composition (mol%)	Melting endotherm (°C)			T_m (°C)	ΔH_f (J g^{-1})	Crystallization range (°C)			T_c (°C)	ΔH_c (J g^{-1})	$\Delta S_f = (\Delta H_f/\Delta T_m)$
	T_i	T_f	ΔT			From	To	ΔT			
P_0 MAA/IA = 0	172	195	23	186	58	163	175	12	171	39	6.89
P_1 MAA = 3.2	146	180	34	164	27	123	147	24	143	15	3.18
P_6 IA = 2.3	152	181	29	168	49	139	157	18	148	26	5.83
P_8 IA = 3.2	137	173	37	158	26	126	158	32	145	13	3.18

may be another reason for the single melting endotherm in case of MAA copolymer although the melting range is broader (146–180°C; $\Delta T = 34°C$) than homopolymer (172–195°C; $\Delta T = 23°C$) (Table 2). The least heat of fusion ($\Delta H_f = 26.1$ J g^{-1}) of P_8, P(AN/IA; IA = 3.2 mol%), compared to all other polymers also supports the above hypothesis.

On incorporation of 2.3 mol% IA, the heat of fusion (ΔH_f) is reduced from 58 to 49 J g^{-1}. The reduction in ΔH_f may be attributed to the reduction in crystallinity due to the defects created by the comonomers. The presence of defects reduces the melting point and heat of fusion by disrupting the intermolecular bonding within the crystalline lattice. Comparing P_6 and P_8, (Table 3 and Fig. 5), it could be

noted that an increase in the comonomer content decreases the T_m, as well as ΔH_f.

The entropy of fusion, ΔS_f, per single chain bond (Table 3) calculated using Eq. (2) for PAN is higher (6.83 J °C^{-1}) than the reported values.

$$\Delta S_f = \frac{\Delta H_f}{T_m} \tag{2}$$

A ΔS_f value of 4 J °C^{-1} (dry state) has been reported by Kriegbaum and Takida [31] which is well below the usual range of 6–8 J °C^{-1} for polymers like polyethylene, polychloroprene, etc. This fact indicates in the present case that addition of water enhanced the mobility of PAN single chain bonds (more entropy), which is now comparable
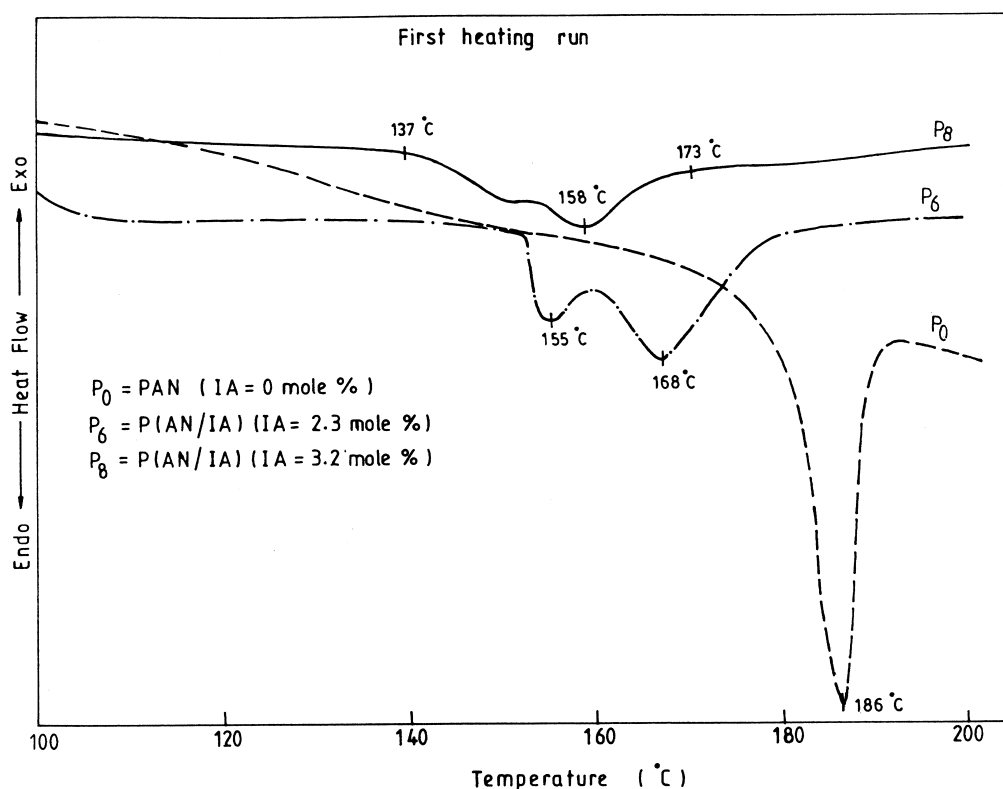

Fig. 5. Effect of comonomer content on the melting behaviour of P(AN/IA) copolymers.
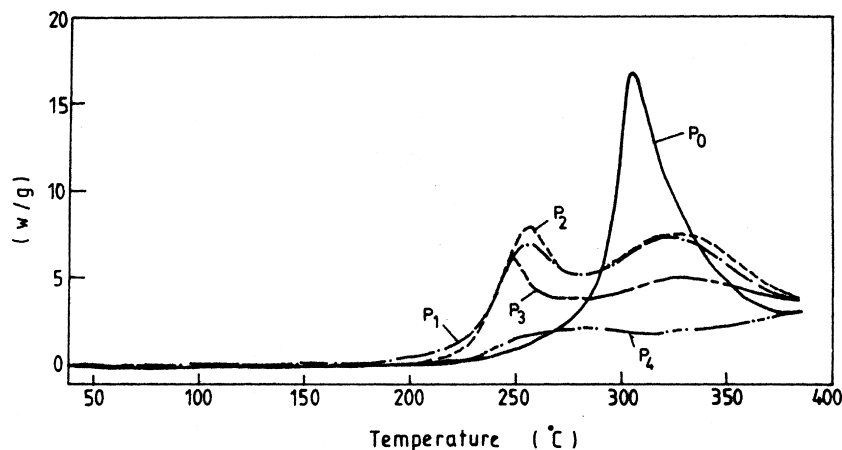
Fig. 6. DSC exotherm of PAN homopolymer and P(AN/MAA) copolymers in air atmosphere. Heating rate 10°C min^{-1}.

with that of other polymers thus demonstrating the lowering of T_m due to hydration of the paracrystalline structure through nitrile bonds.

Another interesting observation is that the ΔS_f decreases with increasing comonomer content. According to Eq. (2) lowering of ΔS_f can be due to two factors, i.e. lowering of heat of fusion ΔH_f or increase in T_m. However, it could be noted that both ΔH_f and T_m decrease with increase in the comonomer content. It may be noted that addition of comonomer has created some degree of disorder initially itself (the same may be confirmed from crystallinity data). When heated, these copolymers undergo transition from an already disordered state to a still higher disordered state and melt due to hydration. Thus, the change in disorder or ΔS_f is apparently low. Also due to the greater degree of hydration, comonomers through carboxylic side groups may resist the molecular movements in the molten state, which can also lead to the lower value of ΔS_f.

3.4. Thermo-oxidative reactions

DSC thermograms of PAN, P(AN/MAA) and P(AN/IA)

obtained in air atmosphere at a heating rate of 10°C min^{-1} are shown in Figs. 6 and 7. At this heating rate, no endothermic transition due to T_m is observed. Instead, strong exotherms were shown. These exotherms are characteristic of the chemical changes in AN sequence of homopolymer and copolymers. The temperature of initiation (T_i), finish (T_f) and their difference or the width of the exotherm ΔT, ($\Delta T = T_f - T_i$), the peak temperature (T_{pk}), and the heat evolved (ΔH) are shown in Table 4.

3.5. PAN homopolymer

The DSC exotherm of PAN homopolymer shows a single, very sharp and intense narrow peak starting from 272°C (T_i) to the final temperature 376°C (T_f). The peak maximum (T_{pk}) is at 322°C. The heat liberated during the reaction (ΔH) was 2810 J g^{-1}. The sharp narrow exotherm indicates that the rate of propagation is very high after the initiation of cyclization reaction. Here, the rate of reaction has been considered as the ratio of heat liberated to the time taken during the exotherm, i.e. $\Delta H/\Delta T$. The higher value of $\Delta H/\Delta T$, 269.2 J g^{-1} min^{-1}, (Table 4) indicates the maximum
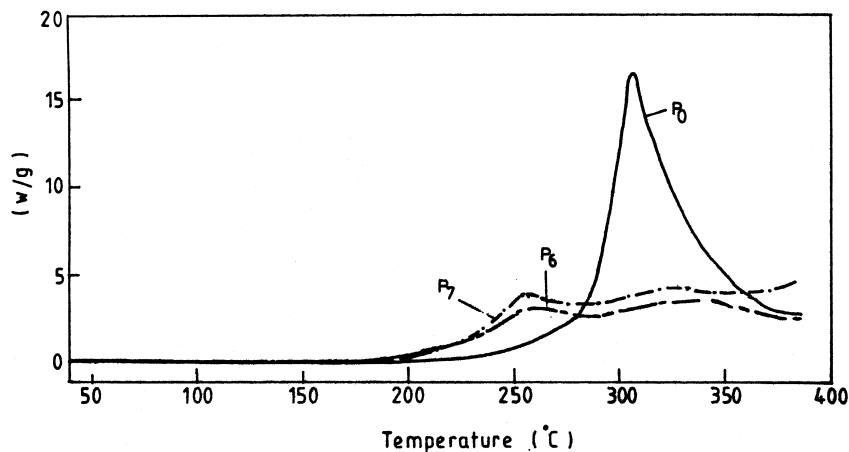

Fig. 7. DSC exotherm of PAN homopolymer and P(AN/IA) copolymers in air atmosphere. Heating rate 10°C min^{-1}.

Table 4
DSC data of homopolymer and copolymers in air atmosphere (rate of heating 10°C)

Polymer code	Copolymer composition (mol%)		[η] (dl g⁻¹)	Exotherm range (°C)		Peak temp. (°C)		$T_f - T_i = \Delta T$	Reaction time (min)	ΔH (J g⁻¹)	$\Delta H/\Delta t$	E_a (kcal mol⁻¹)
	AN	MAA/IA		T_i	T_f	T_{pk1}	T_{pk2}					
P_0	100	0.0	1.76	271	376	322	–	105	10.5	2810	269	30
P_1	96.8	3.2	2.80	217	385	263	335	168	16.9	3250	194	29
P_2	96.3	3.7	2.50	219	385	266	332	166	16.6	3230	195	-
P_3	94.9	5.1	1.36	215	384	254	336	170	17.0	1710	101	-
P_4	93.9	6.1	0.69	220	350	283	329	130	13.0	358	27	18
P_5	98.0	2.0	2.90	208	385	256	324	177	17.7	1810	102	-
P_6	97.7	2.3	2.67	196	374	263	327	178	17.8	939	53	-
P_7	97.4	2.6	1.45	213	374	260	327	161	16.1	843	52	-
P_8	96.8	3.2	0.61	192	369	258	331	177	17.7	466	26	-

rate of cyclization and dehydrogenation for homopolymer as the cyclization of nitrile groups in PAN is considered to be free radical oligomerization. The extent of cyclization or dehydrogenation cannot be calculated independently from the DSC thermogram in air atmosphere as both the reactions are taking place simultaneously. However, the heat of reaction, ΔH for cyclization (31.0 kJ mol⁻¹) and ΔH for dehydrogenation (19.7 kJ mol⁻¹) reaction are found to be different as reported by Dunham and Edie [32].

3.6. Effect of VA comonomers

The introduction of VA comonomers greatly lowered the initiation temperature, T_i of exothermic reaction compared to homopolymer (Figs. 6 and 7). The mechanism of nitrile cyclization in PAN and copolymers is shown in Fig. 8. The doublet characteristic of the exotherm for copolymers, and the increase in exothermic reaction time or width of the exotherm (ΔT) indicates that in copolymers the reactions occur in different steps. The single sharp exotherm of homopolymer suggests that all the reactions are taking place simultaneously. Introduction of 3.2 mol% MAA (P_1) decreased the T_i from 272 to 217.4°C. Also, the rate of exothermic reaction decreased, i.e. $\Delta H/\Delta T$, from 269 to 194 J g⁻¹ min⁻¹. Further increase in comonomer content from 3.2 to 6.1 mol% of MAA did not make any significant change in T_i although the rate of cyclization is decreased to 27 J g⁻¹ min⁻¹.

Polymer code/composition	ΔH (J g⁻¹)	Rate, $\Delta H/\Delta T$, (J g⁻¹ min⁻¹)
P_0 Homopolymer (PAN)	2810	269
P_1 (MAA = 3.2 mol%)	3250	194
P_8 (IA = 3.2 mol%)	466	26

From P_0 to P_1 the ΔH increased from 2810 to 3250 J g⁻¹ and this value decreased on further increment in the comonomer content. The introduction of comonomer (MAA = 3.2 mol%) decreased the activation energy (E_a) of the reaction from 30 to 29 kcal mol⁻¹. When the comonomer content increased to 6.1 mol% the activation energy sharply decreased to 18 kcal mol⁻¹. Similar results are observed in the case of IA copolymers. Dunham and Edie [32] reported an activation energy of 25.7 kcal mol⁻¹ for Caurtaulds, P(AN/MA/IA), special acrylic fibres. For a P(AN/MAA) copolymer Kakida and Tashiro [33] reported an activation energy of 26 kcal mol⁻¹. Comparing P_1 and P_8, copolymers containing equivalent amount of comonomers (3.2 mol%), the values of T_i, T_{pk1}, T_{pk2} and $\Delta H/\Delta T$ follow the order as under.

P(AN/IA) < P(AN/MAA),

while, other properties like ΔT and reaction time ($\Delta T/\phi$) are in the following order:

P(AN/MAA) < P(AN/IA)

This may be due to the presence of two carboxylic acid

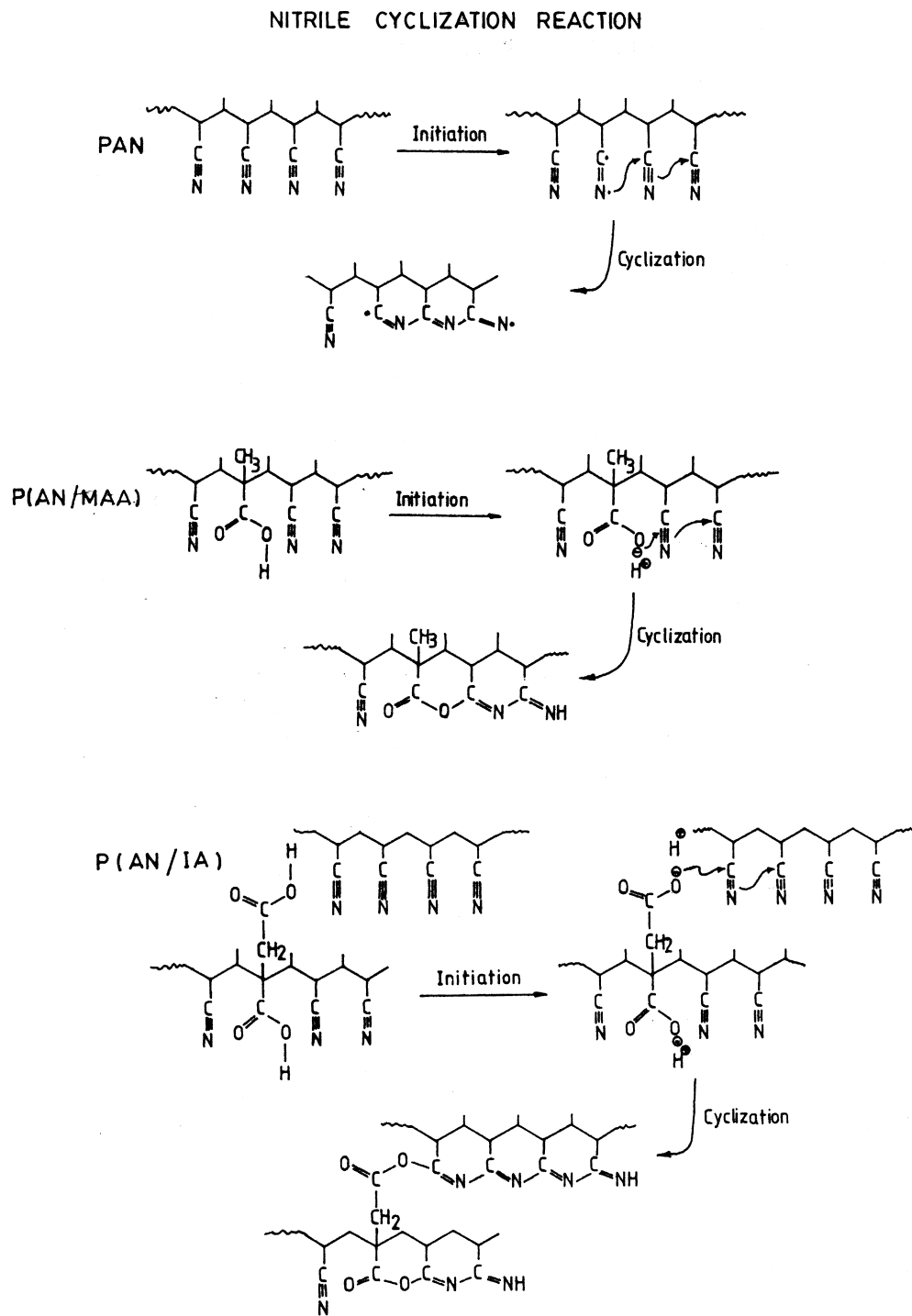## NITRILE CYCLIZATION REACTION

Fig. 8. Mechanism of nitrile cyclization in PAN and copolymers.

groups in IA molecule indicating the role of two acids in cyclization reaction. Further increase in the comonomer content from 3.2 to 6.1 mol% retards the propagation as evident from the decrease in ΔH value (ΔH value at 6.1 mol% of MAA level is only 358 J g^{-1}).

3.7. TGA

TGA and DTG curves of PAN and P(AN/MAA) copolymers show that the weight loss behaviour of homopolymer, and copolymers containing low amount of carboxylic acid
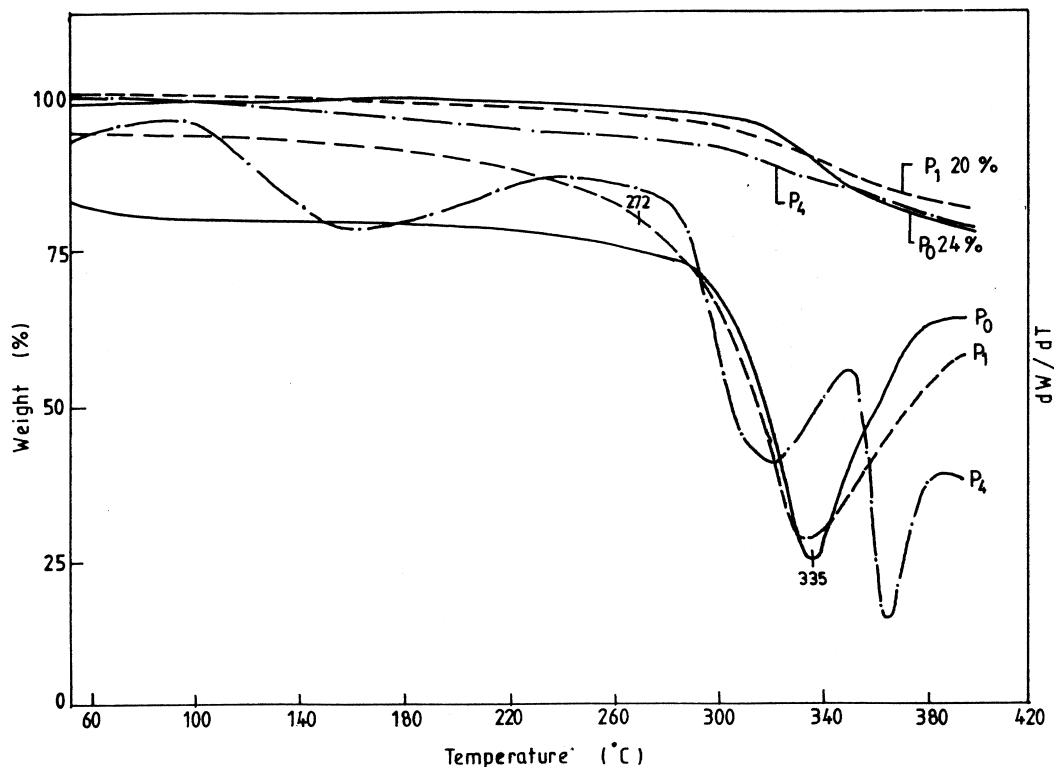
Fig. 9. TG and DTG curves of PAN and P(AN/MAA) copolymers in air atmosphere. Heating rate 10°C min^{-1}.

(P_1, MAA = 3.2 mol%) is essentially a single step process starting from ~272 to 390°C. When the comonomer content increases to 6.1 mol% the weight loss takes place in three steps (Fig. 9). The first step from 100 to 273°C, second step from 280 to 350°C and the third step above 350°C. P(AN/IA) copolymers also show similar degradation behaviour. Grassie [7] observed that the three acid copolymer systems [P(AN/MAA), P(AN/IA) and P(AN/AA)] behave similarly during TGA studies in air.

Recalling the DSC data (Table 4), the degradation or molecular scission in copolymers does not appear to be concurrent with the exotherm ($T_i = 217°C$ for P_1) but takes place gradually at a higher temperature (272°C). However, in P_0 homopolymer, both the reactions are more or less concurrent. In this case the DSC exotherm starts at 272°C, while TGA (Fig. 9) shows that the degradation starts at 280°C. In copolymers, the exothermic nitrile cyclization reaction mechanism is ionic in nature which occurs at a temperature as low as 217°C. Theoretically, the nitrile cyclization reactions should not be accompanied by any weight loss. However, if the reaction rate and the heat liberated are very high, fragmentation of polymer chains may occur producing volatile particles leading to weight loss. As the heat liberated is distributed in a broad temperature range in copolymers, the rate of reaction is low. Thus, initially there is no substantial weight loss for P_1 during nitrile cyclization. In P_0, due to its radical nature of nitrile cyclization initiation starts at a higher temperature and the reaction rate is high

compared to P_1. All types of reaction in P_0 are taking place simultaneously, and the molecular fragmentation is mostly favoured leading to weight loss. The higher weight loss for P_0 (24%) compared to P_1 (20%) may be due to the above reasons.

P_4 shows a three-step weight loss pattern as described earlier. The weight loss in the region of 100–237°C may be due to the dehydration of adjacent carboxyl groups as the VA content in P_4 is maximum (6.1 mol%).

Similar degradation behaviour was reported in MAA homopolymer by Bajaj et al. [34]. The weight loss at higher temperature (>260°C) may be due to the evolution of HCN, NH_3 and CO_2 and H_2O.

4. Conclusions

- Glass transition temperature (T_g) in acrylonitrile polymers is observed between 65 and 72°C and 130 and 135°C. While, homopolymer shows two T_g, some copolymers show an additional baseline shift below 70°C.
- In high-pressure DSC, melting point of PAN is significantly reduced to 186°C under autogenous water vapour pressure. In the second heating cycle all the polymers show T_m at a higher temperature compared to that observed in the first heating cycle.
- Copolymers with acid comonomers P(AN/IA) give two melting endotherms. However, in the cooling cycle a single

crystallization exotherm is exhibited. The T_m and the heat of fusion are reduced on copolymerization.
- The exothermic thermo-oxidative degradation takes place in a single step in case of PAN, while two-step exothermic reaction is noted in copolymers.
- Acid comonomers reduce the initiation temperature (T_i) of cyclization/dehydrogenation, rate of reaction and activation energy E_a, where IA seems to be more efficient than MAA.

Acknowledgements

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