

Effect of the Nature and Mole Fraction of Acidic Comonomer on the Stabilization of Polyacrylonitrile

A. K. GUPTA,* D. K. PALIWAL,¹ and P. BAJAJ

Centre for Polymer Science & Engineering, Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi 110 016, India

SYNOPSIS

Differential scanning calorimetry (DSC) and thermogravimetric analysis measurements were used to study the influence of the acidic comonomers acrylic acid, methacrylic acid, and itaconic acid on the exothermic reactions occurring during the heat treatment of acrylonitrile copolymers under air atmosphere. The presence of these reactions was noticed in the DSC exotherms of the copolymers, which appear as doublets. These doublets were resolved into their constituent peaks, arising due to the occurrence of oxidative and cyclization reactions, and the area under the resolved peaks was considered as the extent of the reaction. The comonomers under study were found to enhance the secondary oxidation reactions and retard the extent of cyclization reactions. The degree of cyclization decreases abruptly with the increase in the comonomer content beyond ≈ 2 mol %. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The effects of various comonomers on the behavior of heat-treated polyacrylonitrile (PAN) have been studied by various workers.¹⁻¹⁵ Grassie and colleagues tried to establish the mechanism of reactions occurring during heat treatment of polyacrylonitrile. They have observed that acrylate and methacrylate comonomers^{6,9} have a diluent effect on the exothermic reactions occurring during heat treatment of PAN, whereas acidic comonomers⁶ initiate the cyclization of PAN nitrile groups at lower temperatures. Some interesting findings on the effect of the acidic comonomer during the heat treatment of PAN in the temperature range corresponding to that used for stabilization of acrylic precursors of carbon fibers were reported in our previous publication¹⁶ and used at a fixed mole fraction in that work. In this paper we report how this role of the acidic comonomers varies for dif-

ferent acidic comonomers and at varying mole fractions of these comonomers.

The heat treatment of PAN and its copolymers in the temperature range of thermal stabilization (i.e., 180–300°C) of the precursor fibers is a highly exothermic process and shows prominent differential scanning calorimetry (DSC) exotherms,^{2-6,17,18} which lead to the formation of ladderlike structure.^{6,19,20} The exotherm in air was much broader than in inert (nitrogen) atmosphere and had a doublet-like character. The role of the acidic comonomer in increasing the separation of the two peaks of the doublet was also recognized in the previous paper.¹⁶ The doublet of the exotherm is attributed to the exothermic cyclization and oxidative reactions.¹⁶ The pre-cyclization reactions (namely, dehydrogenation and oxidation) have some advantages in producing regularity and perfection of the cyclized ladderlike structure of the stabilized precursor fibers.

In this paper, we present the study of the effects of three acidic comonomers—acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA)—by varying their mol % in these reactions and examining their effects on DSC exotherms.

¹ Present Address: Department of Education, Ministry of Human Resource Development, Shastri Bhawan, New Delhi 110 001, India.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 59, 1819–1826 (1996)

© 1996 John Wiley & Sons, Inc. CCC 0021-8995/96/121819-08

EXPERIMENTAL

Sample Preparation

PAN homopolymer and the copolymers of acrylonitrile with AA, MAA, and IA, with 1 to 5 percent by weight in the monomer mixture feed, were prepared by the aqueous suspension polymerization method described elsewhere.²¹ These polymers were characterized by intrinsic viscosity (IV) in N:N dimethylformamide (DMF). The copolymer composition was determined using CHN analysis data recorded on a Perkin-Elmer 240C elemental analyzer. The values of IV and comonomer content of the polymers and copolymers thus prepared, and their nomenclature, are shown in Table I.

Measurements

The Perkin-Elmer Delta Series thermal analyzer was used for DSC and thermogravimetric (TG) studies. The samples were scanned on DSC-7 and TGA-7 modules of this thermal analyzer at a heating rate of 5°C/min under air and nitrogen atmospheres.

RESULTS AND DISCUSSION

DSC Studies

DSC exotherms of PAN homopolymer and the copolymers of acrylonitrile with AA, MAA, and IA with

varying comonomer contents are shown in Figures 1-3. The various parameters obtained from these exotherms—namely, temperature of initiation (T_i); temperature of termination, i.e., the final temperature (T_f); their difference ($\Delta T = T_f - T_i$); peak temperature (T_{pk}); and heat evolved (ΔH)—are listed in Table II.

DSC exotherms of PAN and the copolymers of AN with acrylic acids are attributable to the wide variety of reactions occurring in this temperature range and are shown in Figure 4. Broadly, these reactions may be classified as oxidative reactions and cyclization reactions. Oxidative reactions involve a group of reactions (i.e., dehydrogenation and other elimination reactions) which cause the conversion of C—C structure to C=C structure and which generate oxygen-containing groups such as—OH, >C=O, etc. Cyclization reactions lead to the development of ladder structures by oligomerization of nitrile (C≡N) groups. In the PAN homopolymer the cyclization initiates through a radical mechanism, whereas in AN copolymers with acrylic acid, it follows an ionic mechanism. Cyclization reaction initiated through radical mechanism is faster than the cyclization which is initiated through ionic mechanism.

The T_i values for all the copolymers are about 25°C lower than the T_i value for the homopolymer (i.e., 234°C), suggesting a greater ease of initiation of the exothermic process in the presence of all three comonomers studied. Furthermore, for any given copolymer, the T_i does not show much variation with

Table I Composition of Acrylonitrile-Acrylic Acids Copolymers

Polymer	Code	Comonomer in the Feed (mol %)	Comonomer Polymer Content (mol %)	Intrinsic Viscosity (dL g) ¹
PAN	P	—	—	2.87
P (AN-AA)	PA1	0.99	0.99	2.32
P (AN-AA)	PA2	1.48	2.07	2.40
P (AN-AA)	PA3	2.22	2.65	2.61
P (AN-AA)	PA4	2.96	3.18	2.54
P (AN-AA)	PA5	3.70	3.35	2.70
P (AN-MAA)	PM1	0.62	0.97	3.07
P (AN-MAA)	PM2	1.24	1.52	3.11
P (AN-MAA)	PM3	1.86	2.10	3.16
P (AN-MAA)	PM4	2.48	2.95	3.36
P (AN-MAA)	PM5	3.10	3.95	3.44
P (AN-IA)	PI1	0.41	0.69	3.04
P (AN-IA)	PI2	0.82	1.27	2.84
P (AN-IA)	PI3	1.23	1.83	2.75
P (AN-IA)	PI4	1.64	2.15	2.65
P (AN-IA)	PI5	2.05	2.51	2.58

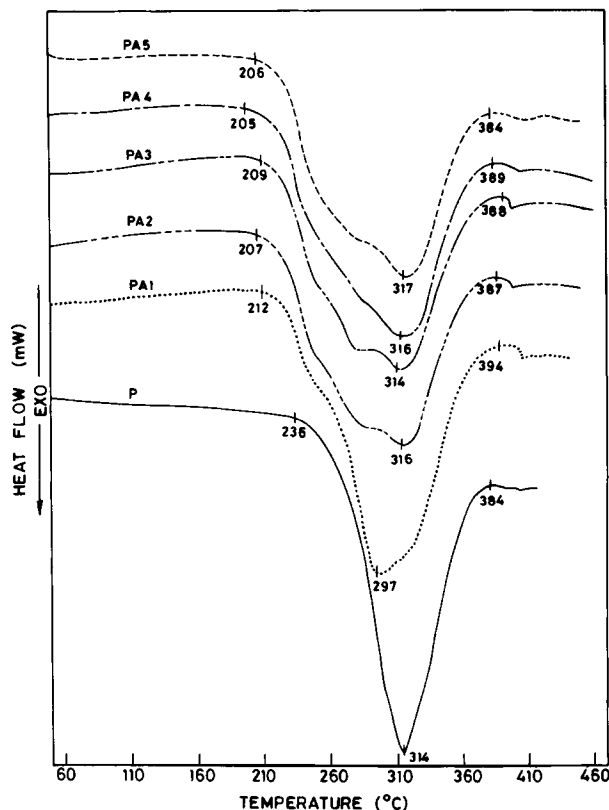


Figure 1 DSC exotherm of PAN homopolymer and P(AN-AA) copolymers recorded under air atmosphere at a heating rate of 5°C/min.

the mol % of the comonomer in the studied range (i.e., 1–4 mol %). This indicates that the initiation of the exothermic reaction is not affected by an increase in the concentration of reaction sites (i.e., the comonomer units, which are believed to initiate the exothermic reaction). In addition to this, acidic comonomers slow the rate of exothermic reaction, as evidenced from the broader exotherm (higher ΔT) in the copolymers than in the homopolymer.

Moreover, DSC exotherms (Figs. 1–3) of the copolymers have the appearance of doublets with superposition of two peaks; however, this doublet characteristic is not very clear in case of the PAN homopolymer. The doublet may be attributed to the exothermic cyclization and oxidative reactions, which may proceed more or less simultaneously; however, initiation of oxidation reaction precedes the onset of cyclization. The first peak of these doublets could be assigned to the oxidative (including dehydrogenation) and cyclization reactions, with the second peak assigned to the secondary oxidative reactions leading to the chain scission which causes the evolution of HCN, CO₂, and CO.^{3,16,22,23} The same observation is also reported in literature,^{3,22,23} which

has been substantiated by TG-FTIR studies in our previous paper.¹⁶ The initiation of these two types of reactions is much more separated in case of the copolymers than the homopolymer, hence the doublet character of the DSC exotherm is more clearly detectable in the copolymer than the homopolymer. The DSC exotherms of P(AN-AA) and P(AN-IA) copolymers have rather a triplet character which slowly converts into the doublet (Figs. 1 and 3) with increased comonomer content. On the other hand, the DSC exotherms of P(AN-MAA) copolymers in all compositions are in the shape of doublet. Greater separation of these reactions and occurrence of some additional reactions in P(AN-AA) and P(AN-IA) copolymers might be responsible for the triplet character in their exotherms. It seems that the overlapping of these reactions (i.e., dehydrogenation and cyclization) increases with increased comonomer contents; this may be responsible for the diminishing of the triplet characteristic of DSC exotherms of P(AN-AA) and P(AN-IA) copolymers with the increase in their comonomer content. In addition, a careful study of Figures 1–3 reveals that the first peak (lower temperature side) decreases whereas the second peak increases in size on in-

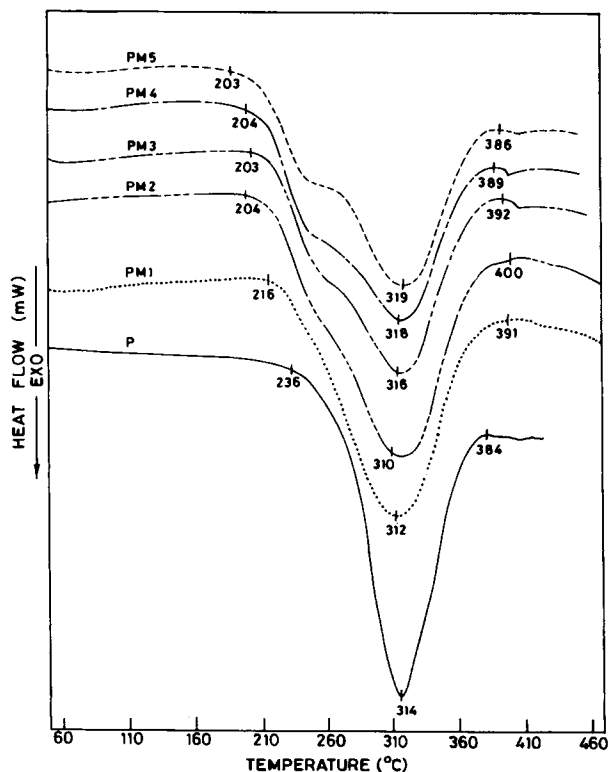


Figure 2 DSC exotherms of PAN homopolymer and P(AN-MAA) copolymers recorded under air atmosphere at a heating rate of 5°C/min.

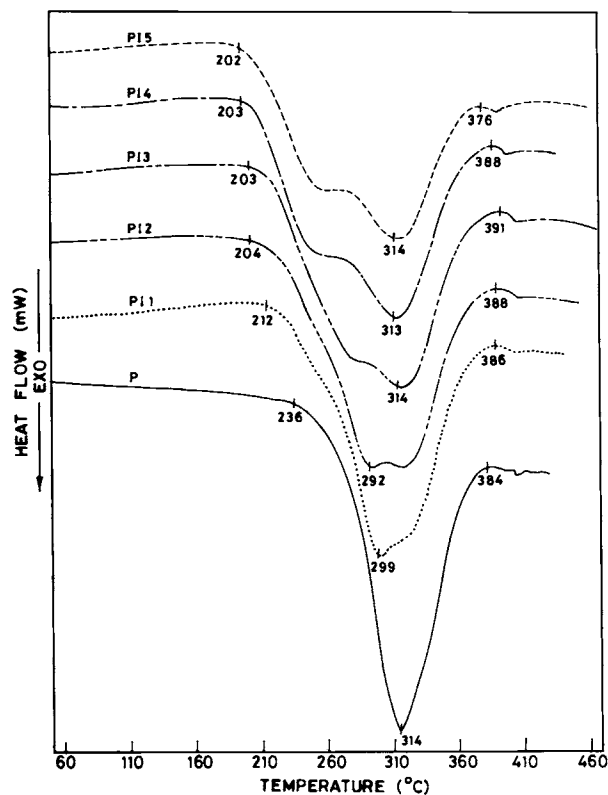


Figure 3 DSC exotherms of PAN homopolymer and P(AN-IA) copolymers recorded under air atmosphere at a heating rate of 5°C/min.

creasing the comonomer content in the copolymer. Thus it may be stated that the reactions occurring at lower temperatures (i.e., cyclization and primary oxidation) are adversely affected by the acidic comonomers, while the reactions which occur at higher temperatures (i.e., secondary oxidation) are favored in the presence of all the three comonomers: AA, MAA, and IA.

Relative Variation of Reactions

The effect of the comonomers (AA, MAA, and IA), on the cyclization and oxidation reactions, occurring during heat treatment of these copolymers under air atmosphere, has been investigated by resolving their DSC exotherms into their constituent peaks. The exotherm was resolved by keeping the peak positions at the temperature of their occurrence in the experimentally observed multiplet and then drawing sufficiently symmetric peaks, such that the total area of the resolved peaks is equal to the area under the entire exotherm. The typical resolved exotherms are shown in Figure 5, where the resolved constituent peaks are labeled as peaks 1 and 2, in increasing

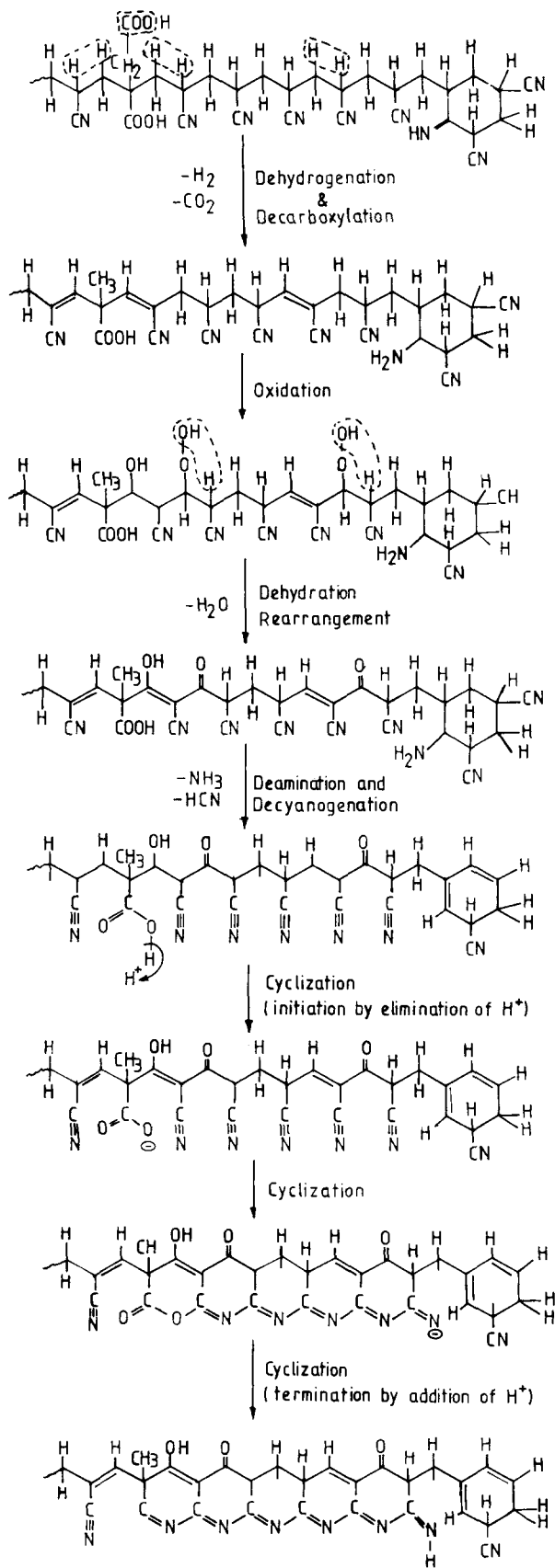
temperature, and are attributed to the oxidation followed by cyclization and secondary oxidation reactions, respectively. A comparison of resolved peaks of the exotherm for the various samples is shown in terms of peak areas and temperatures in Table III.

The fraction of the area under the different resolved peaks with respect to the total area of the exotherm (which is directly proportional to the relative amount of heat of the corresponding reaction, i.e., the extent of that reaction or the extent of the structural changes caused by it) as a function of comonomer content is shown in Figures 6 and 7. The area under peak 1, i.e., the extent of dehydrogenation and cyclization reactions, decreases with the increase of comonomer contents in all the copolymers (Fig. 6). This observation suggests that these acidic comonomers reduce the extent of the cyclization reactions. The reduction of the extent of cyclization by incorporation of the comonomer may be attributed to the interruption in the sequence of CN units in the polymer chain by the comonomer unit, thereby adversely affecting the process of cyclization. Moreover, the decrease in the extent of cyclization reaction as a function of comonomer content is more rapid in case of P(AN-IA) copolymers than those of P(AN-AA) and P(AN-MAA) copolymers, probably due to the bulky size of P(AN-IA), which may cause more steric hindrance. Furthermore, IA

Table II Parameters Obtained from DSC Exotherms of PAN Homopolymer and AN Copolymers with Acrylic Acid, Methacrylic Acid and Itaconic Acid*

Polymer Code	T_i (°C)	T_f (°C)	T_{pk} (°C)	ΔT (°C)	ΔH (J/g)
P	236	384	314	148	4,140
PA1	212	394	297	152	5,063
PA2	207	387	316	180	4,409
PA3	209	388	314	179	4,472
PA4	205	389	316	184	4,625
PA5	206	384	317	178	4,354
PM1	216	391	312	175	4,276
PM2	204	400	310	196	5,198
PM3	203	392	316	189	4,404
PM4	204	389	318	185	4,389
PM5	203	386	319	183	4,124
PI1	212	386	299	174	4,285
PI2	204	388	292	184	4,450
PI3	203	391	314	188	4,691
PI4	203	388	313	185	4,809
PI5	202	376	314	174	3,856

* Recorded under air atmosphere at a heating rate of 5°C/min.



is more effective in decreasing the degree of cyclization above 1.87 mol % in the copolymer. A similar observation was also reported by Muller.²⁵

The variation in the area under peak 2, which is attributed to secondary oxidation reactions¹⁶ with the comonomer content in the copolymers, is shown in Figure 7. It is apparent from the data given in Table III that the extent of secondary oxidation is greater in the copolymers than the homopolymer (Table III) and further increases on increasing the comonomer content in the polymers. This implies that the acidic comonomers promote the secondary oxidation reactions. Moreover, the effectiveness of the comonomers under study in enhancing the degree of secondary oxidation reactions is in the following order: IA > MAA > AA (see Figure 7). This is probably due to the increase in the amorphous phase in the polymer by incorporation of the comonomer unit,²⁵ which may provide greater opportunity for the molecules to come into contact with air. P(AN-IA) with IA as comonomer may have a higher amorphous phase due to the much bulkier size of the IA molecule than MAA and AA, hence may exhibit a higher degree of oxidation reactions. The bulky size of the IA molecule, $\text{CH}_2 = \text{C}(\text{COOH})$, suggests that it may affect the ordering of polymer chains in PAN to a greater extent than AA and MAA do. Thus, its small contents may cause comparatively loose packing of polymer chains. Air may have an opportunity to come in contact with groups present in the loosely packed zone (amorphous phase).

Thermogravimetric Studies

Typical TG curves of PAN homopolymer and AN copolymers with AA, MAA, and IA having approximately same composition (≈ 2 mol % of comonomer) recorded under air atmosphere at a programmed heating rate of $5^\circ\text{C}/\text{min}$ are shown in Figure 8. It is apparent from these curves that the weight loss occurs in three steps. The first weight-loss step is up to 300°C , where it is nominal and occurs at a very slow rate. The rate of weight loss is quite fast in the second step, which extends up to 410°C . The TG curves indicate that the incorporation of the acidic comonomer reduces the rate of weight loss in the second step.

Figure 4 Reaction scheme showing the various exothermic reactions occurring during heat treatment of polyacrylonitrile in the range of stabilization.

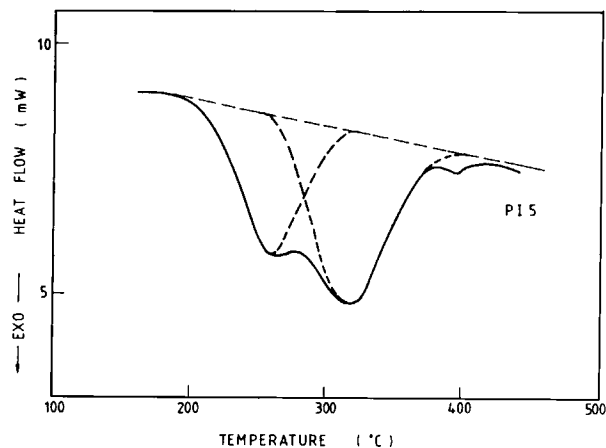


Figure 5 Typical resolved DSC exotherm of P(AN-IA) copolymer PI5.

Figure 9 illustrates the percentage weight loss in the copolymers of AN with AA, MAA, and IA in air, as a function of comonomer content. The weight loss in the copolymers is less than in the homopolymer, and it decreases with increase in the comonomer content up to ≈ 2 mol %; thereafter, it increases. The decrease in the weight loss on incorporation of the acidic comonomer might be due to

Table III Percentage Area and the Peak Temperature of the Peaks Resolved from DSC Exotherms of PAN Homopolymers and AN Copolymers with Acrylic Acid, Methacrylic Acid, and Itaconic Acid

Polymer Code	Area in Percentage		Peak Temperature (°C)	
	Peak 1	Peak 2	Peak 1	Peak 2
P	63	37	314	338
PA1	52.5	47.5	296	318
PA2	50	50	200	315
PA3	50	50	200	315
PA4	46	54	276	316
PA5	44	56	280	317
PM1	56	44	288	313
PM2	52	48	299	313
PM3	46	54	260	315
PM4	39	61	260	315
PM5	31	69	252	319
PI1	53	47	299	320
PI2	52	48	291	317
PI3	49.5	50.5	284	315
PI4	43	57	248	317
PI5	31	68	260	312

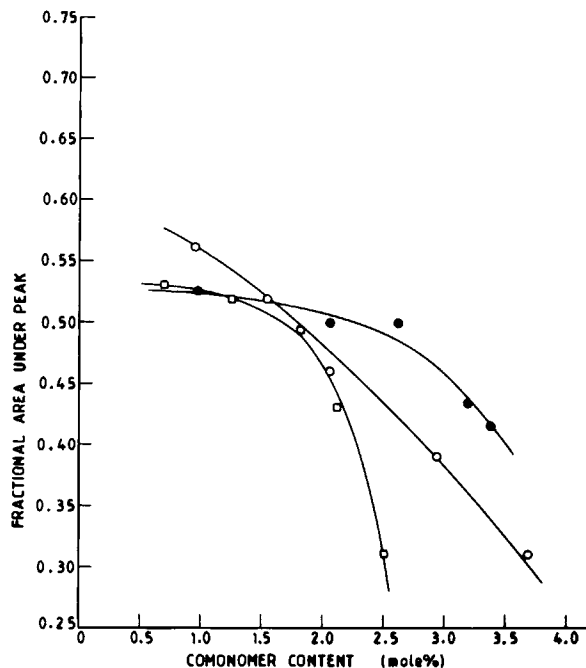


Figure 6 Variation of the extent of cyclization reactions with comonomer content, represented in terms of the area under the exotherm peak: P(AN-AA) ●, P(AN-MAA) ○, and P(AN-IA) □.

the increase in the dehydrogenation reactions, which slow the rate of highly exothermic cyclization.²⁶ Thus acidic comonomers control the evolution of

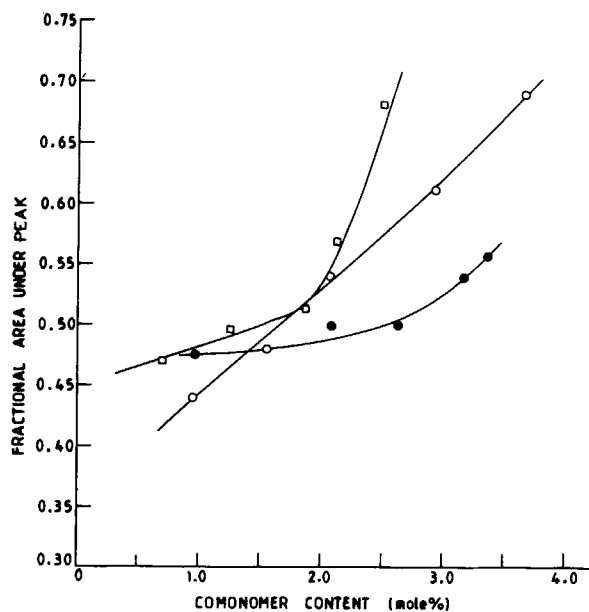


Figure 7 Variation of the extent of secondary oxidation reactions with comonomer content, represented in terms of the area under the exotherm peak: P(AN-AA) ●, P(AN-MAA) ○, and P(AN-IA) □.

heat and thereby minimize the chain scission reactions, leading to the formation of volatile products such as NH_3 and HCN and causing weight loss. But these acidic comonomers also act as reaction sites for the cyclization reaction,⁵ and with increased comonomer content these reaction sites also increase, which leads to the initiation of cyclization reaction at a number of places in the chain simultaneously. This results in the evolution of a sufficient quantity of heat which might increase the formation of volatile products such as NH_3 and HCN , leading to the increase in weight loss. This may be the reason for the increased weight loss when the comonomer content is increased beyond a certain limit, i.e., ≈ 2 mol %.

CONCLUSIONS

The acidic comonomers bring down the temperature of initiation (T_i) and rate of the exothermic process, which occur during the heat treatment of AN copolymers. The T_i decreases considerably at the initial stage of the incorporation of comonomer into the homopolymer, and varies little with the increase in the comonomer content. The exothermic reactions (dehydrogenation, cyclization, and oxidation) are also separated in the DSC exotherms. The degree of cyclization reaction decreases with the increase in the comonomer content, and the extent of the oxidative reactions increases with increased comonomer content. Interestingly, the degree of cy-

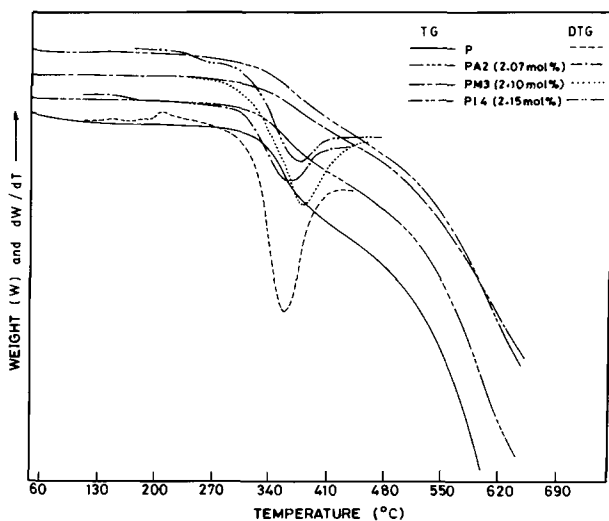


Figure 8 Thermogravimetric curves (TG and DTG) of P, PA2, PM3, and PI4 polymers recorded under air atmosphere at a heating rate of $5^\circ\text{C}/\text{min}$. X-axis scale identical for all four cases but shifted to reveal separation.

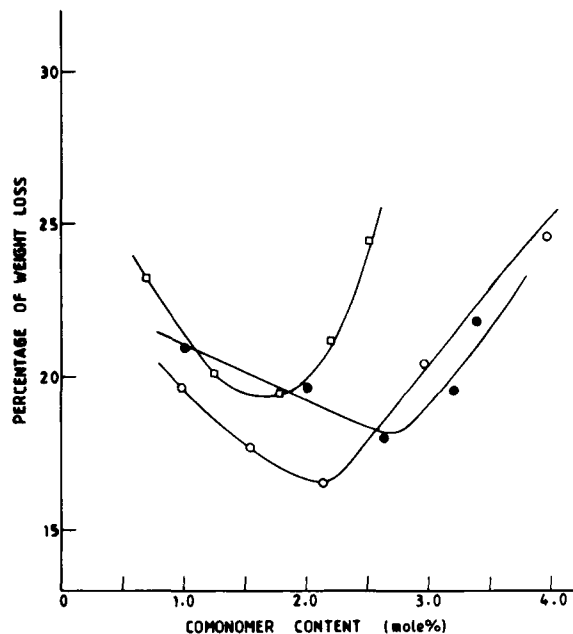


Figure 9 Weight loss in the P(AN-AA), P(AN-MAA), and P(AN-IA) copolymers as a function of comonomer content at 410°C . P(AN-AA) ●, P(AN-MAA) ○, and P(AN-IA) □.

clization decreases abruptly on increasing the comonomer content beyond 1.87 mol % in P(AN-IA) copolymers. The effect of the three comonomers on these reactions is in the following order: IA > MAA > AA.

REFERENCES

1. N. Grassie and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).
2. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **6**, 13277 (1970).
3. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **7**, 1357 (1971).
4. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **7**, 1503 (1971).
5. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 243 (1972).
6. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 257 (1972).
7. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 868 (1972).
8. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **9**, 113 (1973).
9. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **9**, 507 (1973).
10. P. Bajaj and D. C. Gupta, *Eur. Polym. J.*, **15**, 271 (1979).

11. P. Bajaj, P. C. Jain, and D. Gangopadhyay, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 595 (1979).
12. P. Bajaj, D. C. Gupta, and A. K. Gupta, *J. Appl. Polym. Sci.*, **25**, 1973 (1980).
13. P. Bajaj and D. C. Gupta, *J. Macromol. Sci., Chem.*, **A19**, 509 (1983).
14. P. Bajaj and M. Padmanabhan, *Eur. Polym. J.*, **20**, 513 (1984).
15. P. Bajaj and M. Padmanabhan, *Eur. Polym. J.*, **21**, 93 (1985).
16. A. K. Gupta, D. K. Paliwal, and P. Bajaj, *J. Appl. Polym. Sci.*, **58**, 1161 (1995).
17. E. Fitzer and D. J. Muller, *Carbon*, **13**, 63 (1975).
18. Z. Bashir, *Carbon*, **29**(8), 1081 (1990).
19. A. K. Gupta, D. K. Paliwal, and P. Bajaj, *J. Macromol. Sci. Rev.*, **C31**(1), 1 (1991).
20. J. B. Donnet and O. P. Bahl, in *Encyclopedia of Physical Sciences and Technology*, Vol. 2, 1987, p. 515.
21. P. Bajaj, D. K. Paliwal, and A. K. Gupta, *J. Appl. Polym. Sci.*, **49**, 823 (1993).
22. W. N. Turner and F. C. Johnson, *J. Appl. Polym. Sci.*, **13**, 2073 (1969).
23. Y. Tsuchiya and K. Sumi, *J. Appl. Polym. Sci.*, **21**, 975 (1977).
24. A. K. Gupta and R. P. Singhal, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 2243 (1983).
25. T. Muller, *International Fibre J.*, **46** (1988).
26. A. K. Gupta, P. Bajaj, and D. K. Paliwal, *Proc. of Intl. Symposium on Carbon*, Tsukuba, Japan, 1980, p. 238.

Received November 3, 1994

Accepted June 25, 1995