

# Effect of Comonomers on Thermal Degradation of Polyacrylonitrile

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## Synopsis

The thermal degradation of polyacrylonitrile and copolymers of acrylonitrile (AN) with each of vinylacetate (VAC), methallyl sulfonate sodium salt (MASS), and 2-acrylamido 2-methyl propane sulfonate sodium salt (2-AMPSS) i.e., P(AN-VAC), P(AN-MASS), P(AN-AMPSS), and P(AN-VAC-MASS), has been investigated using the technique of thermogravimetry and differential scanning calorimetry (DSC). The initial decomposition temperature (IDT) and integral procedural decomposition temperature (IPDT) for all the copolymers are less than that for polyacrylonitrile irrespective of the nature of the vinyl comonomers. TGA thermograms indicate faster rate of degradation in copolymers compared to polyacrylonitrile. Variation in the glass transition temperature is correlated to the polarity of the functional groups in the polyacrylonitrile copolymers.

## INTRODUCTION

The mechanism of thermal degradation of polyacrylonitrile and its copolymers have been reported by Grassie et al.<sup>1-5</sup> They have illustrated the effect of several comonomers on the rapid exothermic oligomerization of nitrile groups, characteristic of polyacrylonitrile. According to Grassie et al., acrylate and methacrylate comonomers<sup>2,5</sup> have a diluent effect on the exothermic reaction without inhibiting or initiating the nitrile rearrangements. Acidic comonomers<sup>2</sup> have a strong initiating effect on the exothermic reaction. Chlorinated comonomers as vinylidene chloride<sup>5</sup> reduce the intensity of the exothermic reaction, but do not effectively block the oligomerization of nitrile groups in polyacrylonitrile copolymers.

Bajaj and co-workers<sup>6-11</sup> have studied the effect of following comonomers; vinylsilane, hydroxy methacrylates, and their silylated derivatives, haloalkylacrylates, and methacrylates on thermal behavior of polyacrylonitrile. Thermal degradation of polyacrylonitrile and its terpolymers has also been reported by Tomescu et al.<sup>12</sup> Effect of the acrylonitrile-methyllyl sulfonate sodium salt (AN-MASS) ratio on the glass transition temperature of the copolymers by DTA was studied by Romanko et al.<sup>13</sup> We now report the relative influence of vinyl comonomers, e.g., vinylacetate, methyllyl sulfonate sodium salt (MASS), and 2-acrylamido 2-methyl 1-propane sulfonate sodium salt (AMPSS) on thermal behavior of polyacrylonitrile.

## EXPERIMENTAL

Monomers MASS and AMPSS received from M/s Montefibre, Italy through M/s J. K. Synthetic Ltd., Kota, India were used without further purification.

Purification of monomers AN, VAC, and catalyst potassium persulfate ( $K_2S_2O_8$ ) were reported previously.<sup>14</sup> Sulfur dioxide was prepared by reaction of sodium sulfite and concentrated  $H_2SO_4$ . Ferrous sulfate ( $FeSO_4 \cdot 7H_2O$ ) was used without further treatment.

### Copolymerization

The copolymerisation of acrylonitrile with VAC, MASS, and AMPSS were carried out at  $45^\circ C$  using  $K_2S_2O_8-SO_2-FeSO_4$  as redox initiator system. The conditions and details of polymerizations were given in an earlier publication.<sup>14</sup>

The composition of copolymers was determined from their nitrogen content estimated by Kjeldahl's method.

### Characterisation

The molecular weight of acrylic copolymers was expressed in terms of specific viscosity measured at 0.1 g/dL in DMF at  $25^\circ C$  by a standard technique using a Ubbelohde suspension level viscometer.

Glass transition temperature of acrylic polymers were determined using a Perkin-Elmer DSC-2 Model. The thermogravimetric analysis was carried out with Perkin-Elmer thermobalance in static air from room temperature to  $800^\circ C$  at a heating rate of  $10^\circ C/min$ . Thermal stability of polymers is expressed in terms of IPDT calculated according to Doyle's method.<sup>15</sup>

## RESULTS AND DISCUSSION

In Tables I and II are listed a summary of various comonomers, polymerization conditions, and PAN copolymers used in conjunction with this study. Redox initiator system  $K_2S_2O_8-SO_2-FeSO_4 \cdot 7H_2O$  was selected due to high polymer conversion at a commercial scale and the system is presently used at M/s J. K. Synthetics Ltd., Kota (India), for whom this project was under-

TABLE I  
Copolymerization of Acrylonitrile with Other Comonomers

Sample no.	Comonomers	Initiator system	Polymerization conditions	
1. VAC	$\begin{array}{c} CH_2=CH \\   \\ OCOCH_3 \end{array}$	$K_2S_2O_8 - SO_2 - FeSO_4$	Temp pH	$45^\circ C$ 3.0
2. MASS	$\begin{array}{c} CH_3 \\   \\ CH_2=C \\   \\ CH_2SO_3Na \end{array}$		W/M $K_2S_2O_8$	3.0 1%
3. 2-AMPSS	$\begin{array}{c} CH_2=CH \\   \\ CONHC(CH_3)_2CH_2SO_3Na \end{array}$		$SO_2$  Slurry polymerization in water	3%

TABLE II  
Characterization of Polyacrylonitrile and Its Copolymers

Polymer	Composition			Specific viscosity $\eta_{SP}^a$
	Nitrogen content (%)	Comonomer in copolymer (mol %)	Copolymer conversion (%)	
Polyacrylonitrile	26.4	—	85.0	0.150
P(AN-VAC)	24.6	4.4	81.0	0.146
P(AN-VAC)	23.2	7.9	78.0	0.140
P(AN-MASS)	24.0	3.2	71.0	0.180
P(AN-MASS)	23.1	4.6	58.0	0.250
P(AN-AMPS)	24.0	2.3	75.0	0.160
P(AN-AMPS)	22.8	4.3	68.0	0.190
P(AN-VAC-MASS) <sup>b</sup>	24.4	4.4	80.0	0.146
P(AN-VAC-MASS) <sup>c</sup>	24.3	4.4	80.0	0.142

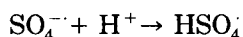
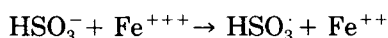
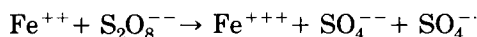
<sup>a</sup> $\eta_{SP}$  (Specific viscosity) measured at 0.1 g/dL in DMF at 25°C.

<sup>b</sup>MASS = 0.26 mol %.

<sup>c</sup>MASS = 0.42 mol %.

taken. In this system  $K_2S_2O_8$  acts as a catalyst,  $SO_2$  as an activator, and  $FeSO_4$  as promotor for free radical generation in aqueous medium.

Mechanism of free radical generation using this system was studied in detail by many investigators.<sup>16,17</sup> In these studies bisulfite was used in place of sulfur dioxide but the essential mechanism remains the same. Catalyst and activator employed as redox initiators for free radical polymerization serve as the prime source of functional end groups in acrylic polymers:



Two radicals,  $HSO_4^{\cdot}$  and  $HSO_3^{\cdot}$ , generated by  $K_2S_2O_8$  and  $SO_2$ , respectively, initiate polymerization and become strong acid groups at chain ends in acrylic polymers.<sup>17</sup> The presence of these end groups in acrylic fibers is responsible for their basic dye ability.

It is noted that slurry polymerization of acrylonitrile with these vinyl sulfonates and vinylacetate gives polymers of high molecular weight as indicated by their higher specific viscosities at 0.1 g/dL in DMF at 25°C. These polymers are of spinnable fiber grade having molecular weight in the range  $1.0-2.0 \times 10^5$ . Peebles<sup>18</sup> has reported the kinetics of polymerization of the acrylonitrile-vinylacetate system using the peroxydisulfite-bisulfite-iron system and calculated the molecular weight of P(AN-VAC) copolymer using the Cleland and Stockmayer equation. Since values of constants for calculating molecular weight are not available for these polymers, P(AN-MASS) and P(AN-AMPSS) molecular weights could not be calculated and specific viscosities in DMF at 25°C are reported.

P(AN-MASS) copolymers are of highest specific viscosities in comparison to P(AN-AMPSS) and P(AN-VAC) copolymers at approximate equal molar comonomer present in the PAN chain (Table II).

### Differential Scanning Calorimetry (DSC)

DSC data for PAN and its copolymers are given in Table III.  $T_g$  data of the copolymers from DSC studies show lower  $T_g$  in P(AN-VAC), P(AN-MASS), and P(AN-AMPSS) copolymers compared to that of polyacrylonitrile. A decrease in  $T_g$  of P(AN-VAC) copolymers may be due to the introduction of comonomer, VAC into PAN chain, which reduces the intermolecular interactions between the molecular chains due to structure loosening. Further the reduction of  $T_g$  is higher as the amount of VAC into PAN increases.  $T_g$  of polyvinylacetate<sup>19</sup> was reported to be 28°C; thus introduction of VAC into PAN chains will reduce the  $T_g$ .

Similarly introduction of MASS into PAN chains reduce the  $T_g$  of P(AN-MASS) copolymers.  $T_g$  of AN-MASS copolymers ( $M_2 = 3.2$  mol %) is 75°C. With the increase in the amount of MASS into PAN,  $T_g$ , however, increases instead of reducing as seen by higher  $T_g$  value, i.e., 80°C of AN-MASS copolymer ( $M_2 = 4.6$  mol %). Increase in  $T_g$  value of this copolymer may be related to the polar sulfonate groups associated with the MASS comonomer.<sup>13</sup> These two factors (decrease in intermolecular interactions due to introduction of MASS and effect of polar groups) act differently on  $T_g$  and, depending on the MASS content, one factor or the other will predominate and decide the  $T_g$  of the polymer. Thus introduction of MASS into PAN first decreases  $T_g$  of the copolymers and further increase in MASS amount leads to  $T_g$  at higher temperatures.

Introduction of AMPSS into PAN chains led to decrease in the  $T_g$  of PAN copolymers. A decrease in  $T_g$  may be explained on the basis attributed to the chemical nature and size of side group



As the bulkiness of the side substituent increases, total cohesive energy

TABLE III  
Thermal Degradation of Polyacrylonitrile and Its Copolymers

Polymer	Comonomer in copolymer (mol %)	$T_g$ (°C)	IDT (°C)	DT at different wt losses (°C)				$D_{\max}$ (°C)	IPDT (°C)
				10%	30%	50%	80%		
PAN	—	105	300	340	525	590	670	395	581
P(AN-VAC)	4.4	90	290	330	500	565	615	380	552
P(AN-VAC)	7.9	80	260	325	475	540	595	295	515
P(AN-MASS)	3.2	75	285	335	500	550	606	350	545
P(AN-MASS)	4.6	80	275	315	480	535	575	305	477
P(AN-2AMPSS)	2.3	88	275	330	475	540	595	295	505
P(AN-2AMPSS)	4.3	82	245	315	450	535	580	260	457
P(AN-VAC-MASS) <sup>a</sup>	4.4	—	295	340	480	545	595	380	536

<sup>a</sup> MASS = 0.26 mol %.

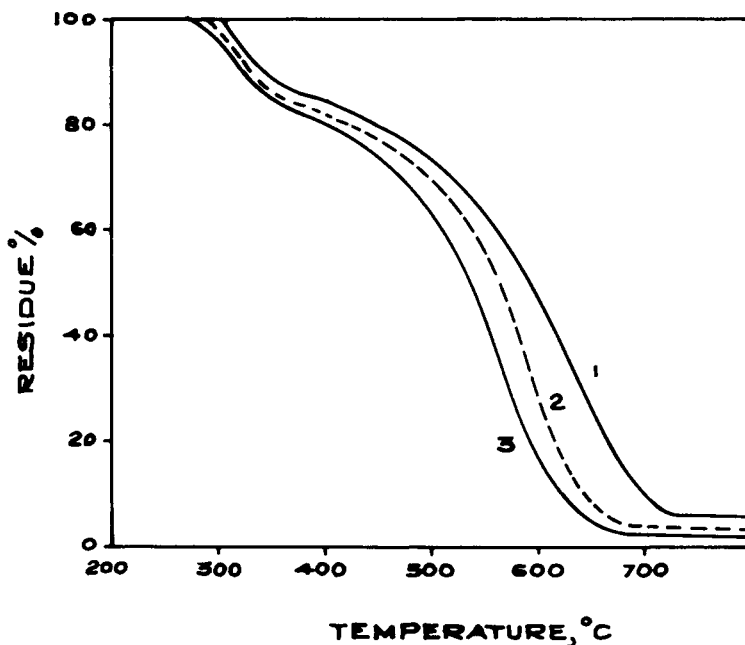


Fig. 1. TGA thermograms for (1) PAN; (2) P(AN-VAC),  $m_2 = 4.4$  mol %; (3) P(AN-VAC)  $m_2 = 7.9$  mol %.

density of the polymer system decreases, leading to low  $T_g$  values. In fact by introducing bulky side groups, chain mobility is hindered sterically. However, in the present case, bulky side substituent (AMPSS) reduces the intermolecular interaction considerably, thus leading to low  $T_g$  values.<sup>8,9</sup> The presence of polar groups ( $-\text{SO}_3\text{Na}$ ) being remotely attached to the vinyl bond does not influence the value of  $T_g$  as observed for AN-MASS copolymers.

#### Thermogravimetric Analysis

Effect of vinyl acetate and vinyl sulfonates (MASS and AMPSS) on thermal stability of polyacrylonitrile was studied by thermogravimetric analysis. Typical thermograms obtained by plotting percentage residual weight against temperature for PAN and P(AN-VAC) are given in Figure 1.

TGA curves clearly show the two stages of the oxidative degradation for PAN. The weight loss (20%) in stage I may be associated with the nitrile oligomerization which produces volatile products ( $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{CH}_3\text{CN}$ , etc.) and subsequent chain scission.<sup>10,11</sup> Since this stage of degradation is related to the nitrile oligomerization, cyclization of nitrile groups is mostly intramolecular.

The stage II of degradation in PAN is related to the thermal oxidative reactions leading to greater weight loss compared with the thermal degradation reactions.

The thermal analysis data in Table III show that threshold degradation temperature is lowered by the introduction of vinyl comonomers in PAN. The IDT of P(AN-VAC),  $m_2 = 4.4$  mol %, is 290°C, in P(AN-MASS),  $m_2 = 4.6$  mol %, IDT is 275°C, and IDT of P(AN-MASS),  $m_2 = 4.3$  mol %, is 245°C in

comparison to IDT of PAN (300°C). The present study indicates that introduction of these comonomers enhances the rate of degradation. The higher rate of degradation observed in the copolymers may be due to the higher amount of chain scission instead of nitrile oligomerization.

Further copolymers are less thermally stable than PAN as indicated by lower  $D_{\max}$  and IPDT values due to their less compact structure than PAN (Table III). P(AN-AMPSS) copolymers are of poorest thermal stability due to the bulky nature of AMPSS:



This may be due to the size of AMPSS being bulkier than VAC and MASS, the steric requirement for cyclization being less easily satisfied in P(AN-AMPSS) than the rest of the copolymers of AN with VAC and MASS; hydrogen abstraction and chain scission become more predominant, which may be responsible for poor thermal stability of these copolymers.<sup>8</sup>

These copolymers may be arranged in order of decreasing thermal stability as per their IPDT values in the following order:



The above thermal stability data led us to the conclusion that nature of comonomer plays an important role in changing the thermal stability of polyacrylonitrile.

Authors are thankful to Dr. K. R. K. Rao, Director, ERDL, Pune, for his permission to publish this paper.

### References

1. N. Grassie and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).
2. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 257 (1972).
3. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 868 (1972).
4. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **9**, 113 (1973).
5. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **9**, 507 (1973).
6. P. Bajaj and D. C. Gupta, *Eur. Polym. J.*, **15**, 271 (1979).
7. P. Bajaj, P. C. Jain and D. Gangopadhyay, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 595 (1979).
8. P. Bajaj, D. C. Gupta, and A. K. Gupta, *J. Appl. Polym. Sci.*, **25**, 1973 (1980).
9. P. Bajaj and D. C. Gupta, *J. Macromol. Sci. Chem.*, **A19**, 509 (1983).
10. P. Bajaj and M. Padmanaban, *Eur. Polym. J.*, **20**, 513 (1984).
11. P. Bajaj and M. Padmanaban, *Eur. Polym. J.*, **21**, 93 (1985).
12. M. Tomescu, I. Demetrescu, and E. Segal, *J. Appl. Polym. Sci.*, **26**, 4103 (1981).
13. O. I. Romanko, N. N. Zakhrova, I. N. Andreeva, L. A. Volkov, A. T. Kalashnik, and M. P. Zverev, *Fibre Chem.*, **3**, 197 (1983) [*Khim. Volokna*, **3**, 17 (1982)].
14. D. C. Gupta, *J. Appl. Polym. Sci.*, **30**, 4187 (1985).
15. C. D. Doyle, *Anal. Chem.*, **33**, 77 (1961).
16. P. Fritzsche and J. Ulbricht, *Faserforsch. Textiltech.*, **15**, 93 (1964).
17. *Encycl. Ind. Chem. Analysis*, Wiley-Interscience, New York, 1967, Vol. 4, p. 227.
18. L. H. Peebles, Jr., *J. Appl. Polym. Sci.*, **17**, 113 (1973).
19. *Encyl. Polym. Sci. and Technol.* Interscience, New York, 1966, Vol. 5, p. 435.

Received February 26, 1988

Accepted June 20, 1988