Melting Behavior of Acrylonitrile Polymers

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ABSTRACT: Melting of acrylonitrile polymers (which have a tendency to degrade before melting) was detected during their heat treatments at high heating rates (i.e., 80° C min⁻¹ or above). The probable reason for their melting at such higher heating rates is discussed. The melting behavior of acrylonitrile polymers was also studied by sealing the polymer with water in a specially designed pressure pan and then heating it in the differential scanning calorimetry cell. The phenomenon of melting is found to be influenced by the rate and environment of heating, molecular weight, and nature of the comonomer. Water suppresses the melting point (T_m) of the polymer due to its plasticization effect; however, it causes the hydrolysis of some CN groups during this process of melting. The nature of melting endotherm has been correlated with the structure of the polymer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2703–2709, 1998

Key words: melting; acrylonitrile polymers; differential scanning calorimetry

INTRODUCTION

Polyacrylonitrile (PAN) and its comonomers at low comonomer content tend to degrade well below their melting point, because they undergo certain exothermic reactions leading to the formation of ladder structure.¹⁻⁴ This typical thermal behavior of these acrylonitrile (AN)-based polymers render them difficult to process. Hinrichsen⁵ reported the melting of these polymers on heating at very rapid heating rates (i.e., above 100°C min⁻¹). Frushour¹ developed a new thermal analytical technique to melt and investigate the structure of AN homopolymer and its attendant fiber-forming copolymers. In this technique, the polymer is mixed with water and sealed in a capsule that is heated in the differential scanning calorimetry (DSC) cell. Water acts as a plasticizing agent and minimizes dipolar interactions among CN groups, thereby bringing down the melting point (T_m) of the polymer. On the basis of this technique, melt spinning of some AN-based polymers was also tried,^{4,6,7} where the other plasticizing agents, such as water-soluble polyethylene glycol, were used. In the present study, we have explored both techniques: i.e., heating the polymer at high heating rates, as well as heating the polymer with water in a sealed pressure pan. An attempt has been made to investigate the effect of the heating rate, medium, molecular weight, and comonomers on the melting behavior of some AN-based polymers used for fiber manufacture.

EXPERIMENTAL

Samples

AN homopolymer and AN-acrylic acid (AA) copolymer were prepared by the method described elsewhere.⁸ A mixture of AN and AA containing

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Polymer	Composition (mol %)	Intrinsic Viscosity (dlg ⁻¹)	
PAN	AN-100	1.88	
PAN	AN-100	2.87	
PAN	AN-100	3.26	
PAN	AN-100	3.44	
	AN-96.65		
P(AN-AA)	AA-3.35	2.70	
	AN-92.17		
	VA-7		
P(AN-VA-SMS)	SMS-0.30	1.10	

Table I Characteristics of PAN Homopolymers, AN Copolymer with AA, and AN-Terpolymer with Vinyl Acetate (VA) and Sodium Methallyl Sulfonate (SMS)

3.75 mol % of distilled AA was used for the synthesis of P(AN-AA) copolymer. AN terpolymer with vinyl acetate and sodium methallylsulfonate was received from J. K. Synthetics Ltd. [Kota (Rajasthan) India]. These polymers were characterized for intrinsic viscosity in N : N dimethylformamide. The composition of the polymer was estimated on the basis of their CHN analysis data recorded on Perkin–Elmer 240C elemental analyzer. The intrinsic viscosity, molecular weight, and composition of the polymers are given in Table I.

Measurements

DSC measurements were done on a Perkin– Elmer Delta Series thermal analyzer using a DSC-7 module. Dry samples were scanned under a nitrogen and air atmosphere at a heating rate of 80° C and 160° C min⁻¹.

Polymer samples wetted by water were placed in a specially designed gold-plated pressure pan capable of withstanding the vapor pressure of water up to 250°C and fits in the sample holder of the DSC module. An equal amount of water was added to the polymer, and then the pan was sealed. The sealed pan was left for 12 h and then scanned at a heating rate of 5°C min⁻¹, which was much lower than the heating rate used for dry samples (*viz.* 80° and 160°C min⁻¹).

Infrared spectra of the samples before and after the heat treatment in the pressure pan were recorded on Nicolet 5-DX Fourier transform infrared spectrometer. The transmission mode was used on finely powdered samples prepared as KBr pellets. X-ray diffraction patterns of the powdered specimens were obtained on Rigaku X-ray diffractometer, using nickel-filtered CuK_{α} radiation. Crystallinity was calculated from the X-ray scans by dividing them into crystalline and amorphous regions, according to the method suggested by Bell and Dumbleton.⁹ Average crystal size (L_c) was calculated by using the Scherrer equation¹⁰:

$$L_c = K\lambda/B \cos \theta$$

where the constant *K* is taken as 0.89, *B* is the half-width of the diffraction peak in radiation, θ is half of the diffraction angle of the concerned diffraction maxima, and λ is the wavelength of the X-rays.

RESULTS AND DISCUSSION

DSC Studies

Nitrogen Atmosphere

DSC scans of the PAN homopolymer at a heating rate of 80° and 160°C min⁻¹ under the nitrogen atmosphere are illustrated in Figure 1. These scans show an endotherm just followed by an exotherm. The endotherm may be attributed to melting of the PAN homopolymer, whereas the exotherm indicates the occurrence of certain exothermic cyclization reactions¹¹ of the PAN homopolymer at this temperature. The scanning electron micrographs shown in Figure 2 of the sample taken out after the DSC experiment show



Figure 1 DSC scans of a PAN homopolymer recorded at a heating rate of 80° C min⁻¹ and 160° C min⁻¹ under a nitrogen atmosphere.



Figure 2 Scanning electron micrograph of the droplet of the PAN homopolymer formed as a result of its melting.

drop-like structures that support the melting of PAN powder under DSC experiments. The melting point (T_m) , heat of fusion ΔHf and half-width of the peak are given in Table II.

Generally, based on some literature reports,⁵ it is believed that PAN and its copolymers undergo melting only at very high heating rates (i.e., 80°C or above) under a nitrogen atmosphere; whereas, at slow heating rates, they degrade (undergo exothermic cyclization reactions) before melting.⁵ During the heat treatment of AN polymers, the exothermic cyclization process starts in the amorphous phase; and, consequently, the heat is liberated, which causes the slow collapse of the ordered phase (i.e., the crystals), leading to the migration of AN units into the disordered (amorphous) phase.¹⁰ These AN units instantaneously undergo the formation of the ladder structure due to the exothermic cyclization reactions. However, if the polymer is heated at higher heating rates (80°C min⁻¹ or above), the temperature of the polymer very quickly reaches the melting point (T_m) before the exothermic degradation reactions could approach the ordered phase (crystalline phase) from the disordered amorphous phase; thus melting of the polymer is observed. When the polymer is heated at 80°C min⁻¹, melting point is observed as 340°C; whereas, at a heating rate of 160°C min^{-1} , it is 365°C. This difference in the values of T_m is because of the lag in the temperature due to the increase in the heating rate. It is also important to mention that the value of ΔHf (heat of fusion) is low (i.e., $1,059 \text{ J mol}^{-1}$) at lower heating rate (i.e., at 80° C min⁻¹), compared with the higher heating rate (i.e., 160°C \min^{-1}), where it is 1,852 J mol⁻¹. The halfwidth of the peak increases on increasing the heating rate. At a heating rate of 80° C min⁻¹, the exothermic cyclization reactions of the amorphous phase nearly approach the ordered phase; thus, decomposition of small and defective crystallites starts before the temperature of the polymer touches T_m . This may be responsible for the lower value of $\Delta H f$, because only bigger and comparatively perfect crystallites are left for melting. However, at a heating rate of 160°C min⁻¹, the temperature of the polymer rises so fast that it does not allow the exothermic reaction to reach even the small and defective crystallites; thus, they also melt along with more perfect and bigger crystals. This seems to be responsible for the higher values of ΔHf and more half-width of the melting exotherm in the case of higher heating rates.

Table II	Parameters Obtained from	n the Melting Endotherms	of the PAN Homopolymer
Recorded	l under a Nitrogen and Air	Atmosphere at 80°C min ⁻¹	and 160°C min ^{-1}

	T_i (°C)		T_f (°C)		T_m (°C)		$\Delta H f (\text{J mol}^{-1} \text{ of AN units})$		Half-width (Arb. Units)	
Atmosphere	$80^{\circ}C$ min ⁻¹	160°C min ⁻¹	80° min ⁻¹	$160^{\circ}\mathrm{C}$ min^{-1}	80° min^{-1}	$160^{\circ}\mathrm{C}$ min^{-1}	80° min ⁻¹	$160^{\circ}\mathrm{C}$ min ⁻¹	80° min^{-1}	$160^{\circ}\mathrm{C}$ min^{-1}
Nitrogen 1st run	329	349	344	377	340	365	1059	1852	3.5	6
Nitrogen		351		375		365		328		6
Air		362		376		369		375		5



Figure 3 DSC scan of the second run of the PAN homopolymer recorded at a heating rate of 160° C min⁻¹ under a nitrogen atmosphere.

The PAN homopolymer was heated in the DSC cell up to 500°C at a heating rate of 160°C min⁻¹ under a nitrogen atmosphere and then suddenly cooled. This sample was thermally scanned under a nitrogen atmosphere at a programmed heating rate of 160°C min⁻¹, and the DSC scan is shown in Figure 3, which also shows a melting endotherm followed by an exotherm. The value of $\Delta H f$ $(328 \text{ J mol}^{-1} \text{ of AN units})$ is lower this time, compared with the value of $\Delta H f$ of the polymer in the first run (i.e., 1,852 J mol⁻¹); however, the T_m and half-width of the peak remain unchanged. This implies that, in the first run, the entire polymer was not degraded, even after melting; and the undegraded polymer underwent crystallization during sudden cooling, and it formed crystals similar to that of the nonheat-treated polymer, as evident from similar values of T_m and half-width.

Air Atmosphere

Melting behavior of the PAN homopolymer was also studied under a air atmosphere, where it was heated at a heating rate of 80° C min⁻¹ and 160° C min⁻¹, and DSC scans so obtained are presented in Figure 4. It is apparent from these DSC curves that, in case of heating at a rate of 80° C min⁻¹, the melting endotherm appears after the exotherm, whereas the melting endotherm precedes the exotherm in case of heating the polymer at a rate of 160° C min⁻¹. Heat treatment of the PAN homopolymer under the air atmosphere causes certain additional exothermic reactions that initiate at lower temperature and do not occur under a nitrogen atmosphere.¹² The lower initiation temperature of these additional degradation reactions (which also start in the amorphous phase) causes the appearance of the exotherm before the melting endotherm. The appearance of the melting endotherm after the cyclization exotherm also indicates that cyclization reactions occur in the amorphous phase as also observed by Ko and colleagues.¹⁰ On the other hand, in case of the higher heating rates (i.e., 160° C min⁻¹), the polymer attains the melting temperature so quickly that the magnitude of these additional reactions is too low to be detected in the form of a DSC exotherm at this scale. Furthermore, like the case of the nitrogen atmosphere, the values of T_m , ΔHf , and half-width are lower (Table II) in the DSC exotherm recorded at 80°C min⁻¹ heating rate, compared with the DSC exotherm recorded at 160°C min⁻¹ heating rate for the same reason given in case of the nitrogen atmosphere. Because additional reactions (which occur under the air atmosphere) start at a lower temperature, their rate increases more rapidly with the rise in temperature. Therefore, they could reach the ordered phase much earlier and damage the crystallites before the polymers achieve melting temperature. Thus, at the time of melting, only bigger and perfect crystals are left for melting. This may be the reason for the very low value of ΔHf (375 J mol⁻¹ of AN units) under the air atmosphere, compared with its value $(1,852 \text{ J mol}^{-1} \text{ of AN})$ units) under the nitrogen atmosphere.

Effect of Comonomer

The effect of comonomers on the melting behavior of AN copolymer with AA and AN terpolymer



Figure 4 DSC scans of the PAN homopolymer recorded at a heating rate of 80° C min⁻¹ and 160° C min⁻¹ under a air atmosphere.



Figure 5 DSC scans of AN-AA copolymer and ANvinyl acetate-sodium methallyl sulfonate (AN-VA-SMS) terpolymer at a heating rate of 160° C min⁻¹ under a nitrogen and air atmosphere.

with vinyl acetate and sodium methallyl sulfonate was investigated by their thermal scanning. The DSC scans of these polymers under nitrogen and air atmosphere at a heating rate of 160°C min⁻¹ are shown in Figure 5. The AN copolymer with AA does not show any melting endotherm in its DSC scan, whereas a small and comparatively broader (as compared with the melting endotherm of homopolymers) endotherm is apparent in the DSC scan of a AN terpolymer with vinyl acetate and sodium methallyl sulfonate. T_m , ΔHf , and half-width obtained from the melting endotherms of the terpolymer under a nitrogen and air atmosphere are given in Table III.

Whereas the acidic comonomers initiate the exothermic cyclization reaction in the AN copolymers at lower temperatures,¹³ this reaction becomes faster than the reaction in the PAN homopolymer near the crystal decomposition temperature. This might cause the approach of this exothermic degradation reaction to the ordered phase before the polymer attains its melting tem-



Figure 6 X-ray diffractograms of a PAN homopolymer and AN terpolymer with vinyl acetate VA and sodium methallyl sulfonate (SMS).

perature; thus, melting of the polymer is not observed. In the case of the terpolymer, neither vinyl acetate nor sodium methallyl sulfonate seem to lower the temperature of initiation for exothermic cyclization reaction; thus, the melting of this polymer is observed.

The melting point (T_m) of the AN terpolymer (307°C) is well below that of the PAN homopolymer (365°C), and the melting endotherm also starts at a lower temperature in the case of the terpolymer. This lowering in the T_i of melting endotherm and T_m may be attributed to the incorporation of the comonomers in the polymer chain that might bring down the average crystal size and may also generate the defects in the crystals/ordered phase, thereby decreasing the T_m .¹⁴ The crystallinity index of the PAN homopolymer and AN terpolymer as determined from their X-ray diffractograms (Fig. 6) was 0.49 and 0.24, respectively. The direct correlation of ΔHf with the degree of crystallinity suggests that the observed endotherm is attributable to the melting of crystallites or ordered regions of these homopolymers and copolymers.

Table III Parameters Obtained from Melting Endotherms of AN-Terpolymer with Vinyl Acetate and Sodium Methallyl Sulfonate at a Heating Rate of 160°C min⁻¹

Heating Atmosphere	T_i (°C)	T_f (°C)	T_m (°C)	ΔHf (J mol ⁻¹ of AN units)	Half-width (Arb. Units)
Nitrogen	283	331	307	$\frac{1471.8}{554.38}$	8
Air	290	328	307		5



Figure 7 Melting and crystallization peaks of the PAN homopolymer (wetted with distilled water in a high-pressure pan) recorded at a heating rate of 5° C min⁻¹.

High-Pressure DSC Studies

Homopolymer

The PAN homopolymer was placed in a specially designed gold-plated high-pressure pan, where an equal amount of double-distilled water was added to it and then the pan was sealed. The sealed pan was placed in the DSC cell, and heating and cooling cycles of the sample at a programmed heating rate of 5°C min⁻¹ were recorded (which are illustrated in Fig. 7). The first run of the heating cycle shows a sharp endotherm with its peak at 184°C due to the melting of the PAN homopolymer; on cooling the sample with the same rate, one exotherm with its peak temperature of 148°C and the other having a peak temperature of 169°C appeared due to the crystallization of the polymer melt.¹ The T_m observed through this technique is considerably lower than that observed through ordinary DSC technique at higher heating rates. This is probably due to the plasticizing effect of water (which reduces the polar interactions among nitrile groups), as well as to the temperature lag because of the difference in the heating rates. The second run of the heating cycle shows two melting endotherms with their peaks at 160° C and 185° C. The similar observation was also made by Frushour,¹ who has attributed the small peak at 148° C (in the cooling cycle) to the formation of some unknown structure on cooling the melt, and suggested that the melting of this structure was responsible for the small endotherm at 160° C in the second run of the heating cycle.

The value of ΔHf (2,343 J mol⁻¹ of AN units) is more for melting in the first run, compared with that of the second run (i.e., 1,812.6 J mol⁻¹ of AN units). This decrease in the value of ΔHf indicates the decrease in the crystallinity of the polymer, probably because of the hydrolysis of the CN groups by water under such a high pressure at 200°C.¹⁵ The occurrence of the hydrolysis of some of the CN groups of PAN is also supported by the decrease in the ratio of the intensity of the CN absorption band at 2,240 cm⁻¹ (i.e., $I_{2,240}/I_{1,450}$), from 0.87 for the nonheat-treated PAN homopolymer to 0.52 for the case of the PAN homopolymer taken out of the high-pressure pan after the heating and cooling cycles.

Copolymer

Like the case of DSC studies at high heating rates, $(>80^{\circ}\text{C min}^{-1})$ under nitrogen atmosphere, melting of the copolymer P(AN-AA) could not be observed. However, terpolymer P(AN-vinyl acetate-sodium methallyl sulfonate) showed melting. It seems that the acidic comonomer not only facilitates the cyclization reaction,¹⁶ but also promotes the rate of hydrolysis of the AN units, as reported in the literature,^{17,18} that the hydrolysis of AN units is facilitated in the acidic medium. Thus, this enhanced hydrolysis might be responsible for the absence of melting in case of the P(AN-AA) copolymer. The melting endotherm of terpolymer is shown in Figure 8. This endotherm is broader, starts at a lower temperature, and has a lower peak temperature, compared with those for the AN homopolymer. This is because of the increase in the variation of crystal size and generation of defects in the crystals due to the incorporation of the comonomer.

CONCLUSIONS

Melting of AN polymers may be noticed at higher heating rates (i.e., $>80^{\circ}$ C min⁻¹) under a nitro-



Figure 8 Melting peak of the AN terpolymer with vinyl acetate (VA) and sodium methallyl sulfonate (SMS), wetted (with distilled water in high-pressure pan) and recorded at a heating rate of 5° C min⁻¹.

gen atmosphere, probably because-at such higher heating rates—the polymer attains the melting temperature before degradation reactions could approach the ordered (crystalline) phase. The process of melting is also found to be influenced by atmosphere (i.e., air or nitrogen) and the nature of the comonomers. The value of ΔHf observed to be greater if the polymer is heated under inert (nitrogen) atmosphere and increases by increasing the rate of heating. The acidic comonomers are found to affect the melting adversely probably because they may initiate the exothermic degradation reaction at lower temperatures, whereas other comonomers (vinyl acetate and sodium methallyl sulfonate), which do not facilitate the degradation reactions, bring down the melting point (T_m) of the polymers. Like the case of other polymers, in the case of AN polymers, the nature of the melting endotherm reflects on the structure of the polymer. The T_m of the polymer can be considerably decreased by heating the polymer in a pressure pan in the presence of water, which acts as a plasticizing agent and lowers the interactions among the polar nitrile groups of AN polymers. However, under these conditions of high pressure, some of the nitrile groups might undergo hydrolysis, which is further enhanced in the presence of acidic comonomers that inhibit the melting.

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