

# Effect of Solvent or Hydrophilic Polymer on the Hydration Melting Behavior of Polyacrylonitrile

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## SYNOPSIS

The effect of solvent, DMF, and hydrophilic polymer on the hydration melting behavior of Tae Kwang polyacrylonitrile-based copolymer (T-PAN) was investigated by DSC measurement. The melting temperature ( $T_m$ ) of T-PAN was sharply lowered by incorporating water under autogenous pressure, but leveled off above a critical water content: 23 wt %. However, an additional incorporation of DMF into the hydrated T-PAN further lowered the  $T_m$ , even above the critical water content. On the other hand, addition of water-soluble poly(acrylic acid), poly(vinyl alcohol), and poly(ethylene glycol) or water-swelling starch to the hydrated PAN slightly raised the  $T_m$ . © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polyacrylonitrile (PAN) exhibits an unusually high melting temperature ( $T_m$ ) of 320°C in comparison with other aliphatic polymers.<sup>1,2</sup> The interactions between polar nitrile groups have been recognized to be responsible for the high  $T_m$ .<sup>1</sup> Coxe<sup>3</sup> first found that an addition of a small amount of water to PAN depressed the  $T_m$  enough to permit melt spinning. The depression of  $T_m$  has been ascribed to the formation of some types of complex or association between PAN and water during the melt process.

Direct evidence for the association of nitrile groups of PAN molecules with water molecules has been claimed in patents.<sup>4,5</sup> The Raman active nitrile stretching vibration of PAN is reported to shift from 2234 to 2050  $\text{cm}^{-1}$  upon melting in the presence of water. In addition, Frushour<sup>6</sup> attempted to trace the polymer-water interaction by adopting a wide-line proton NMR. The melting process has turned out to be accompanied by an extreme narrowing of the polymer proton resonance line, which simply indicates an increase in the segmental mobility of polymer chains. However, any concomitant broadening

of the water resonance signal is not reported, which might have been expected if the water molecules were tightly bound to the nitrile groups in the melt. Thus, a formation of some kind of complex or association between the polymer and water has named the melting process the "hydration of PAN."<sup>5</sup>

The hydration of PAN occurs only within a certain elevated temperature range and under at least autogenous pressure. Under these conditions, to one's surprise, a simple extrusion of the hydrated PAN melt led to production of acrylic fiber by manipulating processing parameters.<sup>7</sup> We reported the thermal stability of the PAN melt formed by hydration<sup>8</sup> and the properties of acrylic fiber obtained by simple extrusion.<sup>9</sup> This study investigates the effect of additional additives, a solvent, and several hydrophilic polymers on the hydration behavior of PAN.

## EXPERIMENTAL

### Materials

A suspension-grade acrylonitrile polymer from Tae Kwang Industrial Co. (South Korea) was used, denoted as "T-PAN." According to the supplier, T-PAN is a copolymer composed of 88 wt % acrylonitrile and 12 wt % vinyl acetate. The average mo-

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lecular weight ( $M_v$ ) determined by the intrinsic viscosity at 30°C in dimethylformamide (DMF) was calculated to be 82,000 g/mol by following expression<sup>10</sup>:

$$[\eta] = 2.43 \times 10^{-4} M_v^{0.75}$$

As water-soluble additives, 25 wt % aqueous poly(acrylic acid) (PAA) solution, poly(vinyl alcohol) (PVA) of 88% hydrolysis, and poly(ethylene glycol) (PEG) from Aldrich Chemical Co. were tested, whose average molecular weights were 90,000, 25,000, and 8,000 g/mol, respectively. Soluble starch from Aldrich Chemical Co. was the water-swallowable additive.

### DSC Measurement

DSC measurements were carried out using a Perkin-Elmer DSC 7 calorimeter. Since autogenous vapor pressure of water is generated in the melt state of hydrated acrylonitrile polymers, Perkin-Elmer large-volume stainless-steel capsules (Part 319-0218) were used. T-PAN and water were uniformly mixed and approximately 40–70 mg of the mixture are packed into the bottom of the two-piece capsule. The  $T_m$  and crystallization temperature ( $T_c$ ) were taken as the maxima in the endothermic peak of second heating scan and the exothermic peak of first cooling scan, respectively. The heat of fusion ( $\Delta H_f$ ) is calculated from the peak area using an indium standard.

## RESULTS AND DISCUSSION

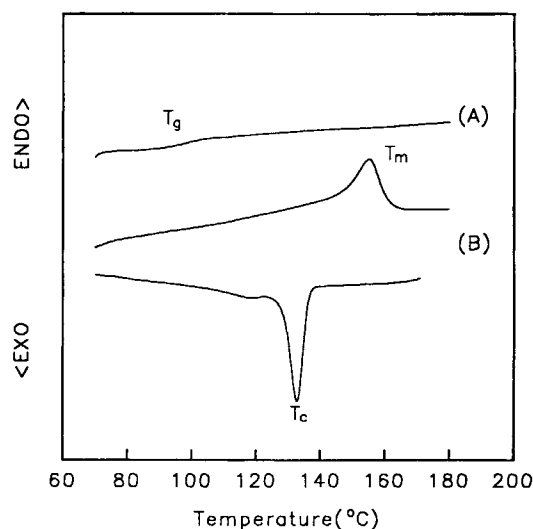
### Melting Behavior of Hydrated T-PAN

It is well recognized that PAN undergoes a cyclization degradation reaction at elevated temperatures in which the adjacent nitrile groups on the polymer chain react to form six-membered rings. This reaction is highly exothermic and tends to obscure the melting endotherm if the heating rate is low, e.g., 10–20°C/min, in the DSC measurement. However, it is possible to record a partial melting endotherm prior to the onset of the reaction exotherm at high heating rates because the cyclization reaction does have an induction time associated with it. At the low heating rate of 10°C/min, the dry T-PAN yielded a sharp reaction exotherm without leaving any trace of melting behavior, whereas a well-defined endotherm was observed at the heating rate of 80°C/min in the vicinity of 275°C.

DSC thermograms of dry T-PAN and wet T-PAN containing 23 wt % water are shown in Figure 1. As predicted, introducing water into T-PAN under autogenous pressure reduces the  $T_m$  from 275 to 155°C. In addition, a definite crystallization exotherm is observed at 132°C in the cooling scan.

Up to the water content 23 wt %, the  $T_m$  of T-PAN is very sharply decreased as water is added. Above the critical water content, ca. 23 wt %, a plateau region of constant  $T_m$  is observed. The implication of the plateau region may be the polymer–water phase separation, i.e., the critical water content is regarded as the very amount of water that is required for the onset of phase separation. It is interesting to see that the critical water content is equivalent to the theoretical value calculated on the assumption that one nitrile group of PAN is combined with one water molecule.

As one may imagine, the nitrile group associates with water through the hydrogen bond. At the room temperature, only the noncoupled nitrile groups would be associated with water, which make up the amorphous region of acrylonitrile polymer. As recognized, the crystalline region of acrylonitrile polymer is made up of coupled nitrile groups, which refers to those nitrile groups along the chains of acrylonitrile polymer molecules coupled by dipole–dipole interaction, i.e., where one nitrile group is attracted to, and associates with, the closest nitrile group or nitrile groups. At the atmospheric temperatures, most acrylonitrile polymers exist in a molecular configuration wherein nitrile groups along one molecular chain are coupled with nitrile groups



**Figure 1** DSC thermograms of (A) T-PAN and (B) wet T-PAN containing 23 wt % of water.

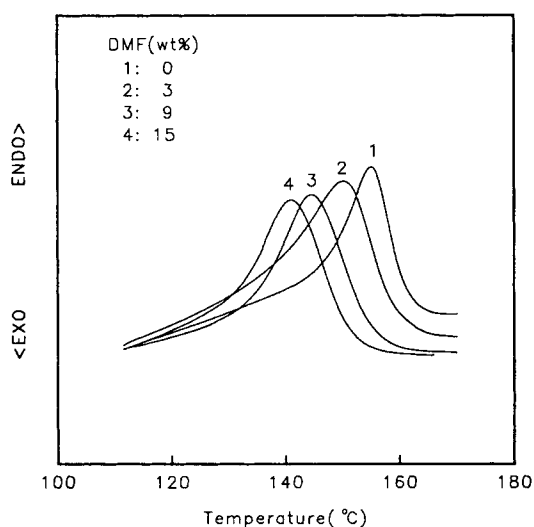
along one or more adjacent molecular chains. Consequently, it may not be possible for water to associate with coupled nitrile groups. At the elevated temperature, however, water would penetrate into the crystalline region to act as a diluent since the coupling strength between nitrile groups becomes much reduced. Owing to the dilution action, the association reaction is endothermic.

Krigbaum and Tokita<sup>1</sup> proposed that the coupled nitrile groups are not arranged freely but distorted due to the repulsions between them, which would make the molecule chains form a semirigid helical structure. They attributed the unusually high  $T_m$  of PAN to the chain rigidity resulting from the repulsions rather than from the attractions. It is worth noting in this conjuncture that variation of  $T_m$  with water content suggests that the hydration of coupled nitrile groups has a more prevalent effect on the  $T_m$  depression than does that of noncoupled ones.

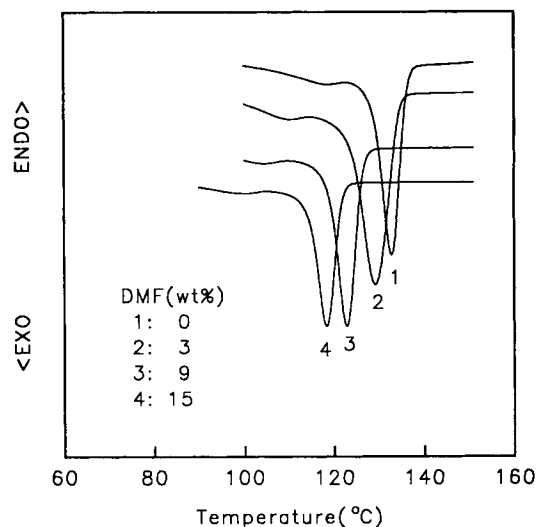
#### Effect of DMF on the Hydration Process of T-PAN

Krigbaum and Tokita<sup>1</sup> examined the melting and gelation behaviors of PAN prepared from concentrated solution in DMF and  $\gamma$ -butyrolactone. It is reported that the  $T_m$  of the PAN gels is increased rapidly with increasing the polymer concentration. This suggests that an incorporation of additional solvent has a profound influence not only on the melting behavior of PAN itself but also on the hydration process of PAN.

Figures 2 and 3 show the variation of the melting endotherms and crystallization exotherms of T-PAN



**Figure 2** Variation of the melting endotherm of T-PAN containing 23 wt % of water with the DMF content calculated on the basis of the polymer.



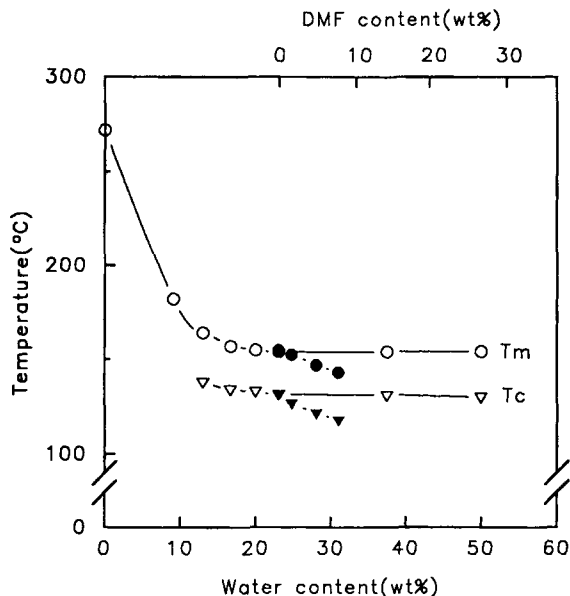
**Figure 3** Variation of the crystallization exotherm of T-PAN containing 23 wt % of water with DMF content calculated on the basis of the polymer.

containing 23 wt % water with the DMF content. Additional incorporation of DMF further shifted both  $T_m$  and  $T_c$  to lower temperatures. In other words, a combined use of water and DMF produces a synergistic effect on the plasticization of T-PAN. The substantial reduction in  $T_c$  by incorporating DMF is ascribed to the fact that the solvent reduces the crystallization rate through retarding the dehydration process. Figure 4 summarizes the effect of DMF and extra water on  $T_m$  and  $T_c$  of T-PAN containing 23 wt % water. As forementioned, the T-PAN with 23 wt % water does not give rise to a further depression of  $T_m$ , although extra water is incorporated but produces a constant  $T_m$ . However, an incorporation of DMF into the T-PAN containing 23 wt % water gives rise to an additional depression of  $T_m$ .

#### Effect of Hydrophilic Polymers on the Hydration Process of T-PAN

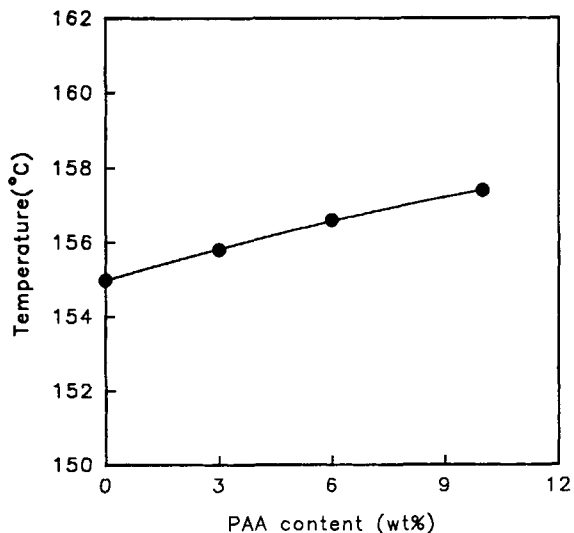
In the melt-spinning process of PAN, controlling the rate of water evaporation of the extrudate is of primary importance. Since the hydrophilic polymers such as water-soluble and water-swallowable polymers are capable of absorbing water, they are expected to be useful for controlling the evaporation rate of water. Three water-soluble polymers, PAA, PVA, and PEG, and a water-swallowable starch were tested. These polymers turn out to be immiscible with T-PAN over the blending compositions observed.

The  $T_m$  of T-PAN saturated with water is plotted against the PAA content in Figure 5. In contrast to

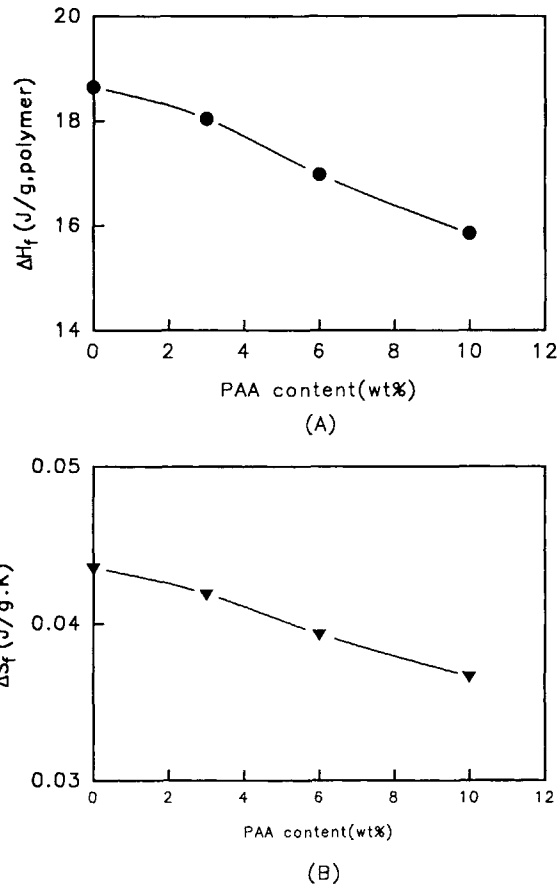


**Figure 4** Effect of incorporating DMF and extra water into the T-PAN containing 23 wt % of water on  $T_m$  and  $T_c$ ; open symbols represent T-PAN containing only water, and closed symbols represent T-PAN containing 23 wt % water and DMF (both DMF and water contents are calculated on the basis of the polymer).

the case of solvent addition, the  $T_m$  of saturated T-PAN is increased with increasing the PAA content. Figure 6 exhibits the effect of PAA on the melting behavior of T-PAN containing various levels of water. The  $\Delta H_f$  is decreased as the PAA content is increased, whereas the  $T_m$  is increased as shown in



**Figure 5** Dependence of the  $T_m$  of T-PAN containing 23 wt % of water on the PAA content calculated on the basis of the polymer.



**Figure 6** Variation of the heat of fusion ( $\Delta H_f$ ) and entropy of fusion ( $\Delta S_f$ ) of T-PAN containing 23 wt % of water with PAA content calculated on the basis of the polymer.

Figure 6(A). Accordingly, the entropy of fusion ( $\Delta S_f$ ), estimated from the following equation, is also diminished with increasing the PAA content as presented in Figure 6(B):

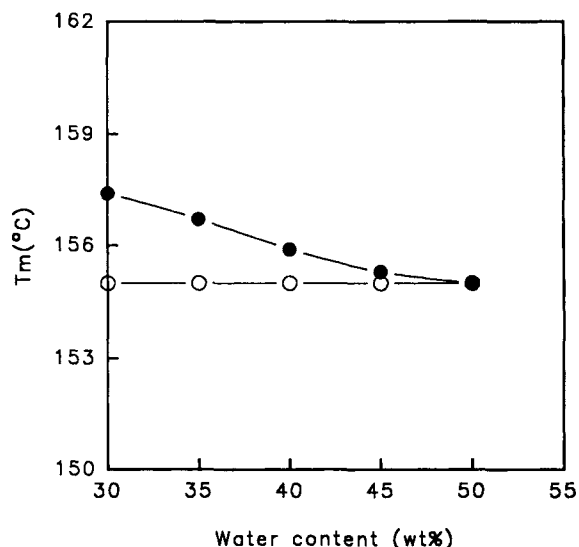
$$T_m = \frac{\Delta H_f}{\Delta S_f}$$

Since it is obvious that the  $\Delta H_f$  of the PAN/water mixture reflects the total absorbed energy during the hydration process between the nitrile group and water, two possible reasons for the decrease of  $\Delta H_f$  with PAA content may be supposed. One is a reduction of the degree of hydration, and the other is a weakening of nitrile interaction of T-PAN molecules by the addition of PAA. If PAA is miscible with T-PAN, the  $T_m$  of wet T-PAN would be depressed as expected in the Flory theory.<sup>11</sup> However, T-PAN has turned out to be immiscible with PAA in the solution of DMF; this suggests that of the

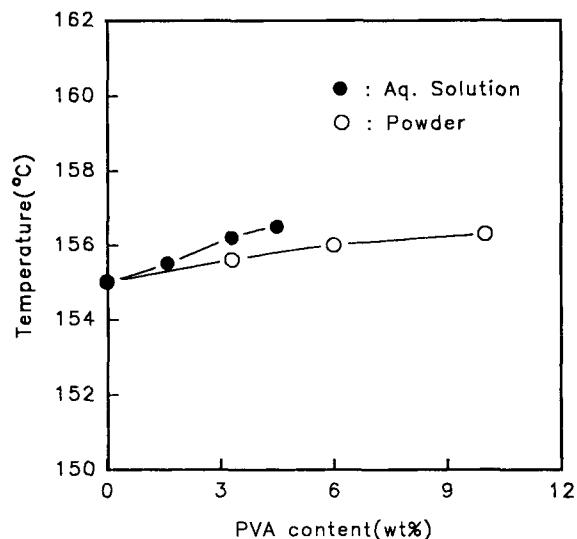
two possible reasons the former is more reasonable. The decrease of  $\Delta S_f$  indicates that the polymer chain in the melt state became less mobile as the PAA content was increased because  $\Delta S_f$  is a parameter related to the chain flexibility. In other words, an addition of PAA reduces the effect of hydration that makes the PAN chains move freely by removing the dipole-dipole interactions of nitrile groups.

In addition, it should be noted that in the given water content of 23 wt % an addition of PAA would reduce the amount of water to hydrate with PAN because PAA absorbs a part of water. Accordingly, the two reactions of hydration and absorption may take place in a competitive way. In consequence, the increase of  $T_m$  by addition of PAA is attributable mainly to the hygroscopicity of PAA. However, if an extra water is added to PAN, enough to make up for the amount of water absorbed by PAA, the  $T_m$  is lowered again and, finally, returns to the original value as shown in Figure 7.

PVA imparts a similar effect to PAA on the melting behavior of T-PAN saturated with water, as depicted in Figure 8. The  $T_m$  of the saturated T-PAN is decreased with increasing PVA content. Additionally, as shown in the figure, the physical state of added PVA affects the efficiency of the plasticization of PAN. As seen, an aqueous PVA solution is more effective than is a powdery PVA. It is due mainly to the difference in the degree of mixing of water and PVA.

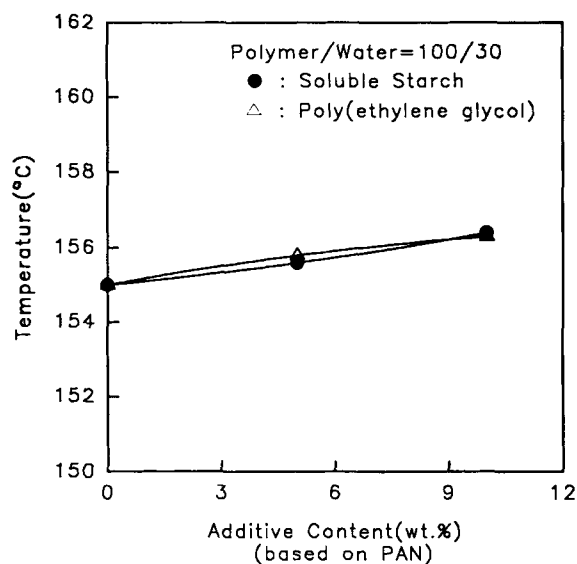


**Figure 7** Variation of the  $T_m$  of T-PAN with the water content showing the effect of adding extra water to T-PAN saturated with water; open circles represent T-PAN containing 10 wt % of PAA and closed circles represent T-PAN without PAA.



**Figure 8** Effect of PVA on the  $T_m$  of T-PAN containing 23 wt % of water showing the effect of the physical state of added PVA (the PVA content is calculated on the basis of T-PAN).

Nishio et al.<sup>12,13</sup> reported that both PVA and PAN are miscible with cellulose because the hydroxyl groups in PVA and the nitrile groups in PAN can give rise to hydrogen bonding with the hydroxyl groups in cellulose. This suggests that there may be a miscibility between PVA and PAN. However, PAN and its copolymers exhibit little miscibility with PVA in the solution blending experiments using



**Figure 9** Effect of the content of soluble starch and PEG content on the  $T_m$  of T-PAN containing 23 wt % of water (the additive content is calculated on the basis of T-PAN).

DMSO as a cosolvent (Nishio et al. used DMAc-LiCl as a cosolvent because cellulose is insoluble in DMSO). Hence, it is obvious that the increased  $T_m$  of saturated T-PAN with incorporating PVA is also obliged to the water absorption by PVA. Other hydrophilic polymers such as starch and PEG exhibit a similar effect on the hydration melting behavior of T-PAN to PAA and PVA, as illustrated Figure 9.

## CONCLUSIONS

It is very essence of the melt-spinning process of hydrated PAN to control the rate of water evaporation. Lowering the  $T_m$  of hydrated PAN is of help to the melt spinning because a reduction in the spinning temperature suppresses the evaporation rate of water. In addition, an incorporation of hydrophilic polymers to the hydrated PAN is also helpful in controlling the evaporation rate of water, although they raise  $T_m$  a little. A relevant formulation by adopting these results possesses a strong potential for the production of PAN fibers with desirable properties by the melt-spinning process.

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