

## Thermal Analysis of Polyacrylonitrile. Part I. The Melting of Polyacrylonitrile

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### Synopsis

The melting point of polyacrylonitrile can be determined directly by differential thermal analysis, provided that a sufficiently fast heating rate is used. The experimental value of 326°C agrees well with predicted values of the melting point. The disparity between oxidative and thermal decomposition of the polymer is noted.

### INTRODUCTION

The thermal decomposition of polyacrylonitrile (PAN) is not a simple reaction. Hay<sup>1</sup> considers that at least three distinct reactions are competing in the purely thermal decomposition, while Friedlander and co-workers<sup>2</sup> have demonstrated the complexity of the oxidative discoloration reaction.

The effect of these reactions in differential thermal analysis (DTA) is an exotherm, at about 300°C, of such magnitude that, in normal practice, only major thermal effects are unequivocally identified. Schwenker and Beck<sup>3</sup> studied the DTA of PAN and Orlon and reported the exotherm, and Thompson<sup>4</sup> has shown that the shape and position of the exotherm is influenced by the molecular weight of the polymer. Recently Slade<sup>5</sup> has shown that a relatively small endotherm, before the main exotherm, can be assigned to the melting point in acrylonitrile-vinyl acetate copolymers. Using the Flory relationship he extrapolated from the melting point of these copolymers a melting point for PAN of 322°C, which was in good agreement with the value of 317°C determined by Krigbaum and Tokita<sup>6</sup> using dilatometric methods.

In the present work it is shown that, at sufficiently fast heating rates, DTA allows direct determination of the melting point of PAN before gross reaction occurs. Some observations are made on the thermal decomposition of PAN and a possible second-order transition is noted.

### EXPERIMENTAL

**Polyacrylonitrile (PAN).** The polymer was obtained from the Mitsubishi Rayon Company Limited as a continuous filament fiber. Finish oils were removed from the fiber by ethanol-benzene (1:2) extraction.

**Thermal Analysis.** The thermograms were obtained on a du Pont Model 900 differential thermal analyzer system. For the isothermal studies, and the associated dynamic thermograms at a heating rate of  $20^\circ/\text{min}$ , the standard cell assembly was used; an unweighed fiber sample was wound closely around the thermocouple and inserted in the 2-mm sample tube. An oxygen-free nitrogen atmosphere and a glass bead reference sample were used, and the timing of the induction period was as previously described.<sup>7</sup> In dynamic studies in air, the DSC cell was used. In this case the unweighed sample was chopped into short lengths and encapsulated in crimped aluminum pans to obtain maximum thermal contact. An empty pan provided the reference.

## DISCUSSION

In dynamic DTA studies it was shown that changing the atmosphere from air to nitrogen had only a small effect on the thermograms before the onset of exothermic decomposition of PAN and Orlon.<sup>3,8</sup> There are major differences between the oxidative<sup>2</sup> and thermal<sup>1</sup> decompositions of PAN, and these are more obvious in isothermal DTA studies.

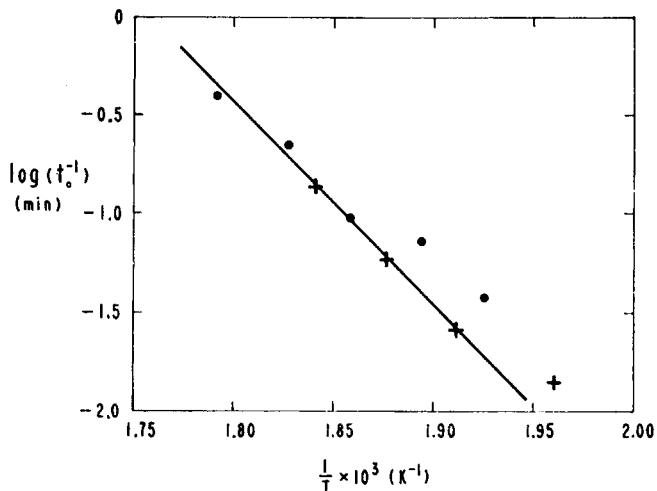


Fig. 1. Arrhenius plot for the induction period ( $t_0$ ) of PAN, under  $N_2$ , at temperature  $T$ : (+) present data; (●) data from Hay<sup>1</sup>.

As reported by Hay<sup>1</sup> the thermal decomposition of PAN in an inert atmosphere is characterized by an induction period, and an Arrhenius plot of this time against temperature allows an estimation of the activation energy of the reaction. Figure 1 shows this plot, both for our own figures and those of Hay. The given line corresponds to an activation energy of 44 kcal/mole and this, it is suggested, is a more realistic figure than that of 30 kcal/mole as previously quoted.<sup>1</sup> The departure from the straight line at

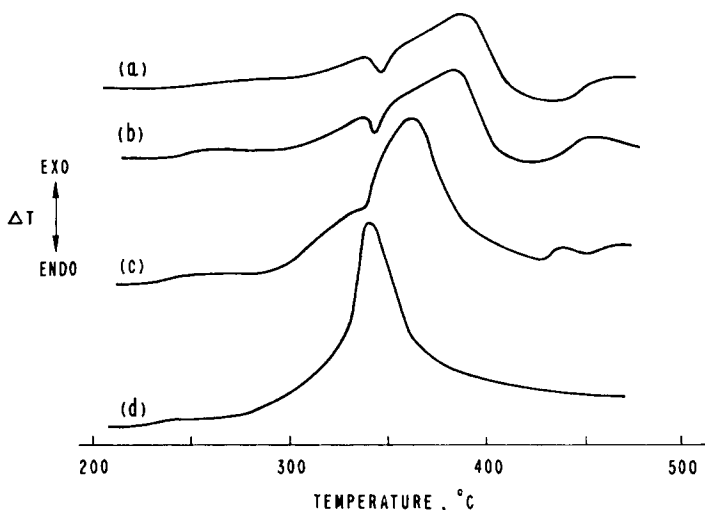


Fig. 2. Effect of heating rate on the DTA of PAN (bracketed figures give relative increase in  $\Delta T$  sensitivity); (a) 100°C/min; (b) 80°C/min; (c) 40°C/min<sup>-1</sup> ( $\times 2$ ), (d) 20°C/min ( $\times 4$ ).

lower temperatures could indicate the presence of a different reaction with a lower activation energy.

Samples of PAN that have been heated isothermally, at temperatures between 240° and 280°C, until completion of the exothermic reaction show no exothermic effects on subsequent dynamic DTA. The material behaves completely differently in air. Not only is there no autocatalytic exothermic reaction when PAN is heated isothermally in air at temperatures between 240° and 280°C for equivalent times, but, after cooling, subsequent dynamic DTA still shows the exothermic effect at 300°C. There is some reduction of the intensity of the exotherm which is dependent on the time and temperature; more prolonged isothermal treatment in air results in a progressively broader and flatter exotherm.

It is apparent that the oxidative decomposition of PAN is slower than the purely thermal reaction and, furthermore, that the presence of air actively inhibits the latter reaction, but not its potential occurrence. Since the thermal reaction is considered to be an autocatalytic cyclization reaction,<sup>1</sup> it is obvious that oxidation of either the initiation sites or the initial reactive intermediates prevents the propagation of the exothermic thermal reaction in air. Mechanisms proposed for degradation of PAN in air will have little relevance to those in an inert atmosphere, and vice versa.

From Figure 1, the induction time for thermal reaction at 300°C would be expected to be about 1 min, and oxidative degradation proceeds more slowly or with less disruption of the original polymer structure. Thus, if the rate of heating is sufficiently great, the melting of PAN should be observed before appreciable reaction can supervene. Figure 2 shows the thermograms of PAN in air, obtained from the DSC cell which allows controlled

heating at rates up to 100°C/min. The melting point is best approximated by the temperature of onset of endothermic deflection from the baseline of the thermogram rather than the point of maximum deflection, in contrast to the standard cell. The observed melting point of PAN is thus 328°, 327°, and 326°C, at heating rates of 100°, 80°, and 40°C/min, respectively. The relative insensitivity of the effect to change of heating rate is a clear indication of a first-order transition; the slight variation is inherent in the cell design. The best value is probably 326°C since, although more decomposition occurs before melting at the lower heating rate, the discrepancy between true and indicated sample temperature will be greater at the faster heating rates. This melting point is in good agreement with the predicted values of 317°C<sup>6</sup> and 322°C.<sup>5</sup>

The thermograms (Fig. 2) also show a slight effect at about 240°C, which is insensitive to changes of heating rate between 5° and 100°C/min. This could be attributed to a previously unreported second-order transition for a PAN with a relatively high degree of crystallinity. This should be confirmed. The effect of heating rate on the thermo-oxidative decomposition is also apparent. The melting of PAN is nearly obscured when the rate is 40°C/min; at lower rates decomposition supervenes, while at higher rates the melting is more evident. The change of shape of the thermogram at higher heating rates is indicative of changing reaction mechanisms, and this is consistent with the known heat stabilization of PAN.

At a heating rate of 100°C/min, the melting endotherm of precipitated PAN is appreciably smaller than that of the continuous filament fiber. We expect that for a PAN fiber of given composition, and thus reproducible decomposition characteristics, high heating rate DTA will provide a useful measure of relative crystallinity.

### References

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