# THE MELTING OF POLYACRYLONITRILE

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ABSTRACT

The melting point of a series of acrylonitrile–vinyl acetate copolymers were measured by differential thermal analysis and the data treated with the Flory relationship for melting-point depression. As a result of this calculation, the melting point of polyacrylonitrile was found to be 322 °C. Additional calculations revealed that the heat of fusion derived from copolymer experiments was about one half the value obtained from diluent studies and that reasonable heats of fusion could be calculated from copolymer melting-point depression experiments if the assumption is made that the effective concentration of the minor component is two times the actual amount present.

INTRODUCTION

Although polyacrylonitrile is usually considered to be an infusible polymer, there have been some reports of its melting[1,2]. Krigbaum and Tokita calculated the melting point of polyacrylonitrile (PAN) to be 317 °C, from the information obtained in a series of dilatometric experiments of PAN in dimethylformamide and γ-butyrolactone. Further calculations utilizing the Flory melting-point depression relationship[3] yielded a heat of fusion of 1.25 or 1.16 kcal/mole of repeat unit with the value dependent on the diluent used. Chiang has discussed the crystallization and melting behavior of PAN in propylene carbonate solutions, but made no extrapolation to the melting point of the perfect crystal.

In this work the melting points of a number of copolymers of acrylonitrile and vinyl acetate were measured by differential thermal analysis and by using the Flory relationship, a melting point was obtained which agrees quite well with the value reported by Krigbaum and Tokita.

EXPERIMENTAL

*Polymer samples*

All of the copolymers used in this study were prepared by the Acrilan Research Section of the Chemstrand Research Center. The vinyl acetate content was determined by an i.r. technique.

*DTA*

The thermograms were obtained with a DuPont Model 900 Differential Thermal Analyzer at a heating rate of 20°/min. A nitrogen atmosphere was maintained throughout the series of experiments.

DISCUSSION

One of the earliest reports of the differential thermal analysis of PAN was by Schwenker[4] in 1960. He presented thermograms of Orlon and PAN and suggested that the most obvious feature of the thermal spectra, a very strong exotherm at about 300 °C, represented the cross linking of PAN chains by elimination of HCN and/or the formation of naphtyridene rings along the chain, as first proposed by Houtz[5] and later confirmed by Burlant and Parsons[6].
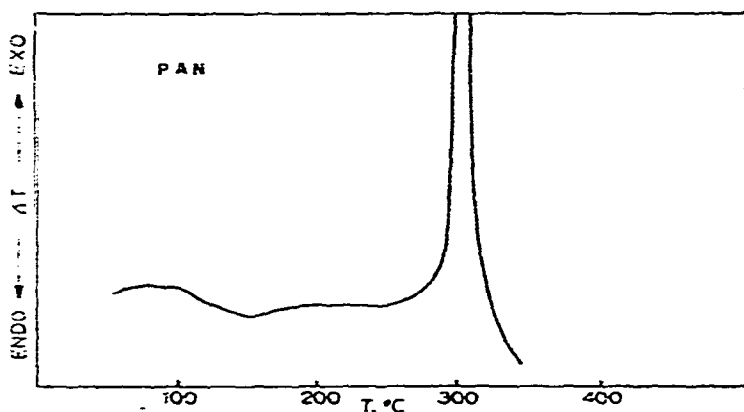


Fig. 1. Typical DTA thermogram for polyacrylonitrile.

A typical thermogram for PAN is shown by Fig. 1. The exotherm precludes any possibility of the observation of a melting endotherm since the quantity of heat evolved is considerably in excess of the amount required for fusion. Another factor that would influence the melting is the compositional change occurring during the exothermic reaction. Even if one could observe PAN melting, the material under observation does not exist as PAN at 320 °C.

Some earlier work in Japan[7] had revealed that a small endotherm was noted at temperatures just below the 300° exotherm when the DTA thermograms of acrylo-nitrile–vinyl acetate copolymers were examined. Thermal spectra obtained in our laboratories contained the same endotherm, but the normal sensitivity used for PAN experiments is very low and these endotherms had not been considered to be significant. By increasing the sensitivity at least an order of magnitude and ending the experiment below the exothermic temperature, melting endotherms were readily seen. A number of additional samples of polymers with varying vinyl acetate content were obtained and, as one would expect, the temperature of the melting endotherm decreased as the vinyl acetate content increased. Fig. 2 is a composite of the melting

behavior of polymers with the vinyl acetate content ranging from 2.7–38.5 weight percent. The broad endotherm is typical of copolymer melting and the low crystallinity[2] of PAN polymers would cause one to expect a shallow peak.



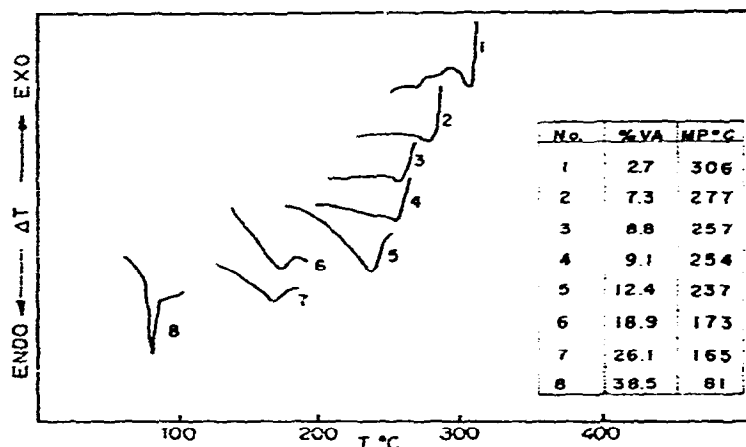| No. | %VA | MP °C |
| --- | --- | --- |
| 1 | 2.7 | 306 |
| 2 | 7.3 | 277 |
| 3 | 8.8 | 257 |
| 4 | 9.1 | 254 |
| 5 | 12.4 | 237 |
| 6 | 18.9 | 173 |
| 7 | 26.1 | 165 |
| 8 | 38.5 | 81 |

Fig. 2. DTA melting points of a series of acrylonitrile–vinyl acetate copolymers.

The melting points and corresponding vinyl acetate concentration were treated with the Flory relationship for copolymers[3].

$$1/T_m - 1/T_m^{\circ} = -(R/\Delta H_u)\ln N_2$$

where $T_m$ is the melting point of the copolymer, $T_m^{\circ}$ the melting point of the pure homopolymer (in this case PAN), $\Delta H_u$ the heat of fusion of the major component, and $N_2$ the mole fraction of the crystallizable component. By a plot of $1/T_m$ vs. $-\ln N_2$, the melting point of crystalline PAN and a value for the heat of fusion can be calculated. Fig. 3 shows this plot where the extrapolated intercept of the line resulting from a least squares regression of the data points is the reciprocal of the melting
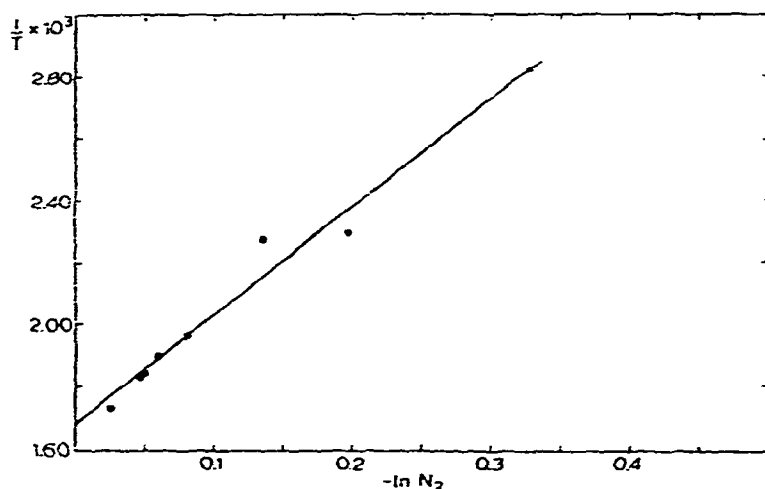


Fig. 3. Flory relationship for acrylonitrile–vinyl acetate copolymers.

point and the slope is $-R/\Delta H_u$. The melting point calculated from these experiments is 322 °C, a value which agrees very well with the 317 °C found by Krigbaum.

The heat of fusion per mole of repeat units calculated from this data is 573 cal. This is considerably lower than that reported by Krigbaum, with 1259 cal/mole listed as the $\Delta H_u$ using $\gamma$-butyrolactone as the diluent and 1160 cal/mole with dimethylformamide.

These data are as expected since both Flory[3] and Mandelkern[8] point out that heats of fusion calculated from copolymer melting-point depression experiments are lower than values obtained from true diluent depression measurements. This is possibly caused by the copolymerized unit having a greater influence on the melting point than a solvent by its interference with the crystal perfection of the pure homopolymer. Barrall[9] has suggested that amorphous regions act as impurities in the crystal lattice and not as diluents. If we accept this premise, some interesting observations can be made on the role of non-crystallizing polymer segments in melting-point depression.

It seems quite reasonable that the minor copolymerized component (vinyl acetate in our experiments) will not be included in the crystal formed by the major component, and it must also affect the ability of adjacent crystallizable repeat units to enter the crystal lattice. There would then be an increase in the number and/or size of the defects which would be related to the effect of the non-crystallizable to crystallizable repeat units. If the assumption is made that the reported heat of fusion value of about 1200 cal/mole is correct and that the melting point of PAN is about 320 °C, the mole fraction of defects can be easily calculated. As an example, a melting-point depression of 66 °C is caused by a defect mole fraction of 0.119; however, a vinyl acetate mole fraction of only 0.058 was copolymerized into the sample that melted this temperature. Since the Flory relationship is a linear function, this factor of a defect mole fraction of twice the vinyl acetate mole fraction holds at all concentrations investigated in these experiments.

Another diluent–copolymer study has been made and this data treated with the same assumptions. The heat of fusion of poly(ethylene terephthalate) has been calculated to be 6560 cal/mole of repeat units when dibutylphthalate was used as diluent in melting-point depression studies and 6654 cal/mole with tricresyl phosphate[10]. If, however, copolymers of ethylene terephthalate and oxydiethyl terephthalate (that is, polymers derived from ethylene glycol and diethylene glycol) are examined for the effect of copolymer content on melting-point depression, the $\Delta H_u$ is found to be 2460 cal/mole. If we again assume that the diluent experiments give the more nearly correct value and using an approximation of 6600 cal/mole, the mole fraction of defects is 2.46 times the mole fraction of the copolymerized DEG–terephthalate repeat unit.

REFERENCES

1 W. R. Krigbaum and N. Tokita, J. Polym. Sci., 43 (1960) 467.
2 R. Chiang, J. Polym. Sci., Part A, 1 (1963) 2765.

3 P. J. FLORY, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, Ch. 13.
4 R. F. SCHWENKER AND L. R. BECK, *Text. Res. J.*, 30 (1960) 624.
5 R. HOUTZ, *Text. Res. J.*, 20 (1950) 786.
6 W. J. BURLANT AND J. L. PARSONS, *J. Polym. Sci.*, 22 (1956) 249.
7 M. VONNEL, Unpublished data.
8 L. MANDELKERN, *Crystallization of Polymers*, McGraw-Hill, New York, 1964.
9 E. M. BARRALL II, Paper presented at the Second DuPont Materials Characterization Symposium, Wilmington, Delaware, 1969.
10 P. E. SLADE AND T. A. OROFINO, in R. S. PORTER AND J. F. JOHNSON (Eds.), *Analytical Calorimetry*, Plenum Press, New York, 1968.