

# Oligomerization Reactions in Acrylonitrile-*N*-Naphthyl-*N'*-Acryloylthiourea Copolymers in the Solid State

S. M. HAMZA\* and I. M. ALY

Chemistry Department, Faculty of Science, El-Menoufia University, Shebin El-Kom, Egypt

## SYNOPSIS

*N*-naphthyl-*N'*-acryloylthiourea homopolymer (PNAT) and a series of copolymers of acrylonitrile (AN) with *N*-naphthyl-*N'*-acryloylthiourea (NAT) have been prepared and characterized by a variety of analytical and spectral methods. Thermogravimetry (TG) and differential thermal analysis (DTA) data showed that the homopolymer (PNAT) undergoes homolytic scission followed by depolymerization and decomposition upon heating. On the other hand the comonomer (NAT) initiates the nitrile oligomerization reaction in the copolymers upon heating. A mechanism for the initiation of the NAT units in the nitrile copolymers was also proposed.

## INTRODUCTION

The thermal degradation of polyacrylonitrile (PAN) and its copolymers in air as well as under nitrogen atmosphere has been investigated by Coleman et al.<sup>1-3</sup> Intramolecular cyclization, intermolecular crosslinking and water elimination have been proposed. Oxidative reactions were a major factor with subsequent heating. Grassie and McGuchan<sup>4,5</sup> have investigated the effect of copolymerization on the oligomerization of the nitrile groups of PAN on heating. It has been argued that since the comonomer is an integrated part of the polymer chain, it may influence the cyclization reaction of the nitrile group either by initiation, participation, or inhibition. Acrylic acid and acrylamide act as initiators for the cyclization reaction. A free radical mechanism followed by homolytic scission of the amide C-N bond has been proposed. Methyl- and benzyl-acrylates and methylmethacrylate participate in the cyclization process and cause a decrease in the intensity of the exotherm without a strong initiating effect. Styrene,  $\alpha$ -methylstyrene, vinyl pyridine, and vinyl acetate, on the other hand, act as blocking

agents for the nitrile oligomerization. Elsabee and co-workers<sup>6,7</sup> have also reported that glycidyl methacrylate and *N*-substituted maleimides belong to the first and second categories of the Grassie classification,<sup>5</sup> respectively.

The present study reports the thermal behavior of poly(*N*-naphthyl-*N'*-acryloylthiourea) (PNAT) and a series of high conversion acrylonitrile-*N*-naphthyl-*N'*-acryloylthiourea (AN-NAT) copolymers in order to find out the effect of NAT units on the oligomerization reactions of the nitrile groups of copolymers.

## EXPERIMENTAL

### Materials

Acrylonitrile (BDH) was purified by distillation before use, azobisisobutyronitrile (AIBN) (Merck) was purified by repeated crystallization from ethanol, and the solvents were purified according to standard methods.

### Preparation of NAT Monomer

The monomer was prepared according to the general method<sup>8,9</sup> by adding 0.01 mol of acryloyl chloride to 0.012 mol of ammonium thiocyanate suspended in

\* To whom correspondence should be addressed.

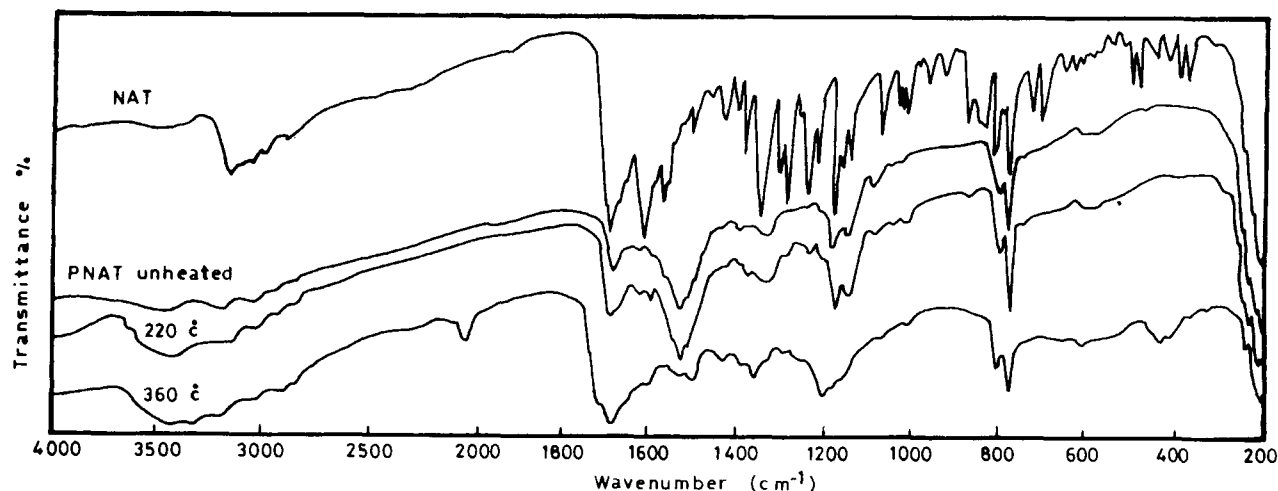


Figure 1 IR spectra of monomer NAT, unheated and heated homopolymer PNAT at different temperatures.

20 cm<sup>3</sup> dioxane. The reaction mixture was heated on a water bath at 65°C for around 10 min. To a stirred solution of the acryloyl isothiocyanate, 0.01 mol of  $\alpha$ -naphthylamine in 20 cm<sup>3</sup> dioxane was added dropwise. The reaction mixture was allowed to stand at 45°C for an hour, then evaporated *in vacuo*. The remaining product was triturated with water and the solid product formed was filtered off and crystallized from ethanol.

### Polymerization Procedures

Ampoules of Pyrex glass were charged with the monomer or monomer mixture, dimethylformamide,

and the initiator (AIBN). The ampoules were then cooled under nitrogen. The polymerization was carried out in a water ultrathermostate at 65°C with stirring for about 9 h. The contents were poured into a large excess of methanol. The polymers obtained were washed several times with hot methanol and dried at 40°C to constant weight.

### Spectral Measurements

<sup>1</sup>H-NMR spectra were recorded on a Varian EM-390 90 MHz NMR spectrometer in deuterated dimethylsulphoxide. IR spectra were measured as KBr discs using a Perkin-Elmer 598 (4000–200 cm<sup>-1</sup>) spectrophotometer.

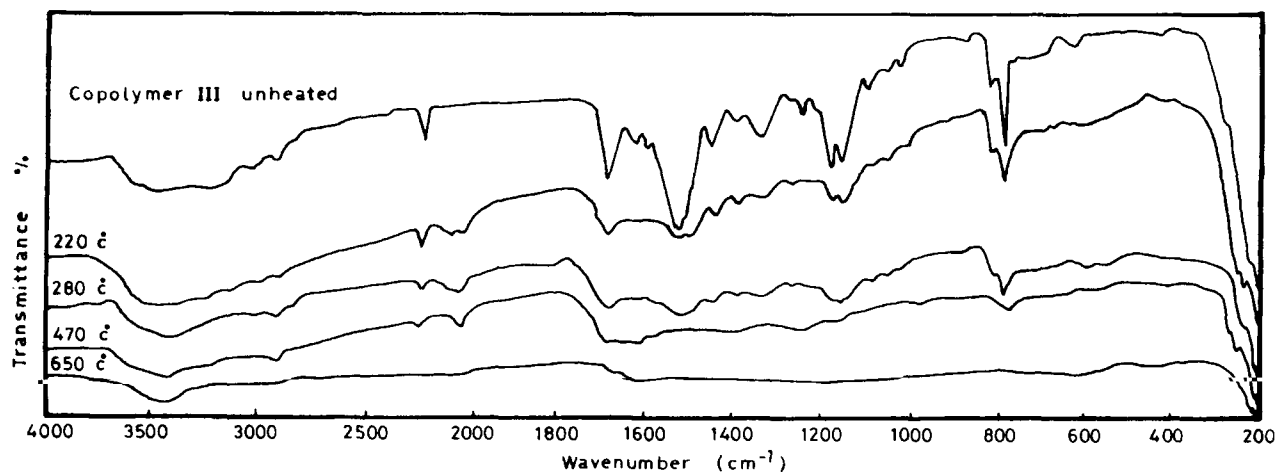


Figure 2 IR spectra of unheated and heated copolymer III (AN-NAT).

### Thermal Analysis

Differential thermal analysis (DTA) was carried out at a heating rate of  $15^{\circ}\text{C min}^{-1}$  using a Shimadzu XD-30 thermal analyzer. Thermogravimetry (TG) thermograms were obtained using a DT-30B thermal analyzer (Shimadzu, Kyoto, Japan).

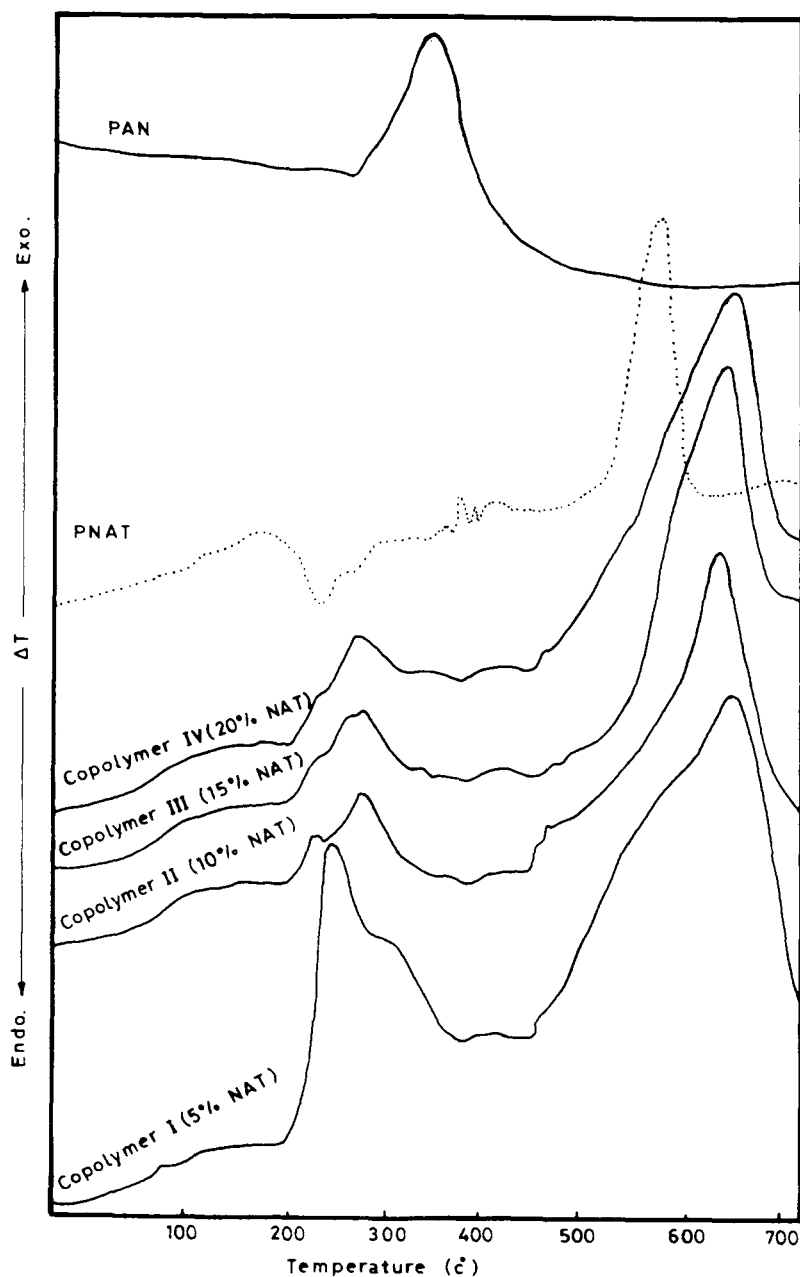
### DC Electrical Conductivity Measurements

The DC electrical conductivity measurements were carried out by using a Keithley 175 autoranging

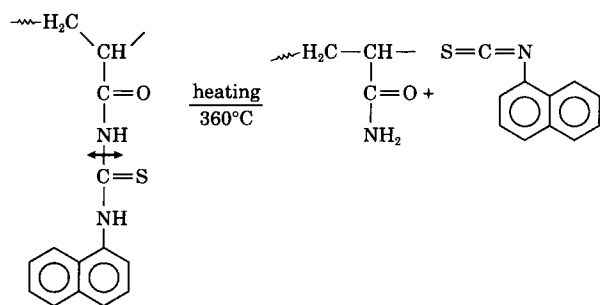
multimeter with applied volt (200 V) and rate of heating ( $1^{\circ}\text{C min}^{-1}$ ). The samples used in the measurements were pressed into cylindrical discs at a pressure of about  $300\text{ kg cm}^{-1}$ . This pressure was chosen as the electrical conductivity was independent on the load.

### RESULTS AND DISCUSSION

A series of high conversion copolymers of AN with NAT in dimethylformamide (DMF) at  $65^{\circ}\text{C}$  were



**Figure 3** DTA curves for PAN, PNAT, and copolymers (AN-NAT) in air.



Scheme 1

prepared and characterized by a variety of spectral and thermal methods in order to find out the effect of NAT on the thermal behavior of copolymers.

$^1\text{H-NMR}$  spectra of NAT and its homopolymer PNAT show that the disappearance of the signal at 7.15–7.3 ppm corresponding to 3H, ( $\text{CH}_2 = \text{CH}-$ ) in the spectrum of homopolymer, compared to that of monomer, indicates the formation of homopolymer.

The IR spectra of NAT monomer, PNAT homopolymer, and AN–NAT copolymer III are shown in Figures 1 and 2. The IR spectra show bands at

3180, 1690, 1630, and  $1157\text{ cm}^{-1}$  attributable to  $\nu(\text{NH})$ ,  $\nu(\text{C}=\text{O})$ ,  $\delta(\text{NH})$ , and  $\nu(\text{C}=\text{S})$ , respectively. The spectrum of the copolymer shows a new band at  $2250\text{ cm}^{-1}$  attributable to  $\nu(\text{C}\equiv\text{N})$ .

### Thermal Behavior

The thermal behavior of polyacrylonitrile (PAN) has been studied in detail by Grassie.<sup>10</sup> In the present investigation a comparison between the DTA and TG data of PAN and those of the copolymers have been made to illustrate the effect of NAT comonomer on the thermal behavior of the copolymers.

The DTA curves of PAN, PNAT, and those of the copolymers are shown in Figure 3. The thermal analysis of PAN in air shows the usual thermogram with an initial decomposition at  $310^\circ\text{C}$  and an exothermic peak with a maximum at  $340^\circ\text{C}$ , which results from the oligomerization of the nitrile groups and formation of some aromatic structures,<sup>10</sup> whereas the DTA curve of PNAT (Fig. 3) shows an endothermic peak at  $280^\circ\text{C}$  followed by exothermic peaks at 360, 395, and  $560^\circ\text{C}$ .

The IR spectra of unheated PNAT and PNAT samples heated at different temperatures are shown in Figure 1. The spectra show no change in the func-

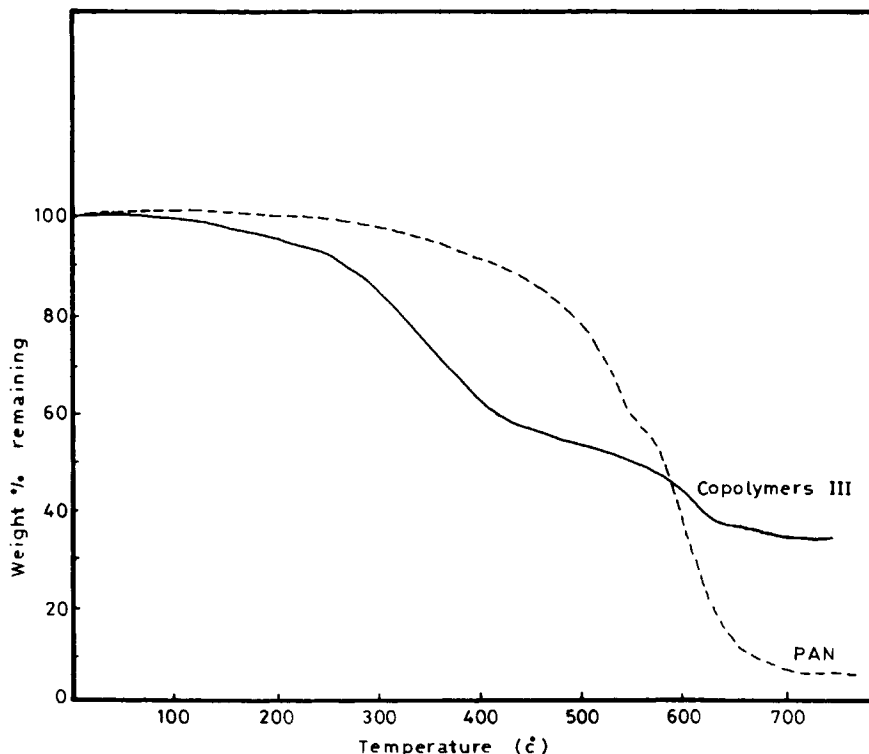


Figure 4 TG curves for PAN and copolymer III (AN–NAT).

tional groups present upon heating up to 218°C. This indicates that the endothermic peak at 218°C may be attributable to a change in the molecular packing in the crystal. On the other hand, the spectrum of a heated sample at 360°C shows a rapid decrease in the intensity of the bands characteristic of  $\nu(\text{NH})$ ,  $\nu(\text{C}=\text{O})$ , and  $\nu(\text{C}=\text{S})$ . In addition a new broad band with shoulder appears at 2028  $\text{cm}^{-1}$ , assigned to the stretching vibrations of the isothiocyanate group,  $\nu(-\text{N}=\text{C}=\text{S})$ . This indicates that a homolytic scission takes place in the C—N

$$\begin{array}{c} \text{S} \\ || \\ (-\text{C}-\text{NH}-) \end{array}$$
 bond in a similar manner as occurs in *N*-acyl-*N'*-aryl-thiourea<sup>11</sup> and poly(*N*-(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazoline-4-yl)-*N'*-acryloylthiourea<sup>12</sup> as shown in Scheme 1.

The preceding arguments indicated that the PNAT (homopolymer) shows depolymerization followed by decomposition. The exotherm at 560°C represents a complete decomposition and 100% weight loss.

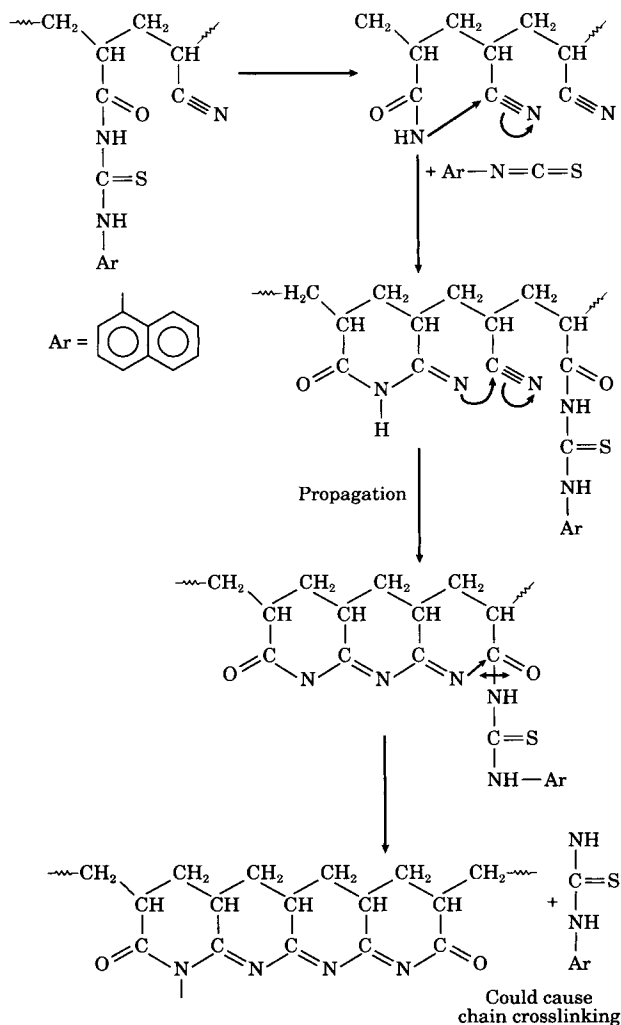
The suggested scission was also conformed by the detection of isothiocyanate among the products of the thermal degradation of the polymer (PNAT). This experiment was carried out by heating the polymer in a sealed ampoule at 360°C for about 50 min and then extracting the residue with a mixture of alcohol and water (70 : 30 v/v). A solution of sodium azide was added to the extract; then dimethylformamide was added. A green color was observed that is characteristic of the presence of the isothiocyanate group.<sup>13</sup>

When PNAT was heated at 360°C, a black soluble mass was left, indicating that no crosslinking reaction occurs.

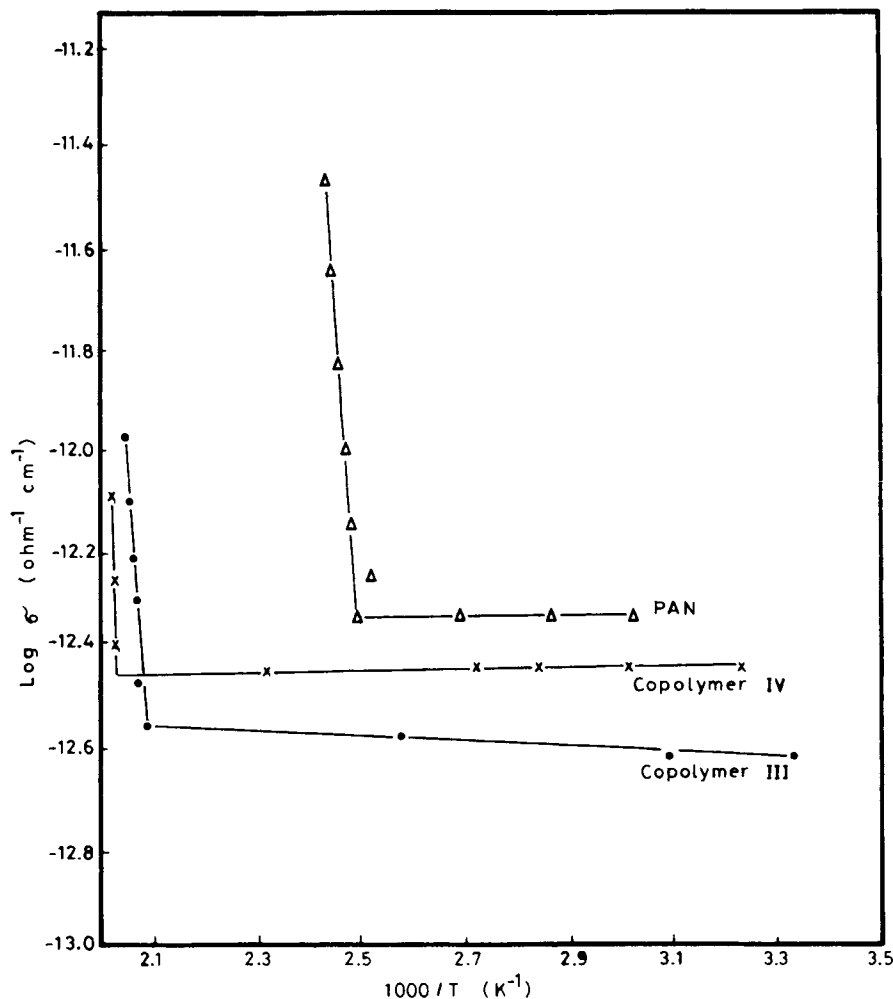
The DTA curves of the AN-NAT copolymers in air (Fig. 3) shown an endothermic peak at 200°C followed by exothermic peaks near 230, 280, 470, and 650°C, reflecting many processes, probably including scission, cyclization, crosslinking, and decomposition at the higher temperature peak. The first stage of degradation is a homolytic scission in the C—N bond in a manner similar to that occurring with PNAT followed by cyclization and crosslinking. The DTA peaks of the copolymers were broadened and shifted to lower temperatures relative to that of PAN, indicating an initiating effect of NAT comonomer on the cyclization process.<sup>6</sup> The TG curve of copolymer III in air (Fig. 4) shows an increase in the weight loss of the copolymer relative to that of PAN. When AN-NAT copolymer III was heated for about 20 min at 280°C, a black insoluble

mass was left, indicating an appreciable crosslinking reaction.

The IR spectra of AN-NAT copolymer III before and after heating at 200, 280, 470, and 650°C are given in Figure 2. The spectra show appreciable broadening and decreasing in the intensities of the nitrile band at 2250  $\text{cm}^{-1}$ ,  $\nu(\text{NH})$  at 3180  $\text{cm}^{-1}$ ,  $\nu(\text{C}=\text{O})$  at 1690  $\text{cm}^{-1}$ , and  $\nu(\text{C}=\text{S})$  at 1160  $\text{cm}^{-1}$ . In addition, the band characteristic of  $\nu(-\text{N}=\text{C}=\text{S})$  appears as a broad band with shoulder at 2025  $\text{cm}^{-1}$  upon heating. These spectral changes reveal radical changes in the copolymer structure and must also be due to a direct interaction between the nitrile group and the functional groups of the comonomer. In this interaction an initiation of the cyclization and crosslinking reactions will occur.



Scheme 2



**Figure 5** The variation of electrical conductivity with inverse temperature for PAN and copolymers III and IV.

Based on the above-mentioned arguments, the mechanism shown in Scheme 2 could be suggested for the thermal behavior of the copolymers.

### DC Electrical Conductivity

The variation of the logarithmic electrical conductivity ( $\log \sigma$ ) versus the reciprocal absolute temperature ( $1000/T \text{ K}^{-1}$ ) for PAN and some of the copolymers was shown in Figure 5. The figure shows that the electrical conductivity of the investigated samples is constant up to 400–482 K. Whereas at temperature above 400–482 K, there is a rapid increase in the electrical conductivity. The temperature range within which the electrical conductivity rapidly increases coincides with the temperature of

the DTA peaks that were assigned to scission, oligomerization, and crosslinking processes. Consequently, the measured electrical conductivity may be associated with the thermally formed cyclized conjugated structures, other by-products, and the generation of a free radical through heating; therefore, the electrical conductivity provides evidence for the previously mentioned mechanism for degradation.

### REFERENCES

1. M. M. Coleman and G. T. Sivy, *Chem. Ser.*, **203**, 559 (1983).

2. M. M. Coleman, G. T. Sivy, P. C. Painter, R. W. Snyder, and B. Gordon, *Carbon*, **21**, 255 (1983).
3. M. M. Coleman and B. Gordon, *Anal. Proc. London*, **20**, 572 (1983).
4. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 243 (1972).
5. N. Grassie and R. McGuhan, *Eur. Polym. J.*, **8**, 8654 (1972).
6. M. Z. Elsabee, M. W. Sabaa, M. G. Mikhael, and S. H. El-Hamouly, *Angew. Makromol. Chem.*, **168**, 91 (1989).
7. M. W. Sabaa, M. G. Mikhael, A. A. Yassin, and M. Z. Elsabee, *Angew. Makromol. Chem.*, **139**, 95 (1986).
8. Y. Matayasu, *Chem. Abstr.*, **87**, 135072 (1977).
9. Y. Matayasu, *Chem. Abstr.*, **93**, 220684 (1980).
10. N. Grassie, *Developments in Polymer Degradation*, Applied Science, London, 1977, p. 137.
11. S. Rajapa, T. G. Rajagopalon, R. Sreenivasan, and S. Kanal, *J. Chem. Soc., Perkin Trans.*, **1**, 2001 (1979).
12. S. H. El-Hamouly, F. A. El-Saied, and M. M. M. Ramiz, *Thermochim. Acta*, **153**, 237 (1989).
13. S. Patai, *The Chemistry of Cyanates and Their Thio Derivatives*, Wiley-Interscience, New York, 1977, p. 206.

Received November 20, 1991

Accepted December 6, 1991