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THERMAL BEHAVIOUR AND ELECTRICAL CONDUCTIVITY OF ACRYLONITRILE–*N*-(2,3-DIMETHYL-1-PHENYL-5-OXO-3-PYRAZOLIN-4-YL)-*N*′-ACRYLOYLTHIOUREA COPOLYMERS

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ABSTRACT

Acrylonitrile was copolymerized with *N*-(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl)-*N*′-acryloylthiourea (antipyrine-acryloylthiourea APAT) in dimethylformamide. The prepared copolymers and homopolymer (PAPAT) were characterized by a variety of analytical, spectral and thermal methods. Thermogravimetry (TG) and differential thermal analysis (DTA) data showed that the comonomer (APAT) initiates the nitrile oligomerization reaction in the copolymers upon heating. A mechanism for the initiation of the APAT units in the nitrile copolymers was also proposed. The electrical conductivities of the copolymers as well as of polyacrylonitrile (PAN) were measured.

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. [1–3]. Intramolecular cyclization, intermolecular cross-linking and water elimination have been proposed. Oxidative reactions were a major factor with subsequent heating. Grassie and McGuchan [4,5] 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 benzylacrylates and methylmethacryl-

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ate participate in the cyclization process and cause a decrease in the intensity of the exotherm without a strong initiating effect. Styrene, α-methylstyrene, vinylpyridine and vinylacetate, on the other hand, act as blocking agents for the nitrile oligomerization. Elsabee and coworkers [6,7] have also reported that glycidyl methacrylate and *N*-substituted maleimides belong to the first and second categories of the Grassie classification [5] respectively.

In the present work a series of high conversion acrylonitrile–antipyrine-acryloylthiourea (AN–APAT) copolymers were prepared and characterized by a variety of spectral and thermal methods in order to determine the effect of APAT on the thermal behaviour. The DC electrical conductivity of PAN and copolymers was also measured.

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 APAT monomer

The monomer was prepared according to the general method [8,9] by adding 0.01 mol of acryloyl chloride to 0.012 mol of ammonium thiocyanate suspended in 20 cm^3 of 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 4-aminoantipyrine in 20 cm^3 of 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 triterated with water and the solid product formed was filtered off and crystallized from ethanol (m.p. = 155 °C, yield = 80%).

Polymerization procedures

Ampoules of pyrex glass were charged with the monomer mixtures, the solvent and the initiator (AIBN). The ampoules were then cooled under nitrogen. The copolymerization was carried out in a water ultra-thermostat at 65 °C with stirring for about 8 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.

Copolymer analysis

The copolymer compositions were calculated on the basis of sulphur content. The analysis was carried out at the microanalytical unit of the University of Cairo.

Spectral measurements

^{1}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^{-1}) spectrophotometer.

Thermal analysis

DTA was performed at a heating rate of 15 °C min^{-1} using a Shimadsu XD-30 thermal analyser. TG thermograms were obtained using a DT-30 B thermal analyser (Shimadzu, Kyoto, Japan).

DC electrical conductivity measurements

The DC electrical conductivity measurements were carried out on the investigated samples using a DC electrometer (type TR-150 I Orion-R.T.V., Budapest). The samples used in the measurements were pressed into cylindrical discs at a pressure of about 300 kg cm^{-2}. This pressure was chosen as the electrical conductivity was independent on the load.

RESULTS AND DISCUSSION

A series of low conversion copolymers of AN with APAT in DMF at 65 °C were prepared by El-Hamouly [10]. The reactivity ratios for the comonomers were calculated using the Kelen–Tüdös equation [11]. The calculated values of r_1 (AN) = 1.60 and r_2 (APAT) = 1.52 indicated that the two monomers are incorporated in the copolymers in a random manner.

The composition data of the high conversion copolymers under investigation, based on their sulphur content, are listed in Table 1.

^{1}H NMR spectra of APAT monomer and its homopolymer (PAPAT) are shown in Fig. 1. The disappearance of the signal at 5.6–6.3 ppm corresponding to 3H, (CH_2=CH–) in the spectrum of homopolymer, compared to that of monomer, indicates the formation of homopolymer.

The IR spectra of APAT monomer, PAPAT homopolymer and AN–APAT copolymer **1** are shown in Figs. 2 and 3. The IR spectra show bands at 3170–3150, 1685, 1655, 1625 and 1160 cm^{-1} attributable to ν(NH), ν(C=O) of the pyrazolone ring [12], ν(C=O) of the acrylolyl carbonyl [12], δ(NH) and ν(C=S) respectively. The spectra of the copolymer show a new band at 2240 cm^{-1} attributable to ν (C≡N).

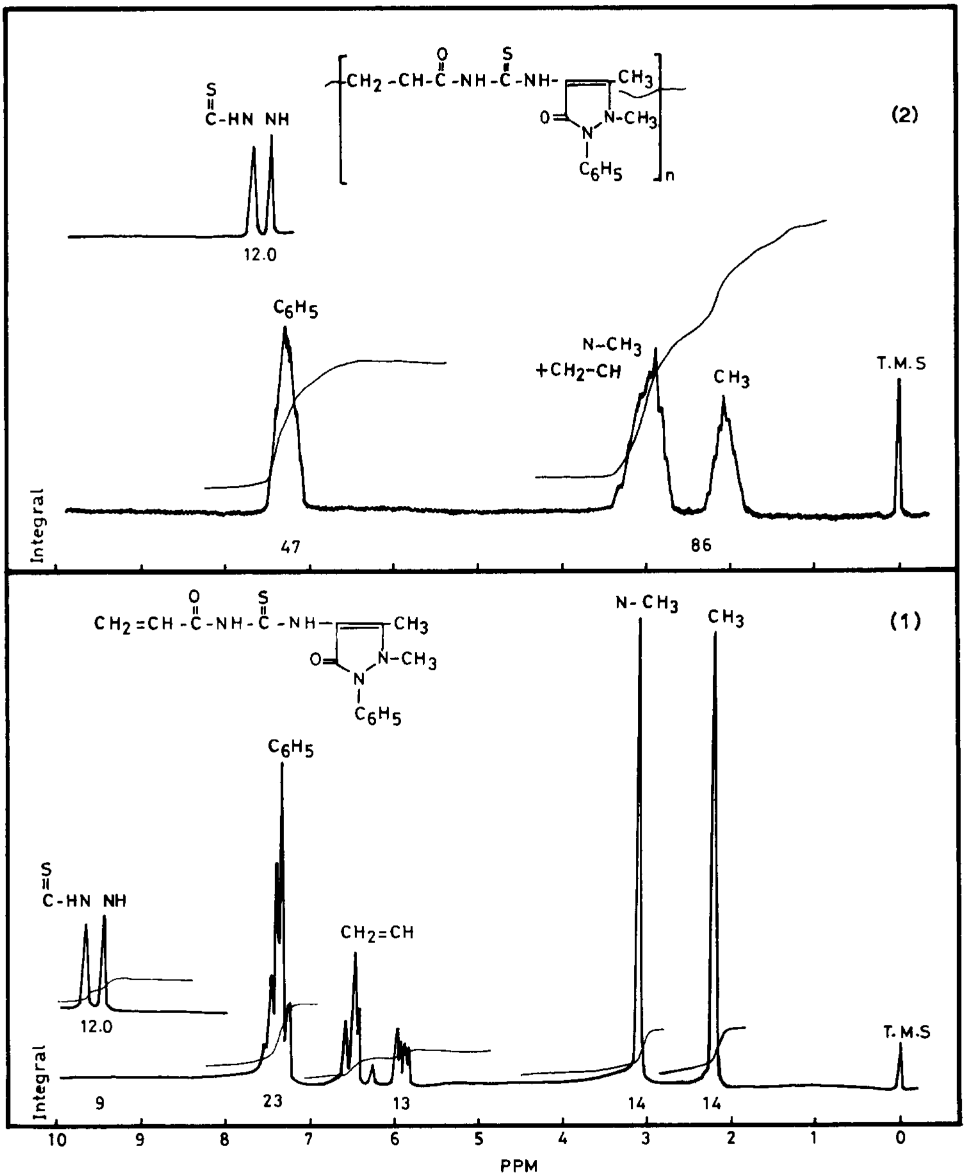


Fig. 1. ^{1}H NMR of monomer antipyrine-acryloyl thiourea APAT (1) and its homopolymer PAPAT (2).

TABLE 1

Copolymerization data for the AN(M_1)/APAT(M_2) system in DMF at 65 °C, AIBN initiator

No.	M_2 (wt.%)	Conversion (S) wt.%	M_2 (mol%)
I	5	1.3	2.4
II	10	3.0	6.6
III	15	3.75	9.0
IV	20	5.25	15.3

Thermal behaviour

The thermal behaviour of polyacrylonitrile (PAN) has been studied in detail by Grassie [13]. In the present investigation, the thermal analysis of PAN is given as a reference, i.e the comparison between the DTA and TG data of PAN and those of the copolymers will illustrate the effect of APAT comonomer on the thermal behaviour of the products.

The DTA curves of polyacrylonitrile (PAN), poly(*N*-(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl)-*N*′-acrylolylthiourea) [poly(antipyrine-acryl-olyl-thiourea) (PAPAT)] and those of the copolymers are represented in

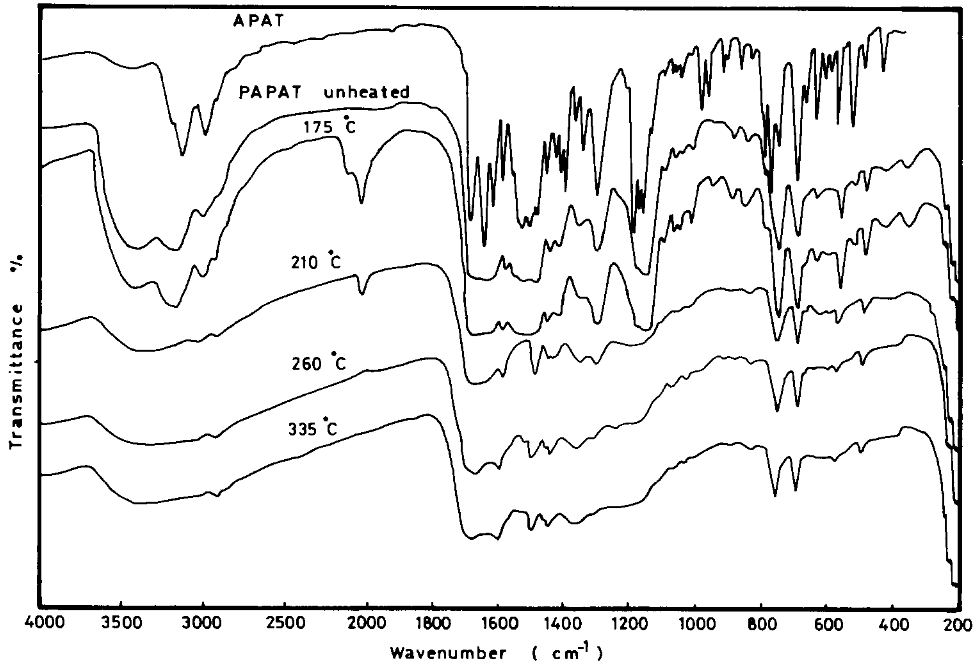


Fig. 2. IR spectra of monomer APAT and unheated and heated homopolymer PAPAT at different temperatures.

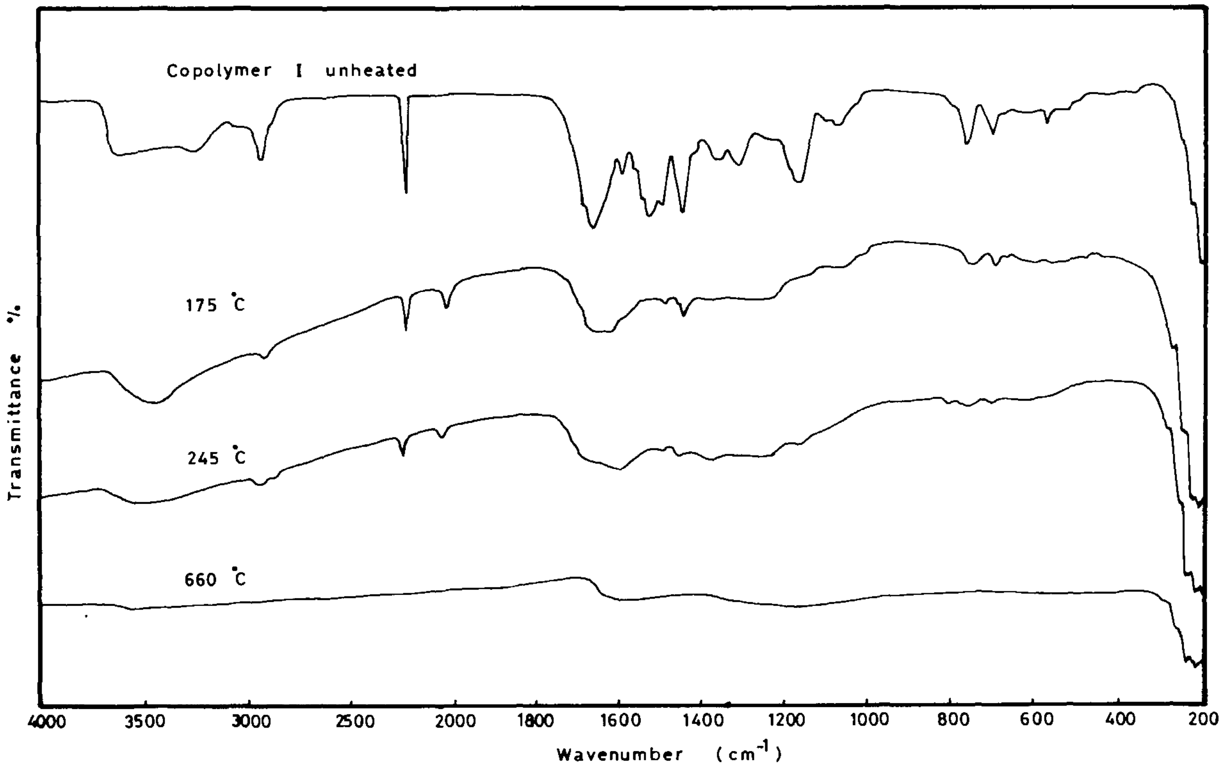


Fig. 3. IR spectra of unheated and heated copolymer I (AN–APAT).

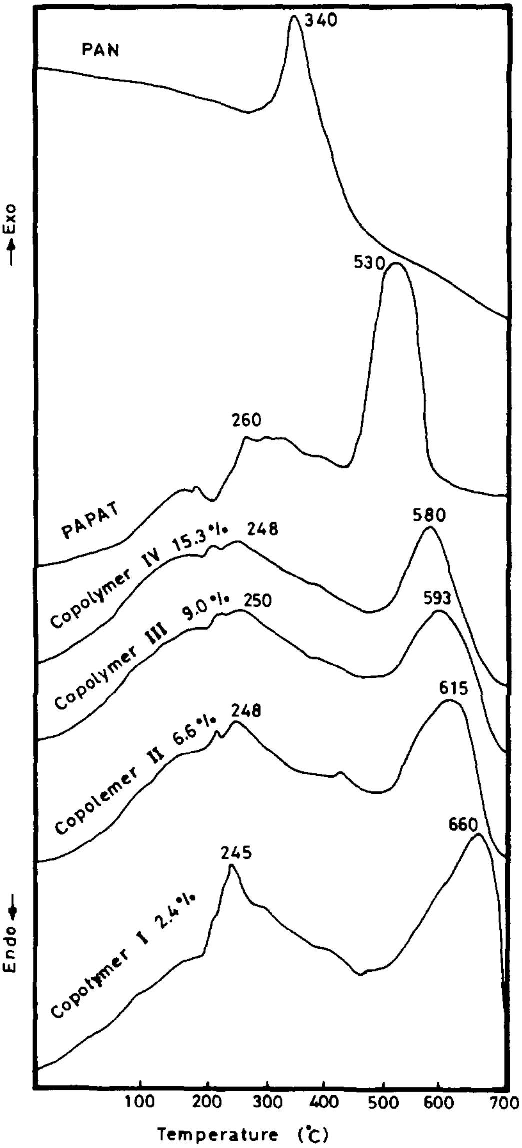
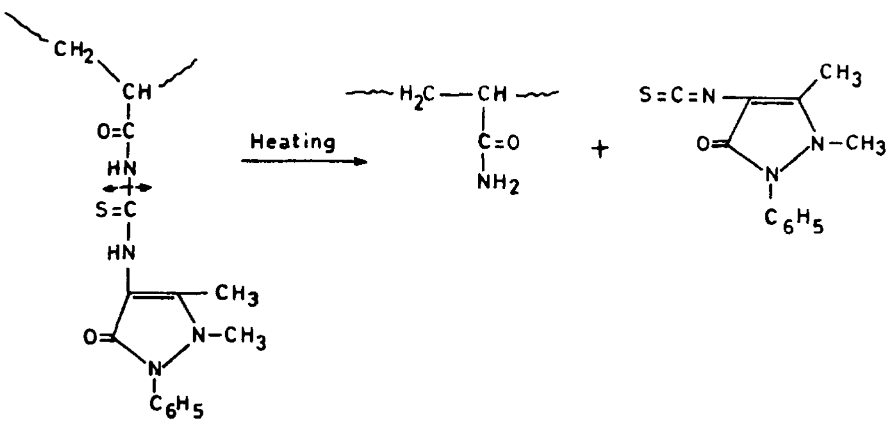


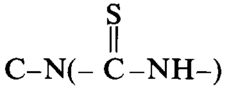
Fig. 4. DTA curves for PAN, PAPAT and copolymers (AN–APAT) in air.

Fig. 4. The thermal analysis of PAN in air shows the usual thermogram with an initial decomposition at 310 °C and an exotherm with a maximum at 340 °C, which results from the oligomerization of the nitrile groups and formation of some aromatic structure [13]. On the other hand, the DTA curve of PAPAT (Fig. 4) shows exotherms with maxima at 165, 175, 260, 335 and 530 °C.

The IR spectra of unheated PAPAT and PAPAT samples heated at different temperatures are shown in Fig. 2. The spectra show no change in



Scheme 1.

most of the functional groups present upon heating up to 175 °C, except that a new band appears at 2040 $\mathrm{cm^{-1}}$, assigned to the stretching vibrations of the isothiocyanate group, $\nu(\mathrm{-N{=}C{=}S})$. This indicates that a homolytic scission takes place in the  $\mathrm{C{-}N({-}\overset{S}{\overset{\|}{C}}{-}NH{-})}$ bond in a similar manner as occurs in *N*-acyl-*N*′-aryl-thiourea [14] as shown in Scheme 1. In contrast, the spectra of the samples heated up to 175 °C show a rapid decrease in the intensity of the bands characteristic of $\nu(\mathrm{NH})$, $\nu(\mathrm{C{=}O})$ and $\nu(\mathrm{C{=}S})$ and the band at 2040 $\mathrm{cm^{-1}}$ disappeared from the spectrum of sample heated at 260 °C. The above arguments indicated that the PAPAT (homopolymer) shows depolymerization and decomposition. The exotherm at 530 °C represents a complete decomposition and 100% weight loss.

The proposed scission was also supported by the detection of isothiocyanate among the products of the thermal degradation of the polymer (PAPAT). This experiment was carried out by heating the polymer in a sealed tube at 175 °C for about 30 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 colour was observed which is characteristic of the presence of isothiocyanate group [15].

In a separate experiment, when PAPAT was heated at 335 °C a black soluble mass was left, indicating that no cross-linking reaction occurs.

The DTA curves of the AN–APAT copolymers in air (Fig. 4) show exotherms at 175, 215 245, 305 and 660 °C, reflecting many processes, probably including scission, cyclization, cross-linking and decomposition at the higher temperature exotherm. The first stage of degradation is a scission in the C–N bond in a manner similar to that occurring with PAPAT, followed by cyclization and cross-linking. The DTA peaks of the copolymers

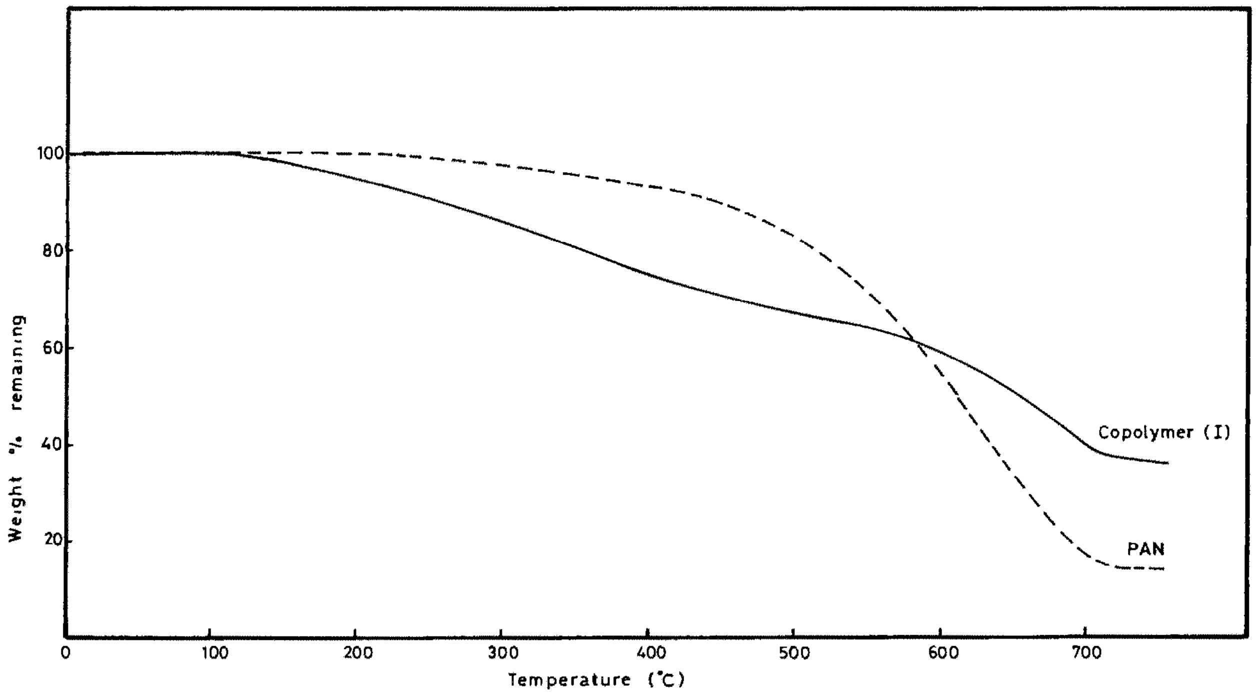
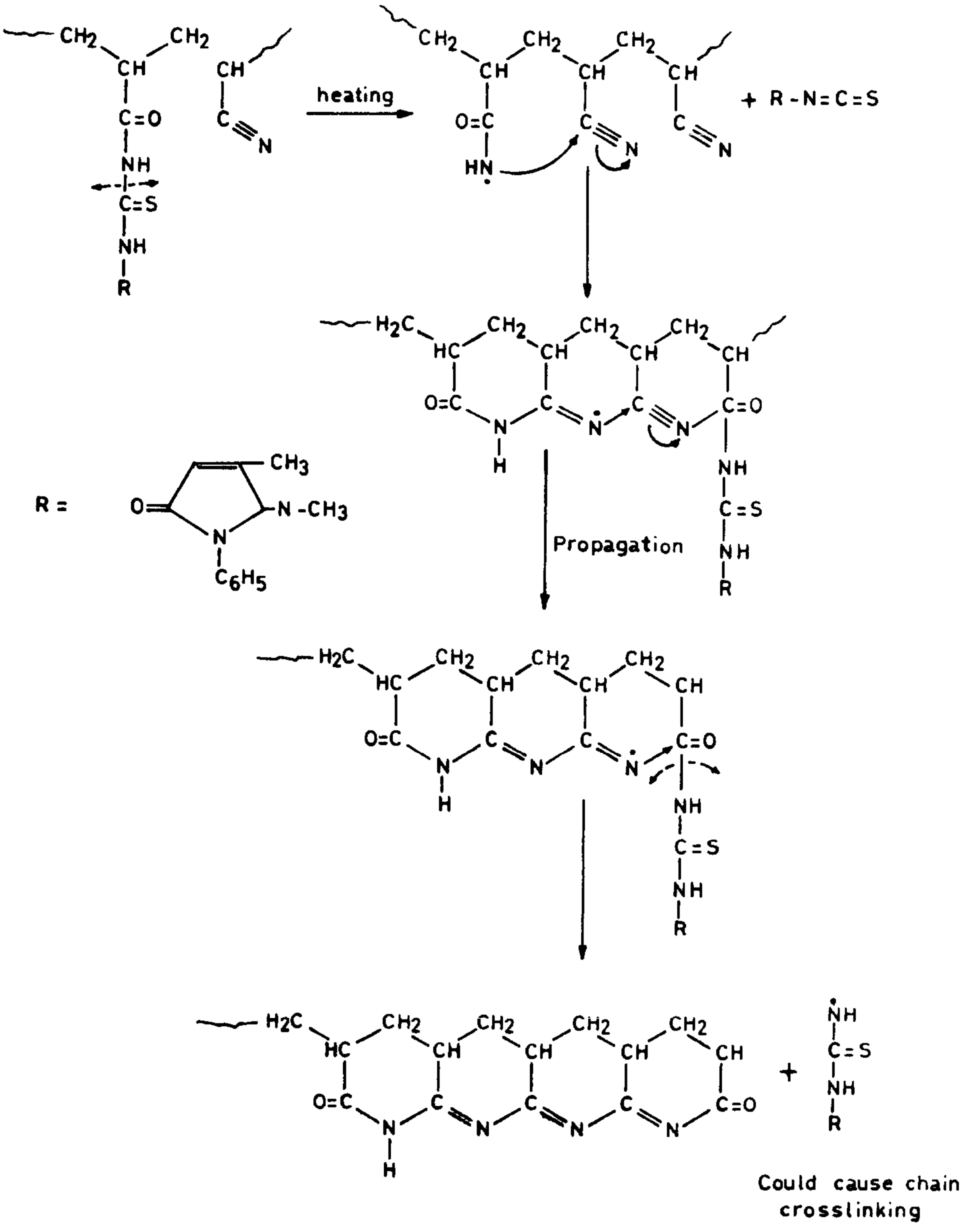


Fig. 5. TG curves for PAN and copolymer **I** (AN–APAT).

were shifted to lower temperatures relative to that of PAN indicating an initiating effect of APAT comonomer on the cyclization process [6]. The TG curve of copolymer I in air, Fig. 5, shows an increase in the weight loss of the copolymer relative to that of PAN. When AN–APAT copolymer I was heated for about 5 min at 245 °C, a black insoluble mass was left indicating an appreciable crosslinking reaction.



Scheme 2.

The IR spectra of AN–APAT copolymer **I** before and after heating at 215, 245 and 660 °C are given in Fig. 3. The spectra show appreciable broadening and decreasing in the intensities of the nitrile band at 2240 cm^{-1}, ν(NH) at 3170 cm^{-1} and ν(C=S) at 1160 cm^{-1}. The band characteristic of ν(–N=C=S) at 2040 cm^{-1} also shows a decrease in its intensity following continuous 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.

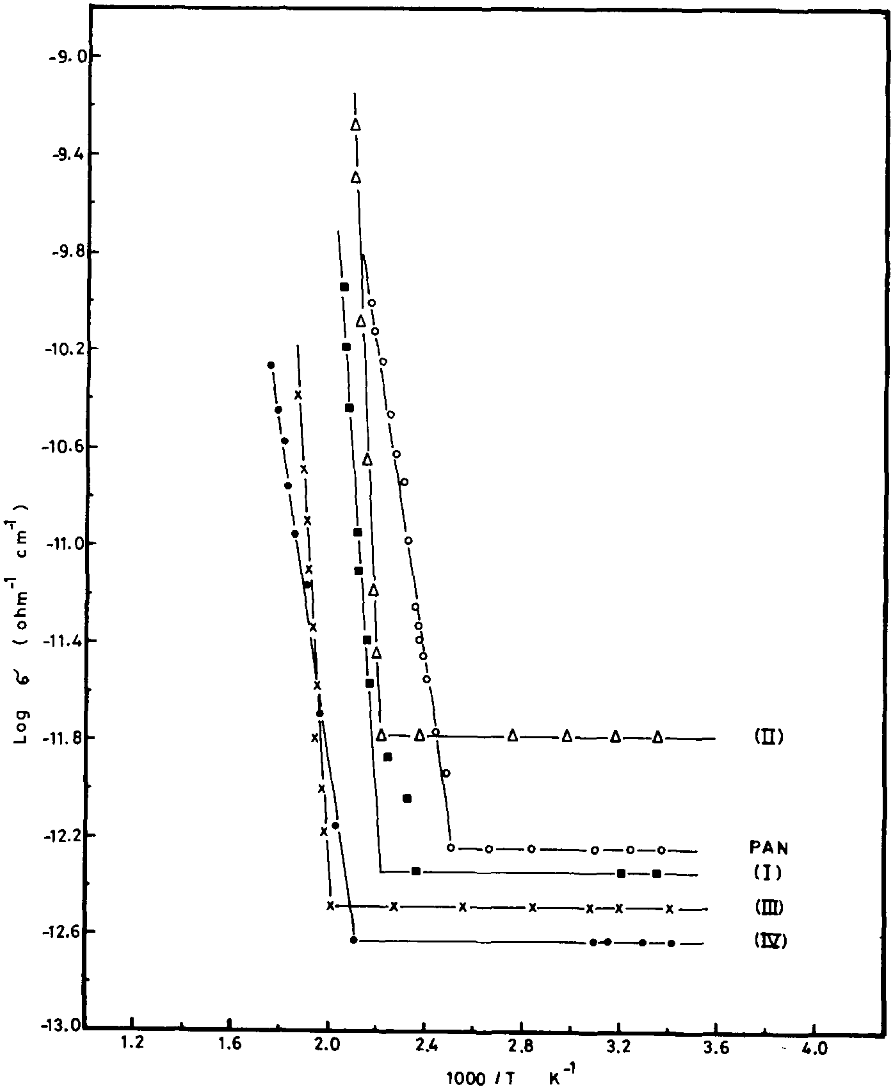


Fig. 6. Variation of electrical conductivity with inverse temperature for PAN and copolymers.

Based on the above-mentioned thermal and spectral data, the mechanism shown in Scheme 2 could be suggested for the thermal degradation of the copolymers.

DC ELECTRICAL CONDUCTIVITY

Figure 6 shows the variation of DC electrical conductivity as a function of temperature for solid state samples of PAN and copolymers. The figure shows that the electrical conductivity of the investigated samples is constant up to 400–492 K. At temperatures above 400–492 K, there is a positive temperature coefficient of the electrical conductivity ($\mathrm{d}\delta/\mathrm{d}T$) for all curves. The temperature range within which the electrical conductivity increases coincides with the temperature of the DTA exotherms 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 biproducts and the generation of a free radical through heating: therefore, the electrical conductivity provides evidence for the previously mentioned mechanism for degradation.

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