Thermochimica Acta, 241 (1994) 57–66
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(94)01711-O

Thermal characteristics of *N*-antipyryl-acrylamide–acrylonitrile copolymers using different spectroscopic techniques

S.H. El-Hamouly [a,*], M.M. Azab [b] and S.A. El-Kafrawi [a]

[a] *Laboratory of Polymer Chemistry, Faculty of Science El-Menoufia University, Shebin El-Kom, Egypt*
[b] *Department of Chemistry, Faculty of Science Benha University, Benha, Egypt*

(Received 8 September 1993; accepted 20 January 1994)

Abstract

N-antipyryl-acrylamide monomer (NAA) (2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl acryloylamine) was copolymerized with acrylonitrile in dimethyl formamide using azobisisobutyronitrile (AIBN) as initiator. The homopolymer and also the copolymers were characterized by a variety of spectral and thermal methods. Thermogravimetry (TG) and differential thermal analysis (DTA) data showed a remarkable improvement in the thermal behaviour of the investigated copolymers. A mechanism for the participation of the acryloyloxy units in the nitrile oligomerization is proposed and confirmed by interpretation of the fragmentation patterns of the mass spectrum of the *N*-antipyryl-acrylamide (NAA) monomer and also the IR spectra of the copolymers after heating.

INTRODUCTION

The technological importance of polyacrylonitrile (PAN) has been disadvantaged by three basic problems: namely processability, dyeability, and degradability. The ultimate solution of these problems was achieved on a large scale by the introduction of comonomers into the PAN chains. Many authors have reported the influence of copolymerization on the exothermic oligomerization and the overall thermal stability of PAN [1–3]. Thus, Grassie and McGuchan [4, 5] showed that as the comonomer is an integral part of the copolymer molecule, it may influence the cyclization reaction 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 acrylate, and methyl methacrylate participate in the cyclization process and cause a decrease in the intensity of the exotherm without a strong initiating effect. However, styrene and α-methyl styrene,

---

[*] Corresponding author.

vinyl pyridine, and vinyl acetate act as blocking agents for the nitrile oligomerization. El Sabee and co-workers [6, 7] have also reported that the glycidyl methacrylate and *N*-substituted maleimides belong to the first and the second categories of the Grassie classification, respectively. Finally, El-Hamouly [8] also studied the *N*-methacryloyloxy phthalimide derivatives which belong to the first category of the Grassie classification.

The present study was conducted in order to find out the effect of introducing an acryloyloxy unit into the polymer chain of PAN. It was expected that the thermal properties of PAN would be greatly affected and, consequently, it is necessary to investigate the thermal behaviour of the copolymers produced.

EXPERIMENTAL

Materials

4-Amino-antipyrine was provided by Fluka, acryloyl chloride and acrylic acid by Aldrich and *N*,*N*′-dicyclohexyl carbodimide (DCCI) by Merck (Darmstadt products). Acrylonitrile (BHD) was purified by distillation at reduced pressure and the middle fraction was retained for use. Azobisisobutyronitrile (AIBN) (Merck) was recrystallized from ethanol. DMF solvent was of reagent grade and was purified according to the standard method.

Synthesis of the monomer

NAA monomer was synthesized either by the acid chloride method or by the *N*,*N*′-dicyclohexyl carbodimide method, as described in our previous work [9].

Polymerization

PNAA and its copolymers with AN were obtained by solution polymerization in DMF ($2\ \mathrm{mol\,l^{-1}}$) under N_2 at 65°C in the presence of 1 mol% AIBN. The overall conversions were <10% in every case. The copolymers were soluble in the reaction mixture and were recovered by precipitation in water. They were redissolved, reprecipitated, washed with water and weighed.

Copolymer analysis

NAA–AN copolymer compositions were calculated from their ^{1}H NMR spectra using a Varian EM-390 spectrometer operating at 90 MHz in deuterated DMS, with TMS as an internal reference.

IR spectra were recorded in KBr discs using a Perkin-Elmer 598 (4000–200 $\mathrm{cm^{-1}}$) spectrophotometer.

The mass spectrum was measured on a Hewlett Packard Model MS 5988 spectrometer at 15 eV.

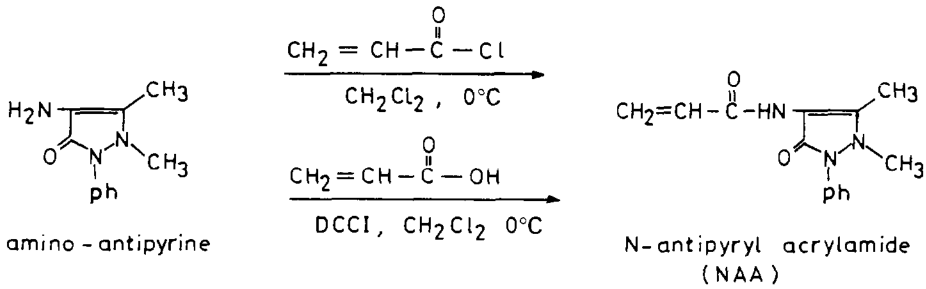
Thermal analysis

DTA was performed at a heating rate of 15°C min^{-1} using a Shimadzu X-D-30 thermal analyser. TG thermograms were obtained at a heating rate of 10°C min^{-1}, using a DT-30B thermal analyser (Shimadzu, Kyoto, Japan).

RESULTS AND DISCUSSION

The *N*-antipyryl-acrylamide (NAA) monomer was prepared according to Scheme 1. The prepared monomer was a white powder, soluble in most organic solvents. The m.p. was 216°C, yield 65%. The ^{1}H NMR and IR spectra of the NAA monomer have been discussed previously [9].

The mass spectrum of NAA monomer is shown in Fig. 1. The fragmentation patterns are represented in Scheme 2 which illustrates the most abundant fragments of NAA monomer.



Scheme 1. Preparation of NAA monomer.

TABLE 1

Characteristic ^{1}H NMR signals and analytical data for NAA–AN copolymers

a	Integral peak area		*b*
	$-C_6H_5$(5H) (7.3 δ)	2(CH_2–CH–) + N–CH_3 + =C–CH_3 (12 H) (3.6–1.2)δ	
0.1111	23	137	0.098
0.2500	28	131	0.214
0.3330	35	144	0.272
0.4285	36	130	0.360
0.5390	53	162	0.483
0.6670	58	165	0.575
1.0000	56	140	0.836

Key: *a* and *b* are the molar ratios of M_1/M_2 in the feed and copolymer respectively.

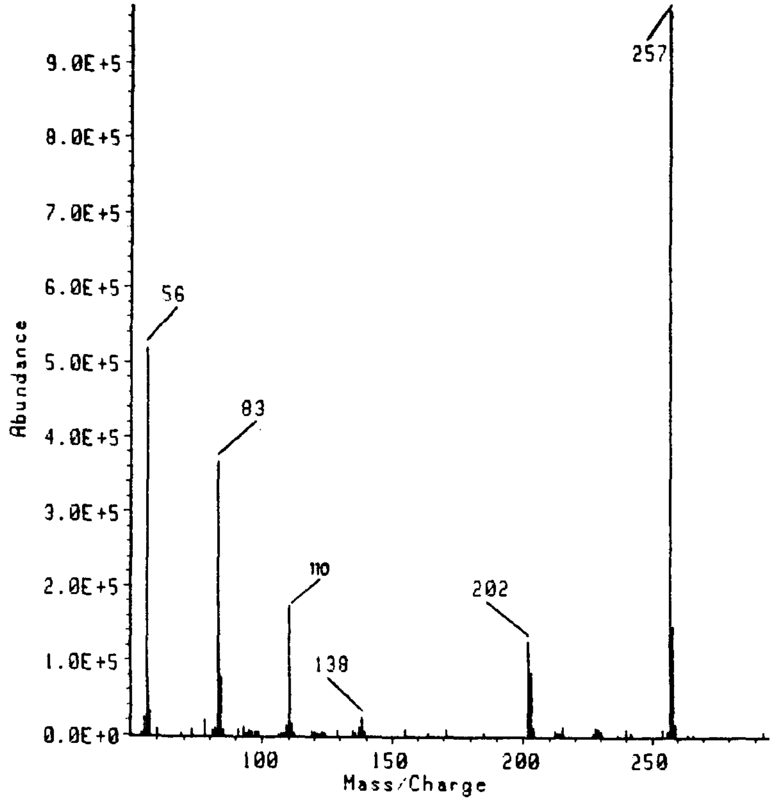


Fig. 1. Mass spectrum of NAA monomer.

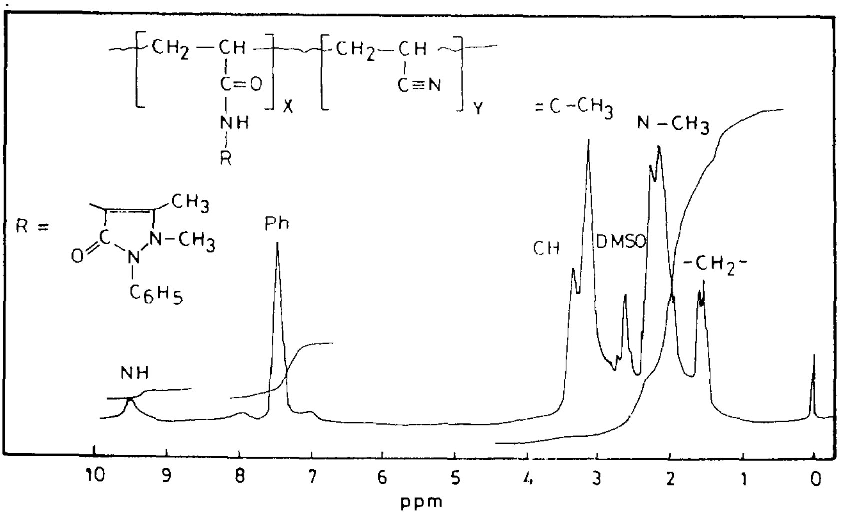


Fig. 2. ${}^1H$ NMR spectrum of NAA–AN copolymer [3].

The composition of the copolymers of NAA–AN was determined by ^{1}H NMR spectroscopy using the approach of Grassie et al. [10]. The characteristic signals used for the quantitative determination of the copolymer composition for equimolar monomer feed are illustrated in Table 1. The ^{1}H NMR spectrum of NAA–AN copolymer [3] is shown in Fig. 2 as an example.

The monomer reactivity ratios, r_1 and r_2, for the comonomers were calculated using the Kelen and Tudos equation [11] and were found to be $r_1(\mathrm{NAA}) = 0.80$ and $r_2(\mathrm{AN}) = 1.14$ [9].

Thermal behaviour

The thermal behaviour of any polymer should be affected appreciably by the introduction of a comonomer in the polymer chain. It was, therefore, important to investigate the thermal behaviour of the prepared copolymers. For this purpose, four NAA–AN copolymers containing 10, 20, 25 and 30 mol% NAA were prepared. The thermal characteristics of PAN have been studied in detail by Grassie [12]. In the present investigation, the thermal analysis of PAN is given as a reference, i.e. the comparison of the DTA and TG data of PAN and those of the corresponding PNAA and copolymers will illustrate the effect of these comonomers on the thermal behaviour of the products.

The DTA curves of PAN and PNAA, and those of the corresponding copolymers with AN are represented in Fig. 3. The thermal analysis of PAN in air shows the usual thermogram with an initial decomposition at 320°C and a broad exotherm with a maximum at 340°C which results from the oligomerization of the nitrile groups and formation of some aromatic structure [12]. However, the DTA curve of PNAA shows exotherms with maxima at 300, 390, 440 and 530°C, respectively, which may represent the homolytic scission and complete decomposition. The proposed homolytic scission of PNAA was suggested from the fragmentation patterns obtained from the mass spectrum of the NAA monomer, Fig. 1. As illustrated in Scheme 2, the most abundant fragmentation is cleaveage of the C–N bond giving a parent ion of m/z 55 (acryloyloxy unit). A similar result has been obtained previously from the fragmentation patterns of *N*-methacryloyloxy phthalimide derivatives [8]. The exotherm at 530°C may represent a complete decomposition. Moreover, in a separate experiment when PNAA was heated at 530°C, a black soluble mass was left indicating that no cross-linking reaction occurs.

The DTA curves of the NAA–AN copolymers show exotherms at 290, 360, 400 and (560–600)°C respectively, reflecting many processes probably including scission, cyclization, cross-linking and decomposition at the higher temperature exotherm. The first stage of decomposition could be attributed to scission of the C–N bond in a manner similar to that occurring in the

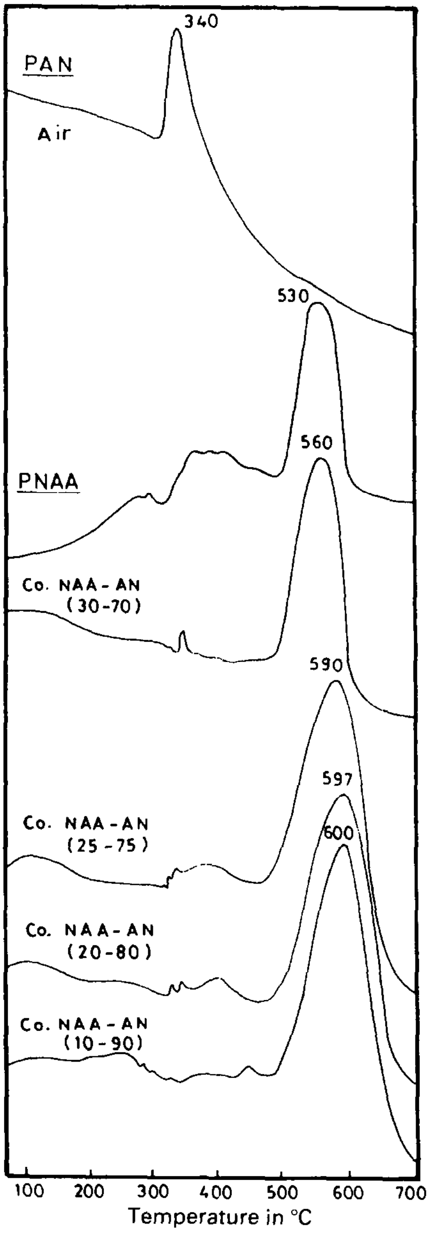
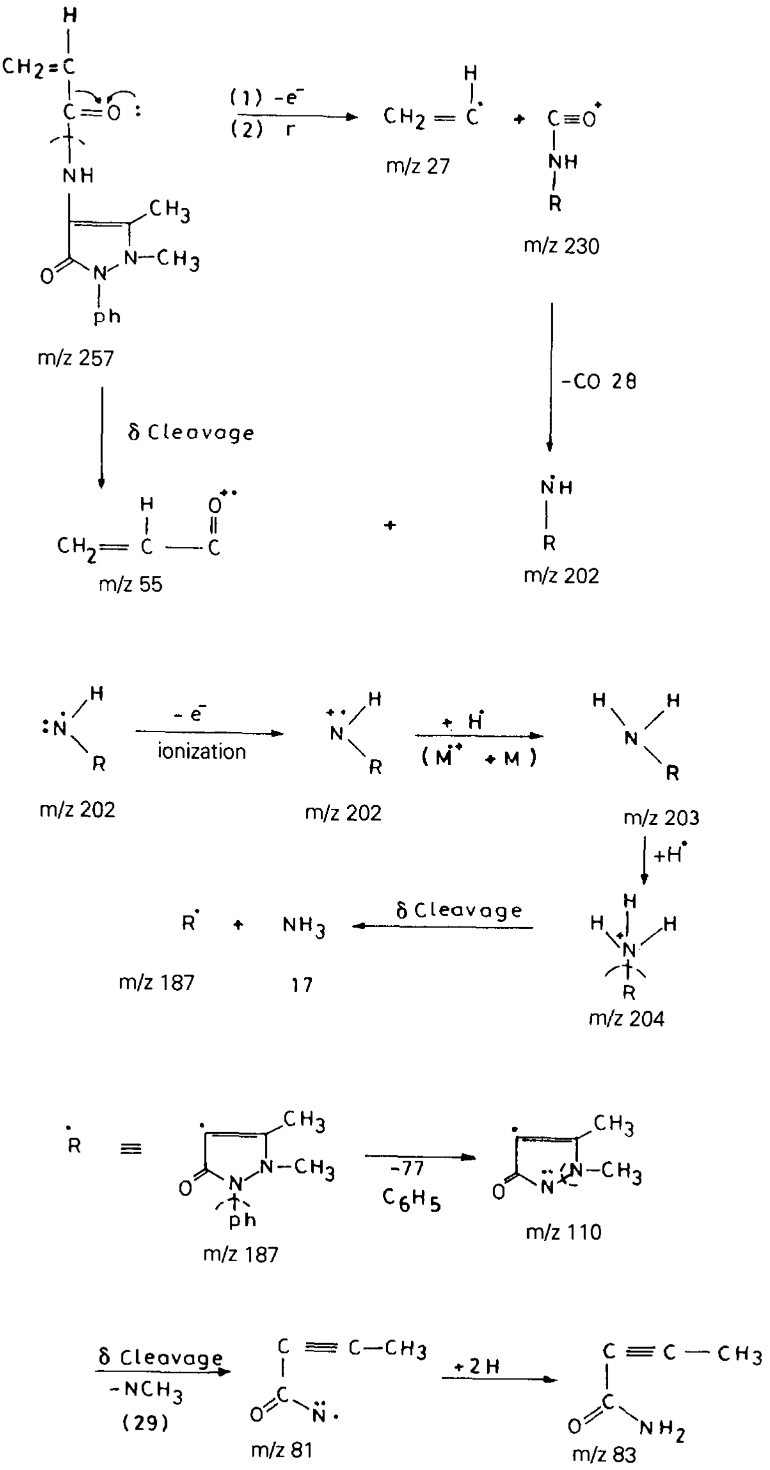


Fig. 3. DTA curves for PAN, PNAA, and (NAA-AN) copolymers in air.

suggested degradation of homopolymers, followed by cyclization and crosslinking. The DTA peaks of the copolymers are shifted to lower temperatures relative to that of PAN, indicating an initiating effect of the comonomers on the cyclization process [6].

The IR spectra for the unheated and heated NAA-AN copolymer [1], Fig. 4, show bands for unheated copolymer at 3150, 2240, 1680, 1645 and



Scheme 2. Fragmentation of NAA monomer, see Fig. 1.

1620 cm^{-1} which are attributed to ν(NH), ν(C≡N), and ν(C=O) of the acryloyl amide (I) (stretching vibration), ν(C=O) of pyrazolone [13] and δ(NH) of amide (II) (bending vibration). However for heated NAA–AN

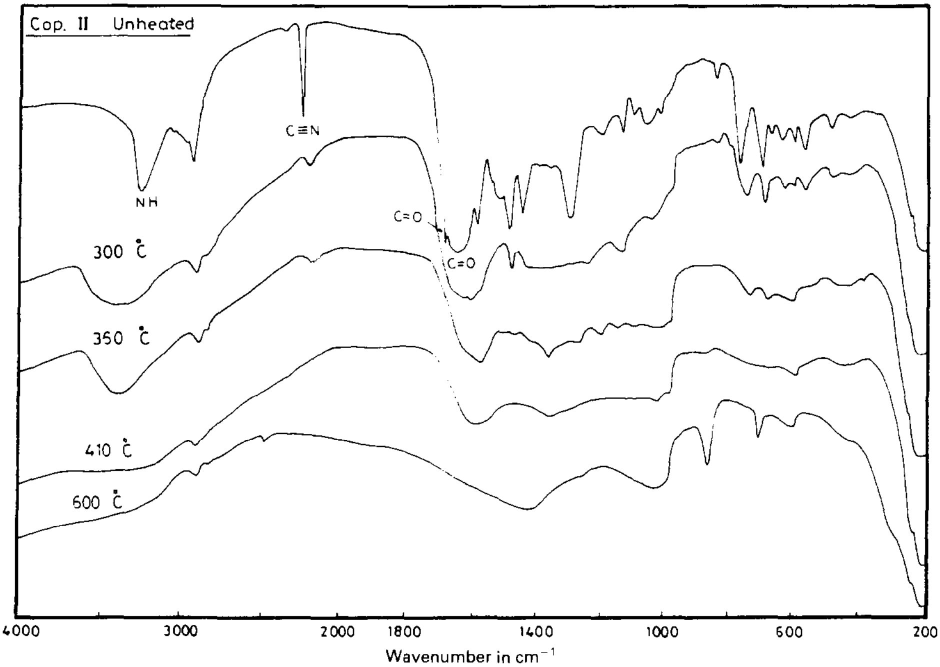


Fig. 4. IR spectra of unheated and heated NAA–AN copolymer [1].

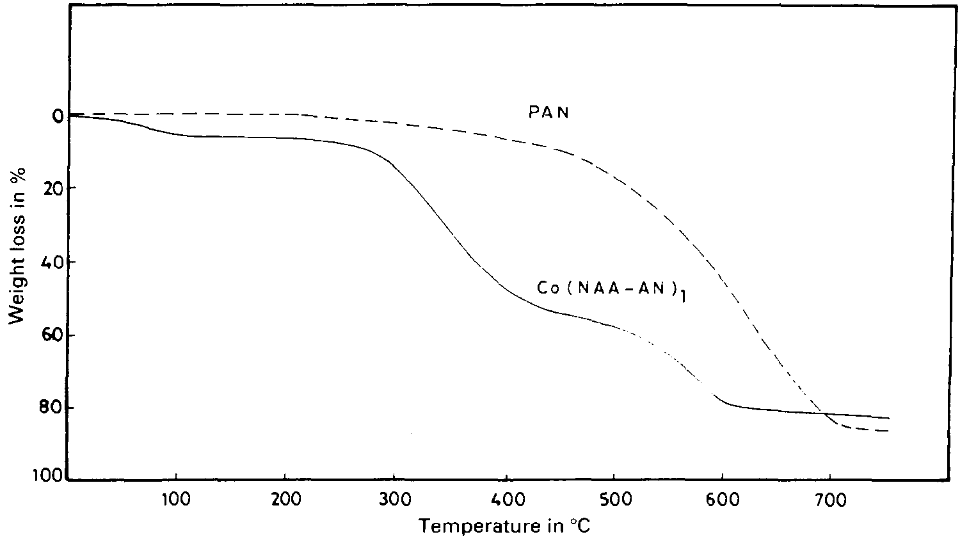
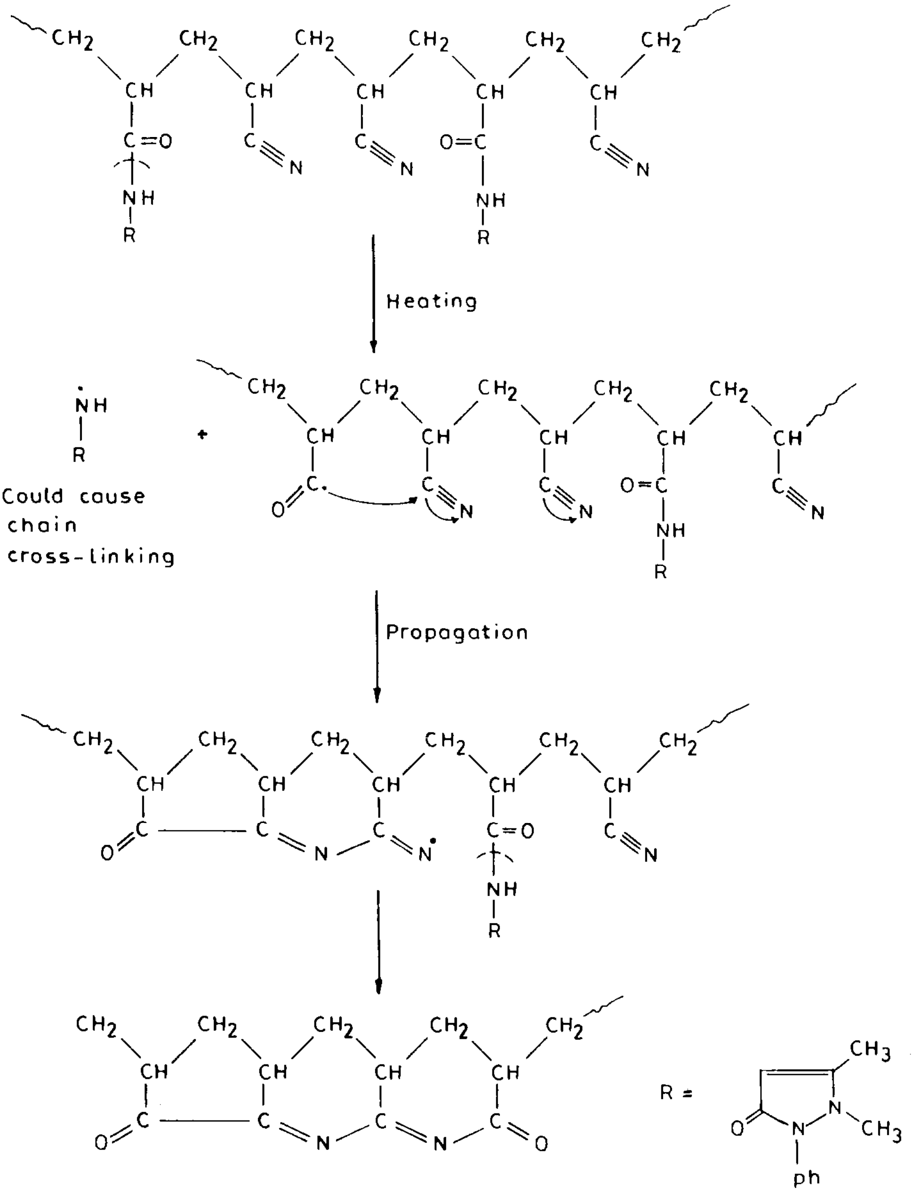


Fig. 5. TG curves in air for PAN (– – –) and NAA–AN copolymer [1] (——).

copolymer at 300, 360, 410 and 600°C, there is an appreciable decrease in the intensity of the C≡N bond at 2240 cm^{-1}. The carbonyl band at 1680 cm^{-1} merges with the band at 1650 cm^{-1}. The bands at 1650 and 1630 cm^{-1} are attributed to the ethylene and imino groups and are enlarged and broadened.

The TG data of PAN and NAA–AN copolymer [1] are represented in Fig. 5. The analysis shows that there is more than one process in the



Scheme 3. Thermal degradation of NAA–AN copolymer.

thermal degradation reaction. It also shows an increase in the weight loss of the copolymer relative to that of PAN. Finally, when NAA–AN copolymer [1] was heated for about 5 min at 410°C, a black insoluble mass was left, indicating an appreciable cross-linking reaction.

From the mass spectrum fragmentation mechanism (Scheme 2) mentioned above, it can be suggested that the lower ionization potential of the C–N bond is responsible for its fission. This confirms our suggested mechanism as represented in Scheme 3.

REFERENCES

1 M.M. Coleman and G.T. Sivy, Adv. Chem. Ser., 203 (1983) 559.
2 M.M. Coleman, G.T. Sivy, P.C. Painter, R.W. Synder and B. Gordon, Carbon, 21 (1983) 255.
3 M.M. Coleman and B. Gordon, Anal. Proc. London, 20 (1983) 572.
4 N. Grassie and R. McGuchan, Eur. Polym. J., 8 (1972) 243.
5 N. Grassie and R. McGuchan, Eur. Polym. J., 8 (1972) 865.
6 M.Z. El Sabee, M.W. Sabaa, M.G. Mikhael and S.H. El-Hamouly, Angew. Makromol. Chem., 168 (1989) 91.
7 M.W. Sabaa, M.G. Mikhael, A.A. Yassin and M.Z. El Sabee, Angew. Makromol. Chem., 139 (1986) 95.
8 S.H. El-Hamouly, Thermochim. Acta, 228 (1993) 111–122.
9 S.H. El-Hamouly, S.A. El-Kafrawi and N.N. Messiha, Eur. Polym. J., 28(11) (1992) 1405.
10 N. Grassie, B.J.D. Torrence, J.D. Fortune and J.D. Gemmel, Polymer, 6 (1965) 653.
11 T.Kelen and F. Tudos. J. Macromol. Sci. Chem., 9 (1975) 1.
12 N. Grassie, Developments in Polymer Degradation, Applied Science, London, 1977, p. 137.
13 M.M. Shoukry, A.K.H. Ghoniem, E.M. Shoukry and M.H. El-Nagdi, Synth. React. Inorg. Met. Org. Chem., 12 (1982) 815.