

Thermal properties of copolymers of acrylonitrile and *N*-methacryloyloxy phthalimide derivatives, using different spectroscopic techniques

S.H. El-Hamouly

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

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Abstract

N-Methacryloyloxy phthalimide (NMph) and *N*-methacryloyloxy tetrachlorophthalimide (NMTCIph) monomers were prepared by the reaction of methacrylic acid with *N*-hydroxy phthalimide and *N*-hydroxy tetrachlorophthalimide in the presence of dicyclohexyl carbodimide (DCCI). The prepared monomers were polymerized or copolymerized with acrylonitrile (AN). The prepared homopolymers as well as the copolymers were characterized by a variety of analytical, spectral and thermal methods.

The thermal behaviour in nitrogen of the homopolymers as well as the copolymers was investigated using differential thermal analysis (DTA) and thermogravimetric (TG) techniques.

NMph and NMTCIph were found to initiate the nitrile oligomerization in the copolymers upon heating. A mechanism for the degradation and initiation of the methacryloyloxy units in the nitrile copolymers is proposed; this was confirmed by interpreting the fragmentation patterns of the obtained mass spectra of the two monomers, as well as the IR spectra of the copolymers after heating.

INTRODUCTION

The copolymerization of acrylonitrile with different comonomers has been used effectively to improve the thermal stability of polyacrylonitrile (PAN).

The thermal degradation of PAN and its copolymers in air as well as under nitrogen has been investigated by Coleman and coworkers [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 upon heating.

It has been argued that because 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 benzylacrylate, and methlymethacrylate participate in the cyclization process and cause a decrease in the intensity of the exotherm without a strong initiating effect. However, styrene, α -methylstyrene vinyl pyridine and vinyl acetate, act as blocking agents for the nitrile oligomerization. El-Sabee 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, respectively [5].

Finally El-Hamouly et al. [8] have also studied the *N*-antipyryl acryloyl thiourea derivative, which belongs to the first category of the Grassie classification.

In the present study, a high conversion of AN–NMph and AN–NMTClph copolymers were prepared and characterized by a variety of spectral, analytical and thermal methods.

EXPERIMENTAL

Materials

Phthalic anhydride and hydroxyamine hydrochloride were purchased from BDH, tetrachlorophthalic anhydride and methacrylic acid from Aldrich, and *N,N*-dicyclohexyl carbodimide (DCCI) from Merck. Acrylonitrile (BDH) was purified by distillation before polymerization. Azobisisobutyronitrile (AIBN), (Merck) was purified by repeated crystallization from ethanol. The solvents used were of reagent grade and were purified according to standard methods.

Preparation of N-methacryloyloxy phthalimide (NMPh) and N-methacryloyloxy tetrachloro phthalimide (NMTClph) monomers

The above monomers were prepared from *N*-hydroxyphthalimide [9]. *N*-Hydroxytetrachloro phthalimide was prepared in a similar manner. The two oximes were reacted with methacrylic acid in the presence of *N,N*-dicyclohexyl carbodimide [10]; 0.2 mol of DCCI as a dehydrating agent was added dropwise to a mixture of a well-stirred cold solution of 0.2 mol *N*-hydroxyphthalimide derivatives and 0.2 mol methacrylic acid in 300 mol methylene chloride. The reaction mixtures were stirred for 20 h at room temperature. The precipitated dicyclohexyl urea was then removed by filtration, and the obtained residue in each case was recrystallized from a benzene/petroleum ether mixture (20:80).

Polymerization and binary copolymerization reactions

Polymerization of NMph and NMTClph monomers, as well as their corresponding copolymers with AN, were obtained by the solution polymerization method in DMF (1.5 mol, 1 l) in the presence of 1.0 mol.%

AIBN as a free radical initiator. The polymerization tubes were flushed with oxygen-free nitrogen for 10 min, and capped and thermostated at 65°C for about 8 h. The resulting homopolymers and copolymers were obtained by precipitation from methanol, washed and dried.

Copolymer analysis

AN–NMph copolymer compositions were calculated from ¹H-NMR spectra; AN–NMTClph copolymer compositions were calculated on the basis of chlorine content in the copolymers. The analysis was carried out at the Microanalytical Unit of the University of Cairo.

Spectral measurements

IR spectra were measured as KBr discs, using a Perkin-Elmer 598 spectrophotometer (4000–200 cm⁻¹). ¹H-NMR spectra were recorded on a Varian EM-390, 90 MHz NMR spectrometer in deuterated DMSO with TMS as an internal reference.

Mass spectra were measured on a Hewlett-Packard Model MS 5988 spectrometer at 15 eV.

Thermal analysis

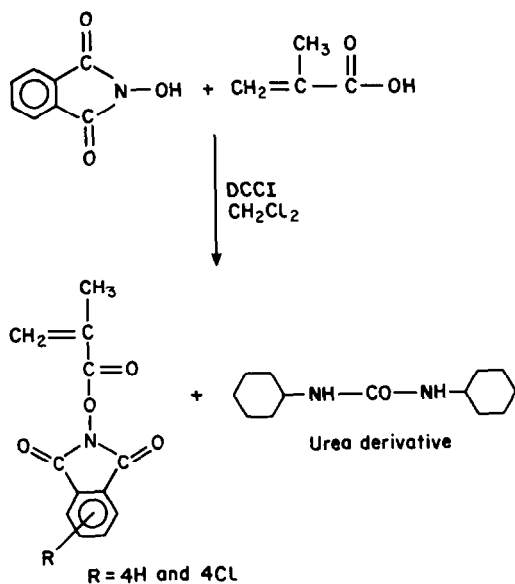
DTA was performed at a heating rate of 15°C min⁻¹ using a Shimadzu X-D-30 thermal analyser. TG thermograms were obtained at a heating rate 10°C min⁻¹ using a DT-30B thermal analyser (Shimadzu, Kyoto, Japan).

RESULTS AND DISCUSSION

NMph and NMTClph monomers were prepared by the reaction of *N*-hydroxy phthalimide and *N*-hydroxy tetrachlorophthalimide with methacrylic acid in the presence of DCCI as dehydrating agent. The mechanism is represented in Scheme 1.

The prepared monomers are pale yellow solids, sparingly soluble in most organic solvents, but easily soluble in DMSO and DMF. The melting point of the NMph monomer is 105°C (yield 75%); for NMTClph it is 147°C (yield 65%). The IR spectra of the prepared monomers are shown in Figs. 1 and 2: these show two strong bands at 1775 and 1720 cm⁻¹ which are characteristic for coupling bands of cyclic imide, a strong band at 1735 cm⁻¹ which is attributed to the ester group of methacryloyloxy, medium bands at 1550 and 1480 cm⁻¹ due to stretching vibrations of aromatic $\nu(\text{C}=\text{C})$, a weak band at 1640 cm⁻¹ which is characteristic for vinyl $\nu(\text{C}=\text{C})$, and a strong band at 1050 cm⁻¹ attributed to the aryl chloride of *N*-methacryloyloxy tetrachlorophthalimide (Fig. 2).

The ¹H-NMR spectra of NMph and NMTClph monomers are shown in



Scheme 1.

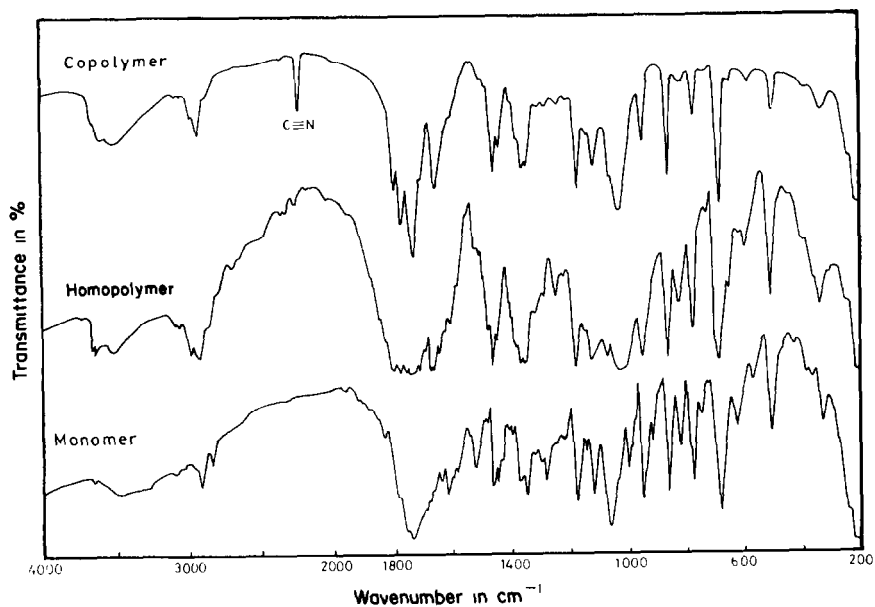


Fig. 1. IR spectra of monomer NMph, homopolymer PHNph, and AN-NMph copolymer (78:22).

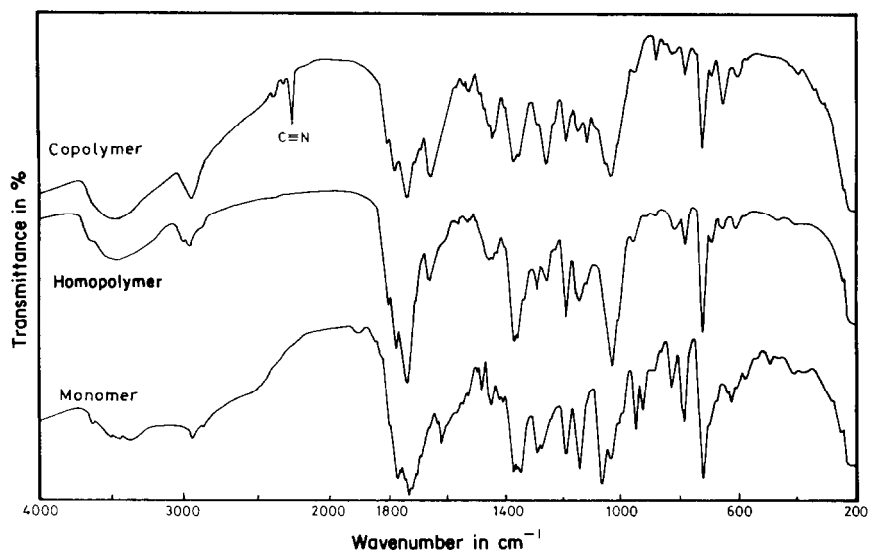


Fig. 2. IR spectra of monomer NMTClph, homopolymer PNMTClph and AN-NMTClph copolymer (88:12).

Fig. 3, A and B. The signals at $\delta = 6.4\text{--}5.8$ are due to the olefinic protons. A signal at $\delta = 2.0$ corresponds to the three protons of $\nu(=\text{C}-\text{CH}_3)$, while the signal at 7.6 (Fig. 3A) is attributed to the 4 protons of aromatic NMph.

The mass spectra of NMph and NMTClph monomers are represented in Fig. 4A and B. The fragmentation patterns are represented in Scheme 2 which illustrates the most abundant fragments of NMph as an example.

Polymerization

NMph and NMTClph were polymerized in DMF at 65°C , using AIBN as a free radical initiator, to give PNMph and PNMTClph. The homopolymers were obtained as pale yellow solids. The yield was 70% for the first monomer and 55% for the second. The homopolymers are soluble in DMSO and DMF, but sparingly soluble in most organic solvents.

The IR spectra of the homopolymers are shown in Figs. 1 and 2: the weak band at 1640 cm^{-1} has disappeared, indicating a complete homopolymerization.

Copolymerization

A series of high-conversion copolymers of AN with NMph and NMTClph were prepared in DMF at 65°C , using AIBN as initiator. The composition data of the copolymers under investigation were obtained from their $^1\text{H-NMR}$ spectra for AN-NMph copolymers, and from their

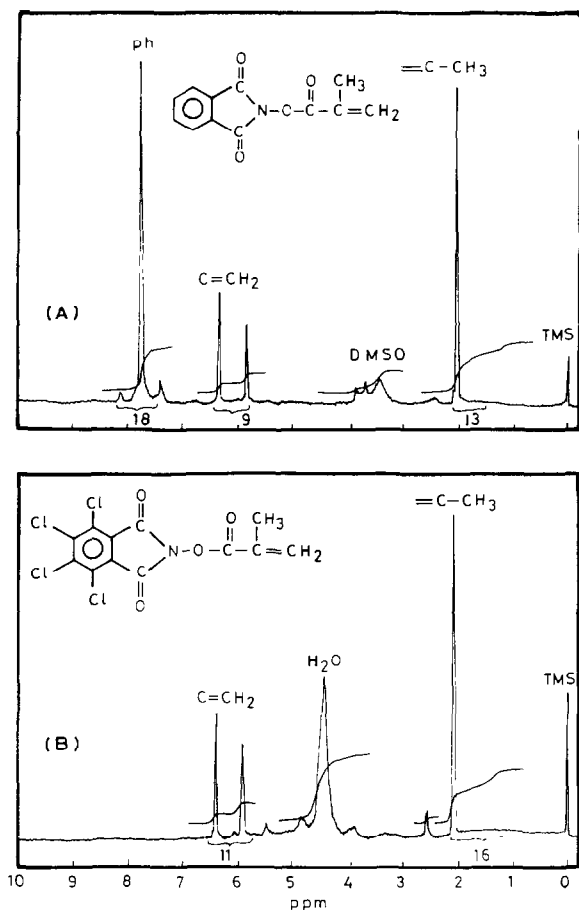


Fig. 3. (A) ¹H-NMR of NMph monomer. (B) ¹H-NMR of NMTClph monomer.

chlorine content for AN-NMTClph copolymers. These are represented in Tables 1 and 2. The IR spectra of the copolymers are also shown in Figs. 1 and 2. The bands at 2240 cm^{-1} indicate the presence of a $\nu(\text{C}\equiv\text{N})$ group in the copolymers.

Thermal behaviour

The thermal behaviour of PAN has been studied in detail by Grassie [11]. In the present investigation, the thermal analysis of PAN is given as a reference: the comparison between the DTA and TG data of PAN and those of the corresponding copolymers will illustrate the effect of these comonomers on the thermal behaviour of the products.

The DTA curves of PAN, PHNph and PNMTClph, and those of the corresponding copolymers with AN are given in Fig. 5, A and B. The thermal analysis of PAN in N₂ shows the usual thermogram with an initial

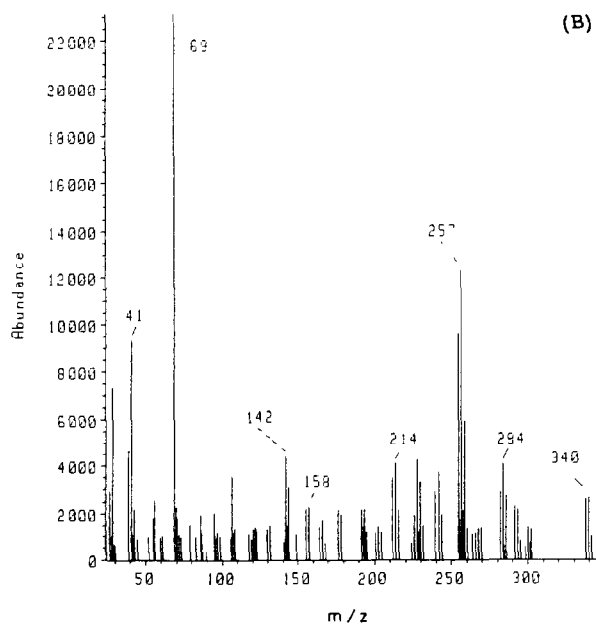
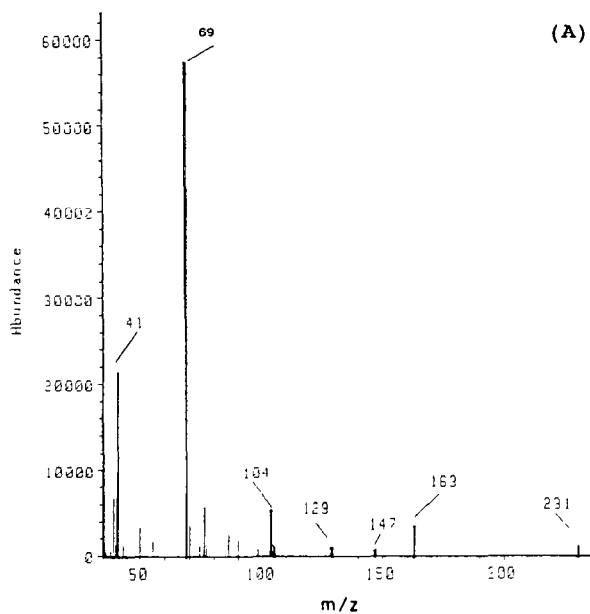


Fig. 4. (A) Mass spectrum of NMph monomer. (B) Mass spectrum of NMTCIph monomer.

TABLE 1

Characteristic $^1\text{H-NMR}$ signals for $\text{AN}(M_1)\text{-NMph}(M_2)$ polymers

Monomer feed/mol%		Integral peak area		Copolymer composition/mol%	
M_1	M_2	C_6H_4 (4H)	X $\text{CH}_2\text{-CH}$ CH_3 Y $\text{CH}_2\text{-C}$	m_1	m_2
90	10	6	28	78.00	22.00
80	20	15	49	63.00	37.00

Solvent, DMF; temperature, 65°C; AIBN, 1 mol%.

TABLE 2

Copolymerization data for the $\text{AN}(M_1)\text{-NMTClph}(M_2)$

Monomer feed/wt. %		Conversion chlorine/ wt. %	Copolymer composition/ wt. %		Copolymer composition/ mol %	
M_1	M_2		w_1	w_2	m_1	m_2
90	10	19.5	51.07	48.93	88.00	12.00
80	20	27.7	30.49	69.51	75.00	25.00

Solvent, DMF; temperature, 65°C; AIBN, 1 mol%.

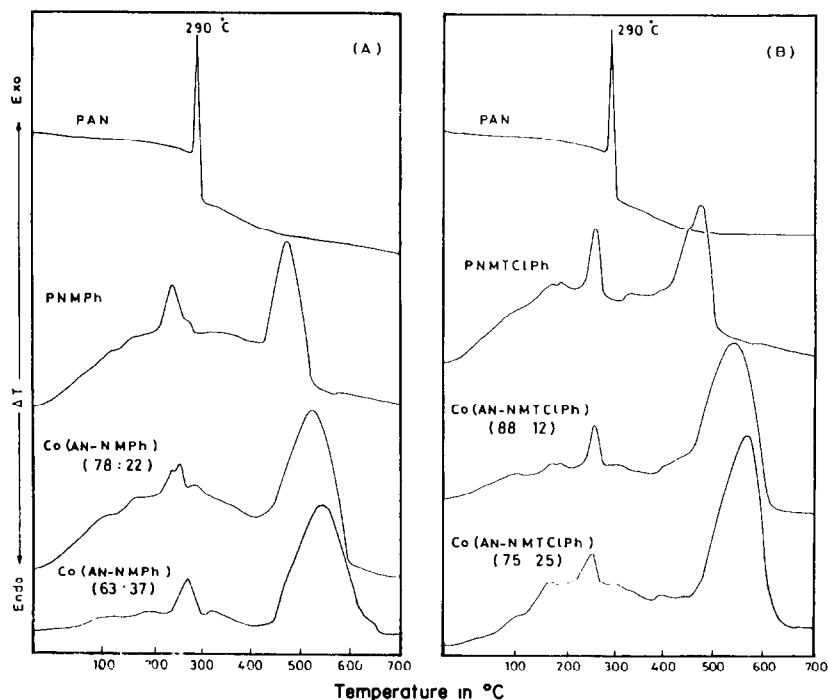
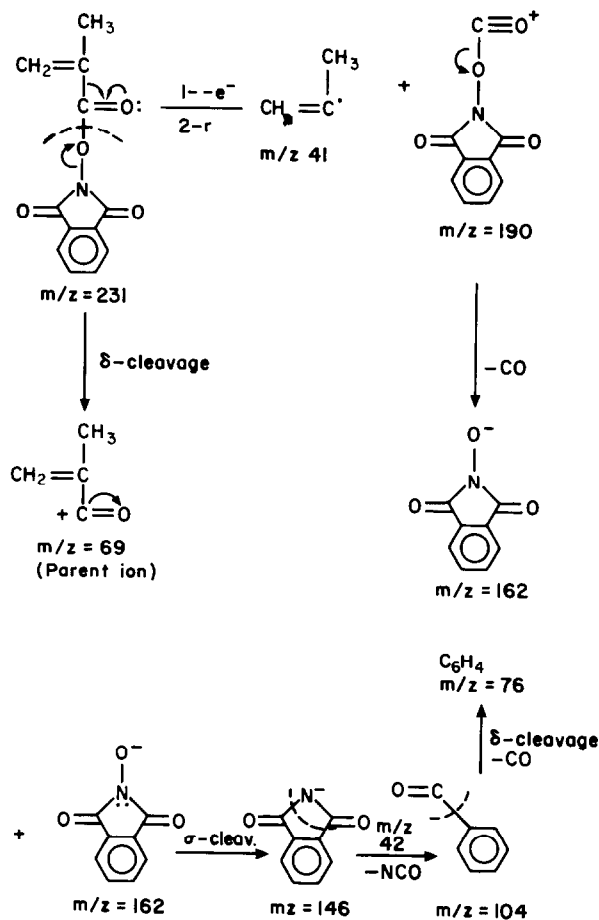


Fig. 5. (A) DTA curves for PAN, PHNph and AN-NMph copolymers in nitrogen. (B) DTA curves for PAN, PNMTClph and AN-NMTClph copolymers in nitrogen.



Scheme 2.

decomposition at 280°C and a sharp exotherm with a maximum at 290°C which results from the oligomerization of the nitrile groups and formation of some aromatic structure [11]. However, the DTA curves of both PNMph and PNMTClph show exotherms with maxima at 260 and 470°C, and 290 and 480°C, respectively, which may represent the homolytic scission and complete decomposition. The proposed homolytic scissions of PHMph and PNMTClph were suggested from the fragmentation patterns of the mass spectra of the corresponding two monomers. As illustrated in Scheme 2, the most important fragmentation cleavage is that of the C–O bond giving a parent ion of $m/z = 69$.

The exotherms at 470°C and 480°C represent a complete decomposition and about 85% weight loss. Moreover, in a separate experiment, when PNMph was heated at 260°C a black soluble mass was left, indicating that no cross-linking reaction occurs.

The DTA curves of the AN–NMph and AN–NMTClph copolymers

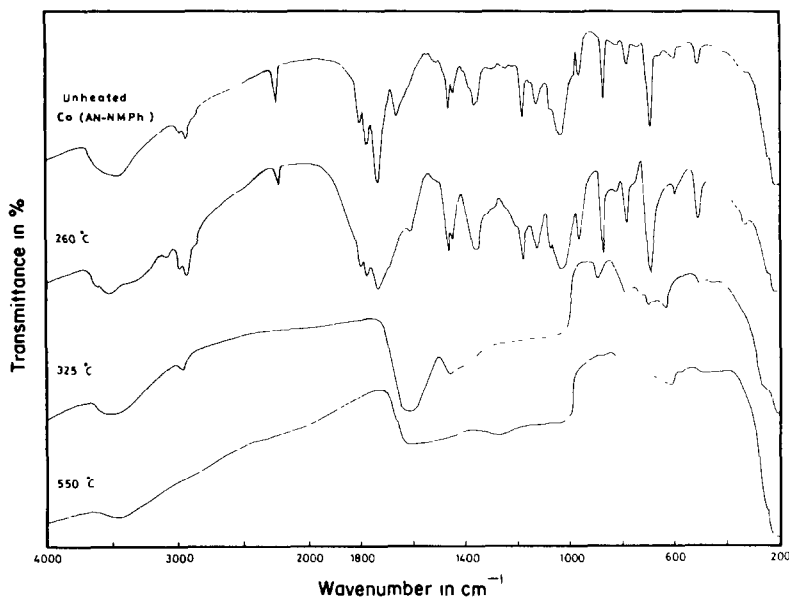


Fig. 6. IR spectra of unheated and heated copolymer AN-NMph.

show exotherms at 260 and 550°C, and 290 and 580°C, respectively, reflecting many processes probably including scission, cyclization, cross-linking and decomposition at the higher temperature exotherm. The first stage of degradation could be attributed to scission of the C–O bond in a manner similar to that occurring in the suggested degradation of the homopolymers, followed by cyclization and cross-linking. The DTA peaks of the copolymers were shifted to lower temperatures relative to that of PAN, indicating an initiating effect of these two comonomers on the cyclization process [6].

The IR spectra for AN-NMph copolymer before and after heating at 260, 325 and 550°C are given in Fig. 6. The spectra show an appreciable

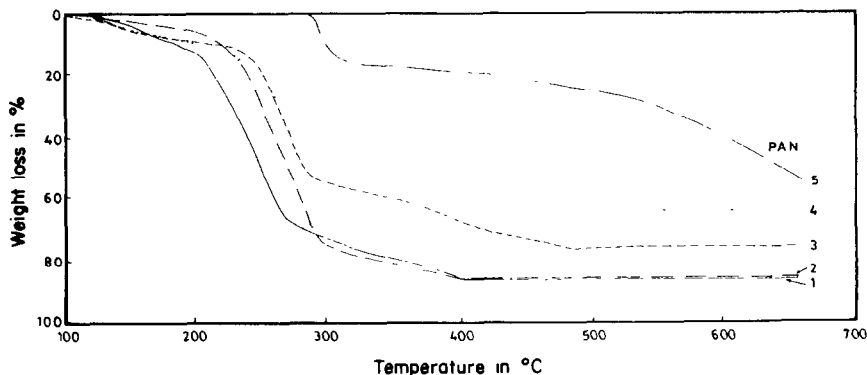
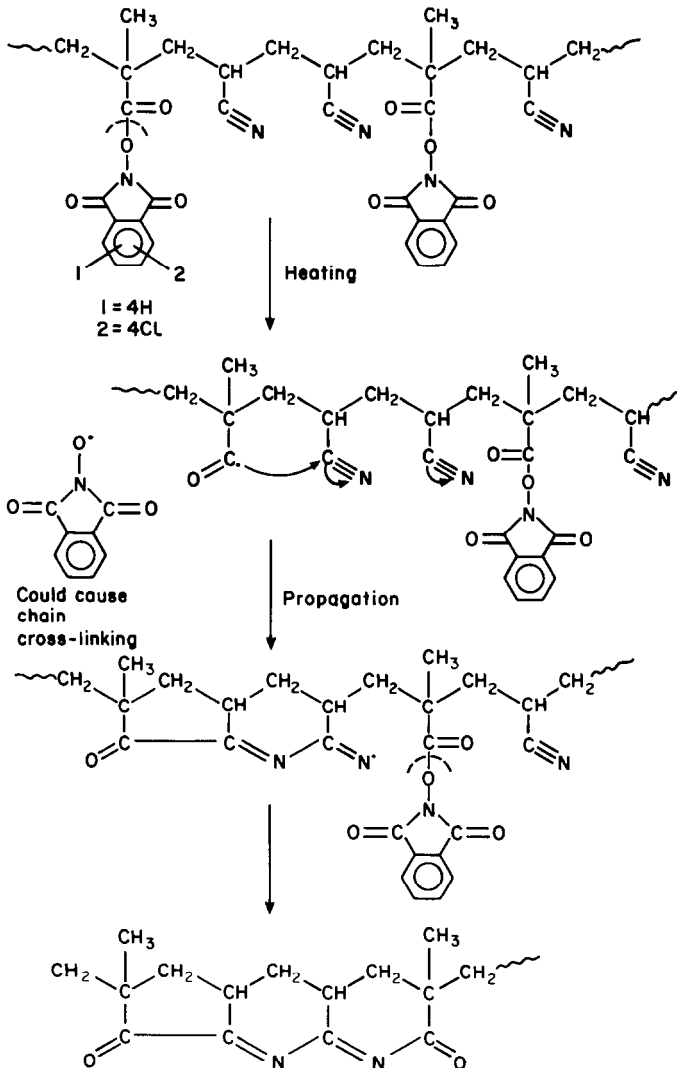


Fig. 7. TG curves in nitrogen, for: 1, PHMph (—); 2, PNMTClph (---); 3, AN-NMph copolymer (78:22) (- · - · -); 4, AN-NMTClph copolymer (88:12) (· · ·); 5, PAN (— · — · —).

decrease in the intensity of the $\nu(\text{C}\equiv\text{N})$ band at 2240 cm^{-1} . The carbonyl band at 1735 cm^{-1} merges into the band at 1690 cm^{-1} . The bands at 1630 and 1690 cm^{-1} , attributed to the ethylene and imino groups, are enlarged and broadened.

The TG data of PAN, PNMph, PNMTClph and those of the corresponding copolymers are represented in Fig. 7. The analysis shows more than one decomposition step, reflecting the presence of more than one process during the thermal degradation reaction. It also shows an increase in the weight loss of the copolymers relative to that of PAN. The weight loss is less



Scheme 3.

pronounced in the case of copolymers containing chlorine, which could be the reason for the high thermal stability of these copolymers. Finally, when AN–NMph copolymer was heated for about 5 min at 325°C, a black insoluble mass was left indicated an appreciable cross-linking reaction.

Depending on the above-mentioned mass spectral fragmentation mechanism, Scheme 2, it could be suggested that the lower ionization potential of the C–O bond is responsible for its fission which consequently confirms our suggested mechanism represented in Scheme 3.

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