Thermal Behavior of 8-methacryloxy-quinoline-Acrylonitrile Copolymers

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Abstract

Acrylonitrile was copolymerized with 8-methacryloxy-quinoline in Dimethylformamide using azobisisobutyronitrile as initiator. The composition of the copolymers was determined by nitrogen analysis and the monomer reactivity ratios (r_1 and r_2) were calculated. Both the homopolymer and the copolymers was characterized by a variety of spectral and thermal methods. Thermogravimetry and differential thermal analysis data showed that the comonomer (MAQ) initiates the nitrile oligomerization reaction in the copolymer upon heating. A mechanism for the initiation of (MAQ) units in the nitrile copolymers was also proposed.

Keywords: 8-methacryloxy-quinoline, Thermal properties, Oligomers, Crosslinking

1. Introduction

The thermal degradation of polyacrylonitrile (PAN) and its copolymers in nitrogen as well as under nitrogen atmosphere was previously investigated by Coleman et al. Intramolecular cyclization, intermolecular crosslinking, and water elimination have been proposed. (El-Hamouly, 1994; Azab, 1994; Meneill, 1998; Jang, 2000; Anathalakshmi, 1999) Oxidative reactions were a major factor with subsequent heating. Grassie and McGuchan (1972) investigated the effect of copolymerization on the oligomerization of the nitrile group of PAN on heating.

The technological importance of PAN is known to suffer from several disadvantages: weak modability, color instability, and weak dyeability. Besides other efforts to abolish these difficulties, several monomers have been

used as comonomers for the production of acrylonitrile (AN) copolymers (Grassie, 1971, 1974) with improved thermal stability.

The present study was conducted to investigate the effect of introducing a methacryloyloxy unit into the polymer chain of PAN. It was expected that the thermal properties of PAN would be greatly affected and, consequently, it was necessary to investigate the thermal behavior of the copolymers produced.

2. Experimental

2.1 Materials

Acrylonitrile (AN) was obtained from BDH (Toronto, Canada) and was purified by distillation before polymerization; 8-hydroxyquinoline was provided by (S.D.finechem.- Ltd., Mumbai, Indi) methacrylic acid (Aldrich) was distilled twice at reduced pressure; N,N-dicyclohexylcarbodiimide (DCCI) and azobisisobutyronitrile (AIBN) were from Merck (Darmstadt, Germany), Dimethylformamide (El gomheria, Cairo, Egypt) triethanolamine (S.D.finechem.- Ltd., Mumbai, Indi) and methacryloyl chloride (Aldrich).

2.2 Synthesis of 8-methacryloloxy-quinoline (MAQ)

MAQ was prepared by the reaction of 8-hydroxyquinoline with the corresponding acid chloride or by the reaction of 8-hydroxyquinoline with the corresponding acid as follows:

2.2.1 Acid chloride method (Ferrnti, 1974)

To a well-stirred solution of 8-hydroxyquinoline (14.5 g; 0.1 mol) and triethylamine (28.5 ml; 0.3 mol) in 350 ml of dry methylene chloride, 8.61 ml (0.1 mol) of methacryloyl chloride was added dropwise under cooling in ice bath (0 –5°C). After the complete addition of methacryloyl chloride, the reaction mixture was then allowed to stand at room temperature for 3 h. the solvent was evaporated. The residue obtained was crystallized from diethyl ether (yield 80%, m.p. 50°C).

2.2.2 N,N-Dicyclohexylcarbodiimide (DCCI) method (Ferrnti, 1975)

To a well-stirred cooled solution (0–5°C) of 8-hydroxyquinoline (2.9 g; 1 mol) and methacrylic acid (3.44 ml; 2 mol) in 300 ml of dry methylene chloride, 4.12g (0.1 mol) of DCCI was added dropwise. The reaction mixture was stirred for 3 h at room temperature and the precipitated dicyclohexyl urea was removed by filtration. The resulting solution was evaporated under reduced pressure and the solid product was crystallized from diethyl ether (yield 70%, m.p. 49-52°C).

<center>**<Scheme 1>**</center>

2.3 Polymerization procedures

Ampoules of Pyrex glass were charged with the monomer mixtures, the solvent (DMF), 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 10 h.

The contents were poured into a large excess of methanol. The polymers obtained were washed several times with hot methanol and dried at 50°C to constant weight. The nitrogen content of the copolymers was determined by a modified Kjeldahl method.

2.4 Spectral measurements

[1]H-NHR spectra were recorded on a Varian MR-400 spectrometer (Varian Associates, Palo Alto, CA) operating at 400 MHz in deuterated $CDCl_3$. IR spectra were recorded in KBr discs using a Shimadzu 470 (4000– 400 cm^{-1}) spectrophotometer (Shimadzu, Kyoto, Japan).The mass spectrum was measured on a Shimadu QP-Zolo plus Model spectrometer(Shimadzu, Kyoto, Japan) operating at 70eV.

2.5 Thermal analysis

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

3. Results and Discussion

8-methacryloxy-quinoline (MAQ) monomer was prepared according to Scheme 1. The prepared monomer was a white powder, soluble in most organic solvents. The ^{1}H-NMR spectrum of MAQ monomer (Fig. 1) showed the following there are three multiplet peak appear near δ 8.86-8.94, δ 8.08-8.21 and δ 7.25 -7.75,corresponding to the protons of quinolyl ring at 3,5,6,7 site, 4-site and 2 site respectively. (s,CH_3) of MAQ appear near δ 2.15 and the peaks for CH_2=C protons of MAQ appear near δ 6.54 and δ 5.82-5.86 respectively corresponding to DMSO.

Structures of the prepared monomer (MAQ), homopolymer (PMAQ), and copolymer with AN were investigated by IR spectroscopy. The IR spectra showed bands at 2918, 1740, 1630, and 1400 cm^{-1} attributable to υ (C-H) aliphatic, υ (C=O), υ (C=C), and υ (C-O), respectively.The spectrum of the copolymer shows a new band at 2363 cm^{-1} attributable to υ (C≡N).

The mass spectrum of MAQ monomer is shown in Figure 2. The fragmentation patterns are represented in Scheme 2, which illustrates the most abundant fragments of MAQ monomer.

The copolymerization data of MAQ with AN in DMF at 65°C are summarized in Table 1 The reactivity ratios for the comonomer were calculated using the Kelen–Tudös equation. (Kelen, 1975) Figure 3 shows a plot for this system. The intercept at ξ=0.403 is equal to r_1 (MAQ) and that at η=0.63is equal to r_2/α, (Tüdö s, 1976) where α is an arbitrary parameter.

3.1 Thermal behavior

The thermal behavior of any polymer should be affected appreciably by the introduction of a comonomer in the polymer chain. It is thus important to investigate the thermal behavior of the prepared copolymers.

For this purpose four MAQ–AN copolymers containing 10, 20, 30, 40,50,60 and 70% MAQ were prepared. The thermal characteristics of PAN were previously studied in detail by Grassie. (Grassie, 1977) In the present investigation, the thermal analysis of PAN is given as a reference; that is, the comparison of DTA and TG data of PAN and those of the corresponding PMAQ and copolymers will illustrate the effect of these comonomers on the thermal behavior of the products.

The DTA curves of PAN and PMAQ and those of the corresponding copolymers with AN are represented in Figure 4 The thermal analysis of PAN in air shows the usual thermogram with an initial decomposition at 320°C and a broad exotherm peak with a maximum at 340°C, which results from the oligomerization of the nitrile groups and formation of some aromatic structures. (Grassie, 1977) However, the DTA curve of PMAQ shows exotherms with maxima at 180, 273 and 459°C, respectively, which may represent the hemolytic scission and complete decomposition.

Proposed homolytic scission of PMAQ was suggested from the fragmentation patterns obtained from the mass spectrum of MAQ monomer (Fig. 2). As illustrated in Scheme 2, the most abundant fragmentation is cleavage of the C-N bond, giving a parention of *m/z*= 69 (methacryloyloxy unit). A similar result was obtained previously from the fragmentation patterns of *p*-acryloyloxy-tri-*n*-butyltin benzoate. (Azab, 1994; 2003) and fragmentation patterns of *p*entachlorophenyl Methacrylate (Azab, 2003) The exotherm at 459°C may represent a complete decomposition. Moreover, in a separate experiment when PMAQ was heated at 459°C, a black soluble mass remained, indicating that no crosslinking reaction occurred.

The IR spectra of unheated MAQ and PMAQ samples at different temperatures are shown in Figure 5 The spectra show no change in most of the functional groups present upon heating to 250°C. Above this temperature, the characteristic bands at 1400, 1740, and 3000 cm^{-1} attributed to υ (C=O), υ C-O, and υ (C-H) aliphatic gradually decrease until they disappear at 600°C. The above arguments indicated that the PMAQ homopolymer decomposed by increasing the temperature. The exotherm at 600°C represents a complete decomposition and 100% weight loss.

The DTA curves of MAQ–AN copolymers in Nitrogen (Fig. 4) show exotherms at 468, 500, 550,585 and 600°C, reflecting many processes probably including scission, cyclization, crosslinking, 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 suggested degradation of homopolymers, followed by cyclization and crosslinking. The DTA peaks of the copolymers were shifted to lower temperatures relative to that of PAN, indicating an initiating effect of the MAQ comonomers by a cyclization process.

The IR spectra for the unheated and heated MAQ–AN copolymer **1** (40 : 60) (Fig. 5) show bands for unheated copolymer at 2240, 1720, and 1400cm^{-1} that are attributed, respectively, to υ (C≡N), υ (C=O), and υ (COO). However, for heated MAQ–AN copolymer at 250, 350, 450 and 600°C there is an appreciable decrease in the intensity of the C≡N band at 2240 cm^{-1}. The carbonyl band at 1720 cm^{-1} merges with the band at 1700 cm^{-1}. The bands at 1700 and 1600 cm^{-1}, characteristic for the (C=O) and (C=N) groups, are enlarged and broadened. (Grassie, 1972) These spectral changes reveal radical changes in the copolymer structure and must also be the result of a direct interaction between the nitrile group and the functional groups of the comonomer. In this interaction an initiation of cyclization and crosslinking reactions will occur.

The TG thermograms for PAN, MAQ, and the four different concentrations of MAQ–AN copolymers are given in Figure 6 The analysis shows the existence of two transitions, probably reflecting more than one process during

the thermal degradation reaction. Also, the TG curves show an increase in the weight loss of the copolymer relative to that of PAN. This could be confirmed when the MAQ–AN copolymer was heated for about 5 min at 330°C; a black insoluble mass remained, indicating an appreciable crosslinking reaction attributed to the cyclization process. Based on the above-mentioned thermal and spectral data, the mechanism in Scheme 3 is suggested for the thermal degradation of copolymers.

4. Conclusions

The thermal stability of the MAQ–AN copolymers showed that the MAQ comonomer initiates the nitrile oligomerization reaction in the copolymers upon heating and formation of some aromatic compounds.

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Table 1. Analytical Data for Copolymerization of MAQ with AN[a]

Feed composition (a)	Conversion (%)	Copolymer composition (b)
0.1111	7.35	0.39
0.25	8.67	0.41
0.6667	9.01	0.724
1.5	6.42	1.38
2.33	5.2	1.63

[a] (a) and (b) are the molar ratios of M_1/M_2 in the feed and copolymer, respectively, and N (%) values were determined by a modified Kjeldahl method.
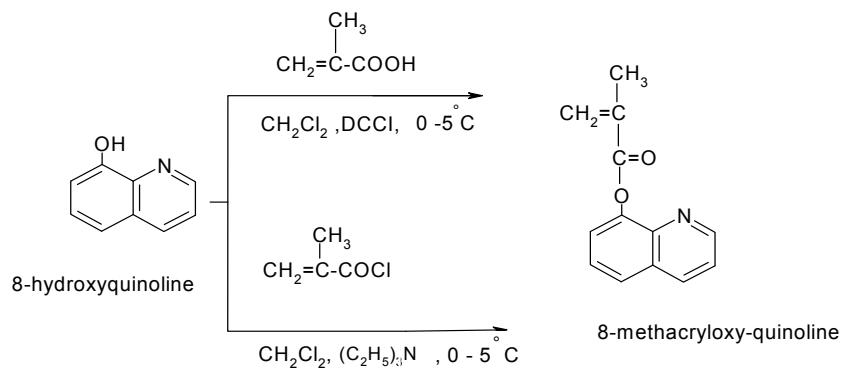
Scheme 1. Preparation of MAQ monomer
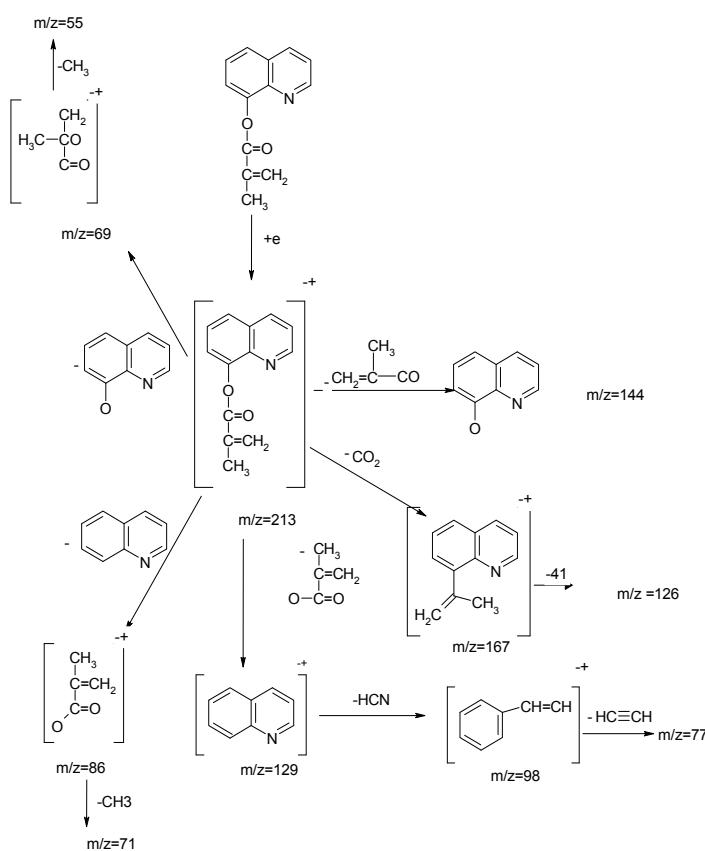
Scheme 2. Fragments of MAQ monomer
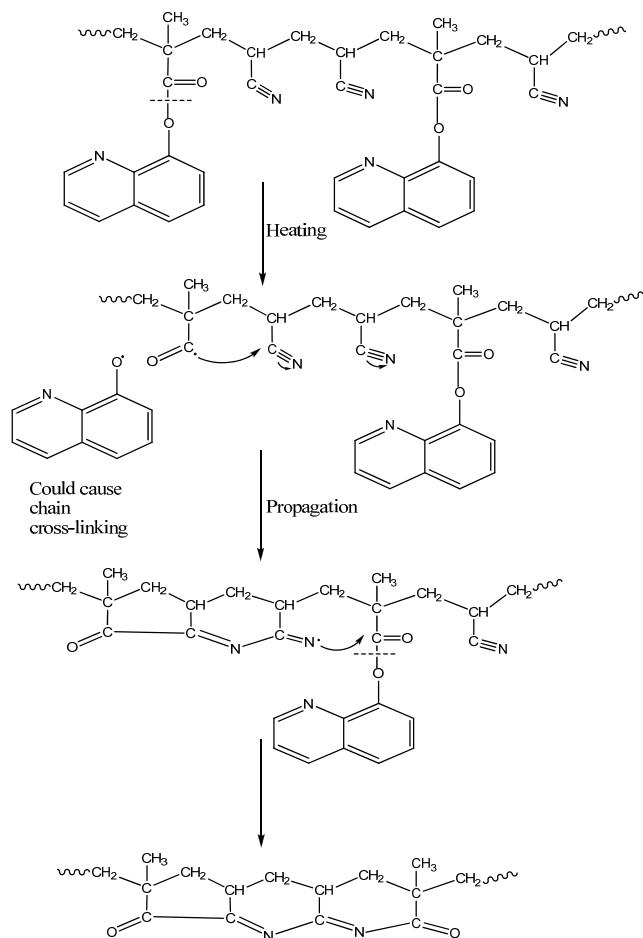
Scheme 3. Thermal degradation of MAQ-AN copolymer
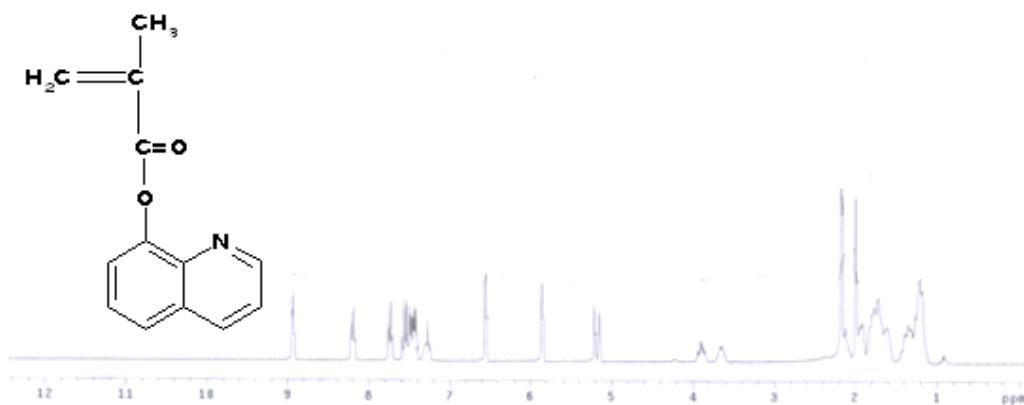
Figure 1. ¹H-NMR spectrum of MAQ monomer
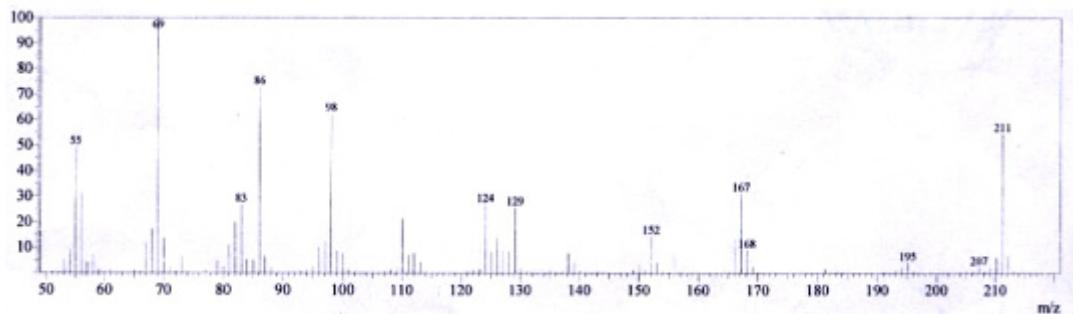
Figure 2. Mass spectrum of MAQ monomer
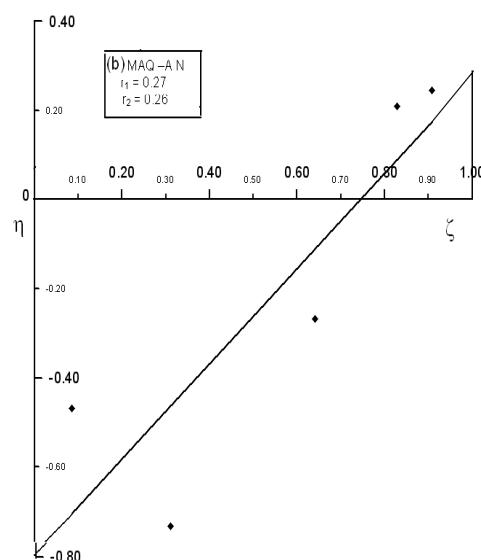
Figure 3. Kelen–Tüdö¨ s plot for copolymerization of MAQ monomer with AN $\xi = [a2/(ab\_a^2)]$ and $\eta = \{[a(b\_1)]/(\_b\_a^2)\}$, where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively; and $=[a_{min}a_{max}/b_{min}b_{max}]^{1/2}$
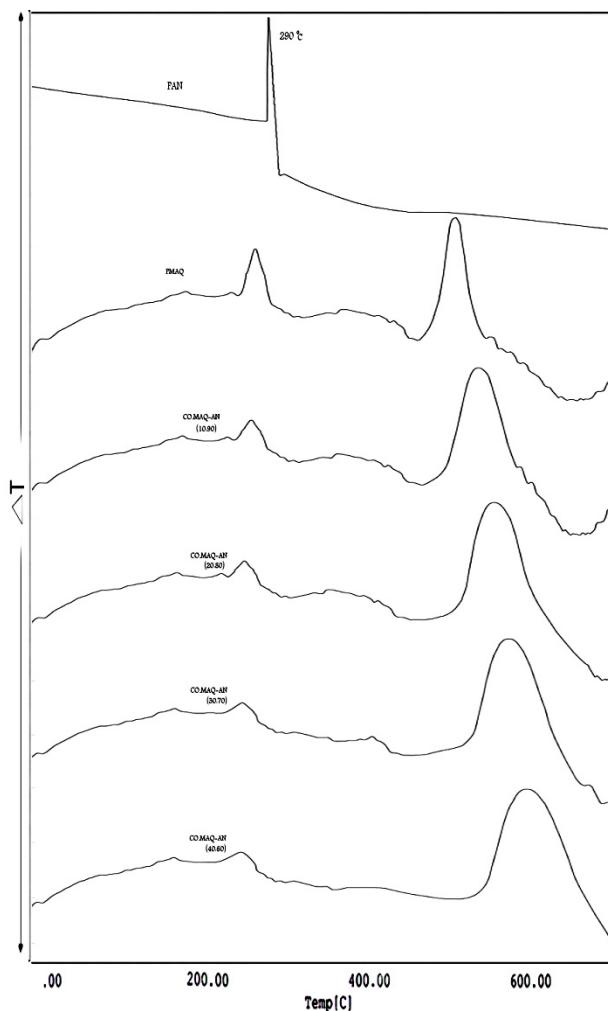
Figure 4. DTA curves for PAN, PMAQ, AN, and copolymer (MAQ–AN) in Nitrogen
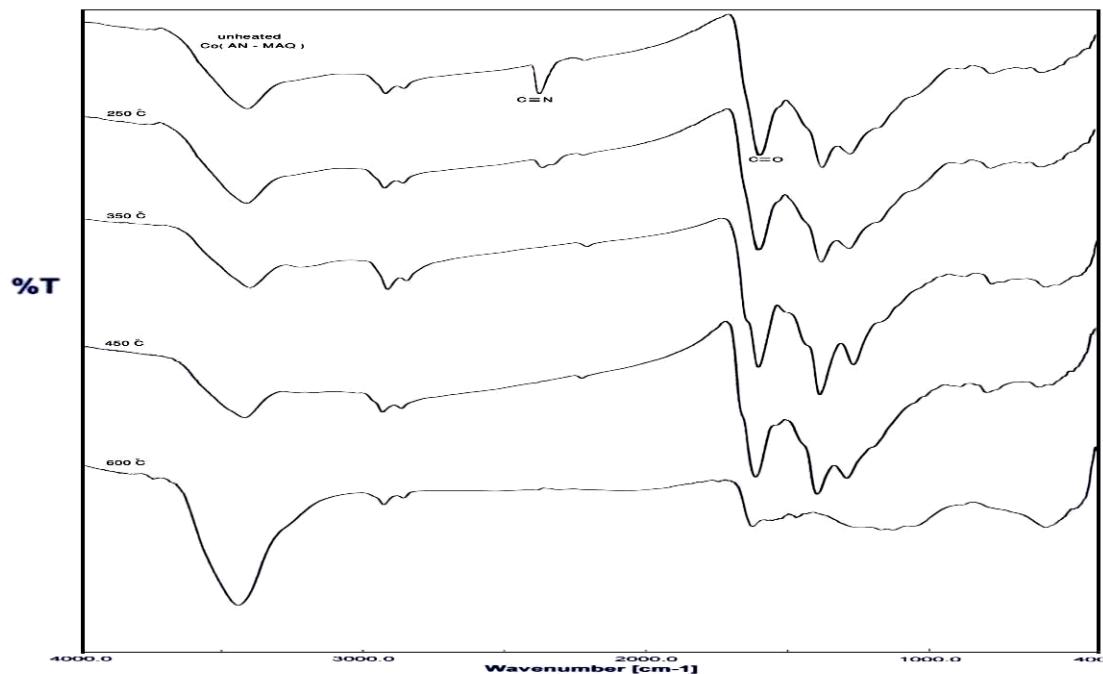
Figure 5. IR spectra of unheated and heated MAQ -AN copolymer
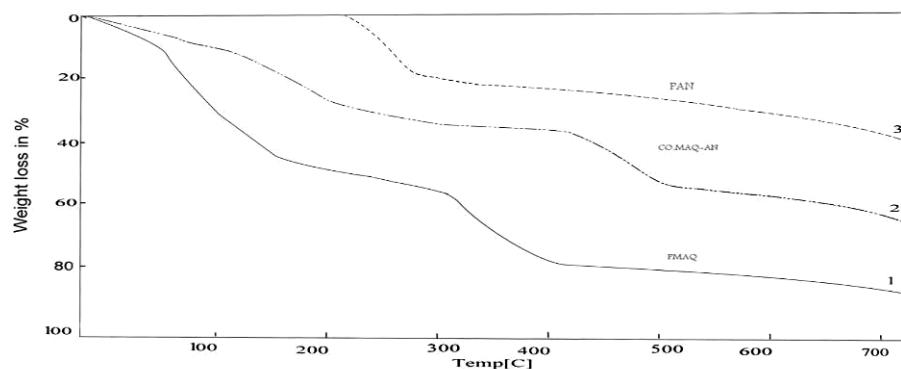
Figure 6. TG curves in N_2 for PAN (------), MAQ -AN copolymer (–··) and P MAQ