

Thermal Stability and Degradation of Poly N-(4-Methoxy-2-methylphenyl)acrylamide Homopolymer and Copolymer of N-(4-Methoxy-2-methylphenyl)acrylamide with Methyl Methacrylate

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ABSTRACT- Different concentrations of copolymer of N-(4-methoxy-2-methylphenyl)acrylamide(MA) with methyl methacrylate (MMA) were prepared and the reactivity ratio values of copolymerization were calculated using Microanalysis technique. Thermal analysis of the copolymers showed that the thermal stability are intermediate between poly(N-(4-methoxy-2-methylphenyl)acrylamide) (PMA) and poly(methyl methacrylate) (PMMA) homopolymers. Thermal degradation products of the PMA were identified by GC-MS techniques. It seems that the mechanism of degradation of PMA homopolymer is characterized by free radical formation followed by recombination along the backbone chain. The activation energies of the thermal degradation of the copolymers were calculated using Arrhenius relationship.

Keywords: N-(4-methoxy-2-methylphenyl)acrylamide, Thermal stability, Degradation and reactivity ratios.

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1 INTRODUCTION

Copolymerization is one of the most important means to improve the performance of thermal stability of polymers. Copolymers are extensively used in industrial processes, because their physical properties, such as elasticity, permeability, glass transition temperature (T_g) and solvent diffusion kinetics can be varied within wide limits [1,2].

Knowledge of a copolymer's composition is an important factor in the evaluation of its utility [3,4]. Controlling the polymer property parameters, such as copolymer composition, copolymer sequence distribution and molecular weight averages, is of particular importance in copolymerization processes. This is because copolymer density and viscosity,

which are two of the most important property measures used by polymer manufacturers, depend on these parameters [5]. Reactivity ratios are among the most important parameters for the composition equation of copolymers, which can offer information such as the relative reactivity of monomer pairs and help estimate the copolymer composition [3].

To calculate the polymerization rate or polymer productivity and copolymer composition, monomer reactivity ratios must be known. The method which is used most often nowadays for estimating monomer reactivity ratios is to perform a low conversion copolymerization at various initial monomers feed compositions. Subsequently, the copolymer composition is determined for each reaction [5]. Reactivity ratio values may be evaluated by various procedures: linear procedures, nonlinear procedures, and other copolymer composition equations [6,9].

Different concentrations of copolymer of N-(4-methoxy-2-methylphenyl) acrylamide with methyl acrylate were prepared and the reactivity ratio values of the copolymerization were calculated using ¹H-NMR technique [10]. Thermal analyses of the copolymers showed that the stability of nitrogenated polymer has been improved by copolymerization with methyl acrylate. The activation energies of the thermal degradation of the copolymers were calculated using Arrhenius relationship.

Most of the thermal degradation results from free radical reactions initiated by bond breaking and depends on the relative strengths of the bonds that hold the molecules together. A large molecule will break apart and rearrange in a characteristic way [11].

In this paper, homopolymers of N-(4-methoxy-2-methylphenyl) acrylamide (MA) and methyl methacrylate (MMA) and different composition of copolymers of N-(4-methoxy-2-methylphenyl) acrylamide and methyl methacrylate (MA-MMA) were prepared, so that the reactivity ratios might be determined using Microanalysis method. The thermal stability of the homopolymers and copolymers were examined. Thermal degradation of the PMA homopolymer was studied using GC-MS apparatus and the activation energies of the thermal degradation of the homopolymers and copolymers were calculated using Arrhenius relationship.

2 EXPERIMENTAL

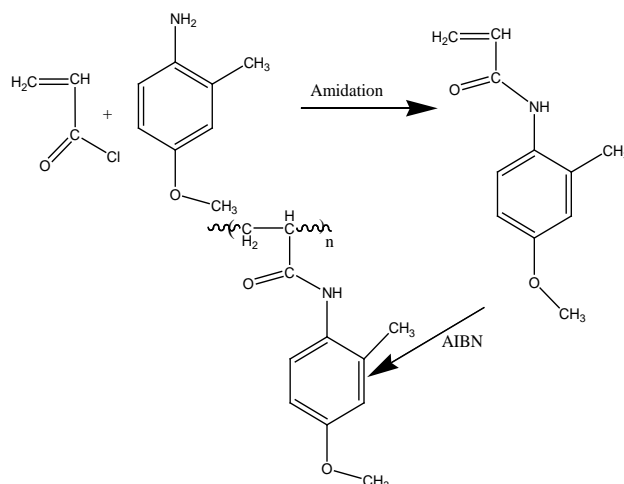
2.1. Materials

Acryloyl chloride (AC) (Aldrich Chemical Co., Inc.) was used without further purification. It was stored below -18°C in a tightly glass-stoppered flask. 2,2'-Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co., Inc.) was used as initiator for all polymerizations. It was purified by dissolving it in hot ethanol and filtering [12]. The solution was left to cool. The pure material was being collected by filtration and then dried. Methyl methacrylate (MMA) (BDH Chemical Ltd.), stabilized with 0.1% hydroquinone was washed with a small amount of sodium hydroxide solution, separated with a separating funnel, distilled on a vacuum line, dried over anhydrous sodium sulphate and stored below -18°C. 2-Methyl-4-methoxyaniline (Aldrich Chemical Co., Inc.) was used without further purification. All other chemicals and solvents were purified by standard procedures.

2.2. Preparation of monomer and polymers

(N-(4-methoxy-2-methylphenyl)acrylamide) (MA) monomer was prepared by the reaction of equimolar amounts of AC and 2-methyl-4-methoxyaniline in dry benzene until the evolution of hydrogen chloride ceased forming a white powder of MA monomer. Poly(N-(4-

methoxy-2-methylphenyl)acrylamide) (PMA) homopolymer was prepared by free radical initiation of MA using 0.1 w/v% AIBN as initiator and DMF as solvent and reflux for 6 hr. The polymer product was precipitated by pouring in distilled water and dried in a vacuum oven for several days at 40 °C.



Copolymers of MA with MMA were prepared using 0.2 w/v. % AIBN as free radical initiator and 50/50 (v/v) DMF as solvent. Different copolymer compositions of MA-MMA were prepared, so that the reactivity ratios might be determined. Polymerization was carried out to about 10% conversion. The polymers were precipitated by pouring into a large excess of distilled water, filtered and dried in a vacuum oven at 40°C for several days.

2.3. Analytical techniques

2.3.1. Infrared spectroscopy (IR)

Spectra were recorded on Pye Unicam SP 2000 spectrometry, for the homopolymers and copolymers in the form of KBr discs.

2.3.2. Nuclear magnetic resonance spectroscopy (NMR)

¹H-NMR spectra were obtained using a Varian EM 390 90 MHz spectrometer with integration and 20 mg samples in dimethylsulphoxide (DMSO) solvent using tetramethylsilane (TMS) as internal reference.

2.3.3. Microanalysis

Nitrogen content determination was performed by the Microanalytical Unit at Cairo University.

2.3.4. Thermogravimetry (TG)

TG measurements were made with a Mettler TG 3000 apparatus. Finely powdered (~10 mg) samples were heated at 10°/min in a dynamic nitrogen atmosphere (30 ml/min); the sample holder was boat-shaped, 10 mm x 5 mm x 2.5 mm deep and the temperature measuring thermocouple was placed 1 mm from the sample holder. TG was also used for the determination of rates of

degradation of the homopolymers and copolymers in the initial stages of decomposition. The activation energies were obtained by the application of the Arrhenius equation.

2.3.5. Thermal degradation of the PMA homopolymer

Samples of ~ 50 mg were heated under vacuum from ambient temperature to 500 °C. The volatile degradation product was collected for qualitative analysis by GC-MS technique. A Saturn GC 3400 with fused quartz capillary column of 30m x 0.25mm coated methyl silicon under programmed heating condition from 60 to 200 °C was used for the identification of the condensable degradation products. The GC is interfaced with a Varian mass spectroscopy equipped with the standard electron impact (E1) or chemical ionization (CI) sources and a DS 55 data system scans from m/e 300 to 20 at a scan rate of 10 s/decade. Perfluorokerosene (PFK) was used for computer calibration and the ion source was maintained at 200 °C. Accurate mass measurements of the CI mass spectra were performed at 1000 resolving power using PFK as internal reference and by a computer interpolation data system.

3 RESULTS AND DISCUSSION

3.1. Characterization of PMA homopolymer and MA-MMA copolymers

The IR spectrum of PMA homopolymer shows a band at 1630 cm⁻¹ is assigned to the antisymmetric stretching vibration of amidic carbonyl group. The bands at 1600, 1545 and 1440 cm⁻¹ are assigned to $\nu(\text{C-H})$, $\nu(\text{C=C})$ and $\nu(\text{C-C})$ bands, respectively [13]. The C-H in plane deformation in the region 1225-1045 cm⁻¹, the ring breathing at 995 and 1005 cm⁻¹, the out-of-plan C-H deformation vibration between 775 and 750 cm⁻¹ and the C-C out-of-plan deformation at 500 cm⁻¹ are assigned. The IR spectrum of MA-MMA copolymer as shown in Fig. (1) exhibit bands at 1637 and 1728 cm⁻¹ assigned to antisymmetric stretching vibration of the amidic carbonyl

group of MA and carbonyl group of MMA in the copolymers, respectively [14]. The bands at 1600, 1545 and 1440 cm⁻¹ are due to $\nu(\text{C-H})$, $\nu(\text{C=C})$ and $\nu(\text{C-C})$ bonds [15], respectively.

Fig. (2) shows the ¹H-NMR spectrum of MA-MMA copolymers. The bands at δ 2.26 and 2.78-2.86 ppm are due to CH₂ and CH protons of MA and MMA in the copolymers [16], the band at δ 8.16 ppm is due to -NH proton of MA in the copolymer [17]. The peak at δ 7.8 ppm due to phenyl protons of MA in the copolymer and peak at 3.52 ppm is due to -OCH₃ protons of MMA units in the copolymers and -OMe protons of MA units in the copolymers.

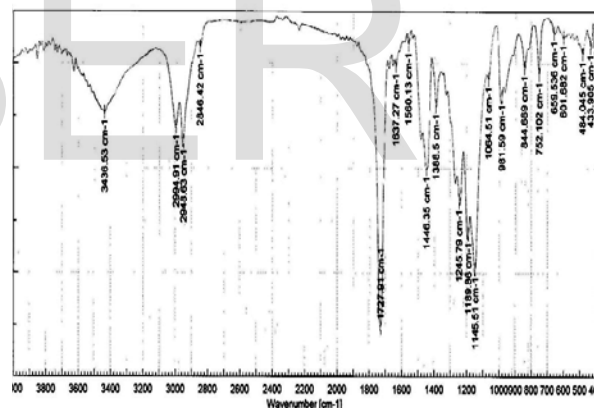


Fig. 1. IR spectrum of MA-MMA copolymers

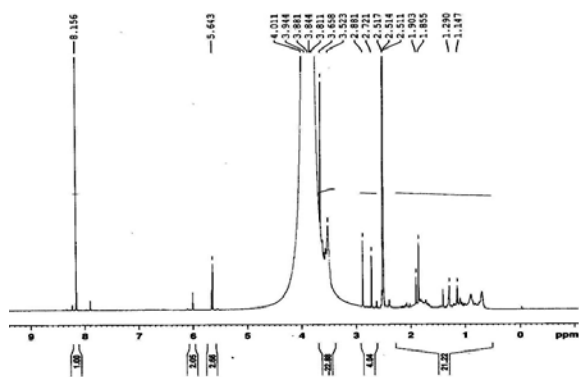


Fig. 2. ¹H-NMR spectrum of MA-MMA copolymers

3.2. Determination of reactivity ratios of MA-MMA copolymers

Three different copolymers of MA-MMA with 40:1, 50:1 and 60:1 mole of MMA-MA covering the entire composition range between PMA and PMMA homopolymers were prepared, so the reactivity ratios might be determined using microanalysis method. This method has already used for the determination of reactivity ratios for butyl acrylate - glycidyl methacrylate copolymer [18] and 2-methyl-N-1,3-thiazole-2-ylacrylamide-glycidylmethacrylate copolymer [19].

Fig. (3) shows the theoretical monomer compositions of the corresponding percentage nitrogen values. Percentage nitrogen data from microanalysis can then be inserted on the curves and the corresponding molar ratio read off from the abscissa.

By knowing the number of moles of the monomer mixture and the molar ratio of the copolymer, reactivity ratios can be calculated by applying the following equation [20]:

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = \frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}r_1 + r_2$$

Where, $F_1 = \frac{M_1/M_2}{M_1/M_2 + 1}$ is the mole fraction of

MMA (M_1) in copolymers, $f_1 = \frac{n_1}{n_1 + n_2}$ is the

mole fraction of M_1 in feed and r_1 and r_2 are the reactivity ratios of MMA and MA, respectively. Fig. (4) is a plot of

$\frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}$ versus $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$, and Fig. (5) is a

plot of $\frac{f_2^2(F_2-1)}{(1-f_2)^2F_2}$ versus $\frac{f_2(1-2F_2)}{(1-f_2)F_2}$ where

$F_2 = \frac{M_2/M_1}{M_2/M_1 + 1}$ is the mole fraction of MA (M_2) in

copolymer and $f_2 = \frac{n_2}{n_1 + n_2}$ is the mole fraction of M_2

in feed. From the slope and intercept in Figures 4 and 5, reactivity ratio values for MA-MMA copolymer are:

r_1 (MMA) = 20 and r_2 (MA) = 10.

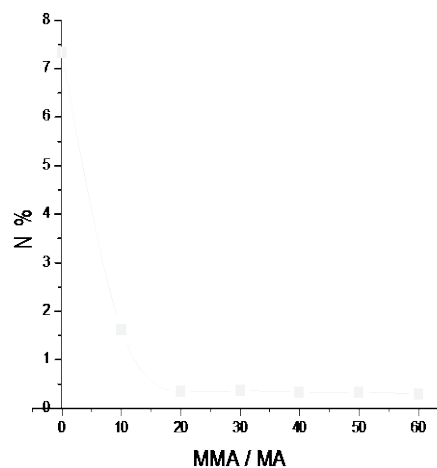


Fig. 3. Theoretical curve Of nitrogen content versus copolymer ratio for MMA-MA copolymers

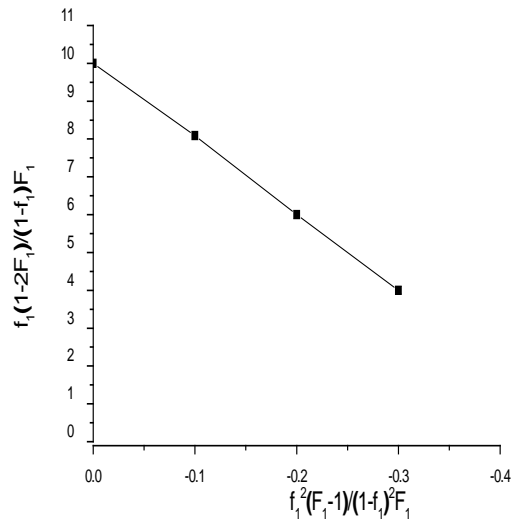


Fig. 4. Graph of $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$ versus $\frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}$ for MA-MMA copolymers.

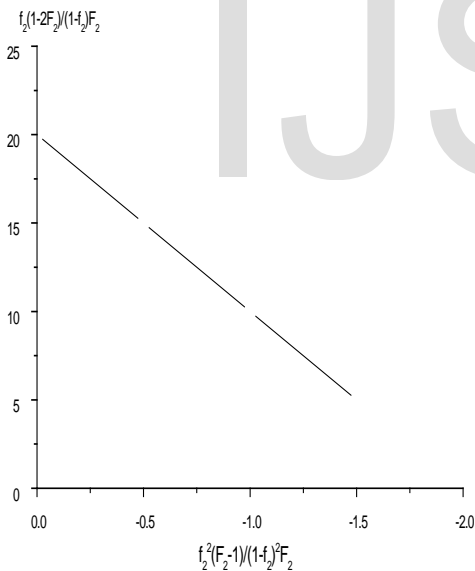


Fig. 5. Graph of $\frac{f_2(1-2F_2)}{(1-f_2)F_2}$ versus $\frac{f_2^2(F_2-1)}{(1-f_2)^2F_2}$ for MA-MMA copolymers.

3.3. Thermogravimetry (TG)

TG curves of PMA and PMMA homopolymers and MA-MMA copolymers are shown in Fig. (6) PMA homopolymer degrades in two stages. The first starts at $\sim 110^\circ\text{C}$ with a weight loss $\sim 6\%$. The second stage starts at $\sim 326^\circ\text{C}$ with a weight loss of $\sim 89\%$.

PMMA homopolymer shows two TG decomposition stages. The first starts at $\sim 250^\circ\text{C}$ with a weight loss $\sim 53\%$. The second stage starts at $\sim 375^\circ\text{C}$ with a weight loss of $\sim 41\%$. There are three TG degradation stages for all the MA-MMA copolymers. The degradation temperature started at $\sim 204, 206$ and 207°C for the copolymers 40:1, 50:1 and 60:1 mole of MMA:MA. Table (1) represents the weight loss percentage and the maximum rate of weight loss shown by derivative TG apparatus. TG curves of the copolymers reveal that the stability of copolymers are intermediate between PMA and PMMA homopolymers.

The most clearly result is the increase of the thermal stability of PMA homopolymer and MA-MMA copolymers towards PMMA homopolymer. The effective activation energies for the thermal degradation of PMA and PMMA homopolymers and MA-MMA copolymers were determined from the temperature dependence of the chain rupture rate. The rate constant of the thermal degradation was plotted according to the Arrhenius relationship Fig. (7). Table (2) lists the activation energies of the homopolymers and copolymers, from which the values of activation energy of the copolymers increasing from 45.73 to 241 KJ/mol were obtained as the MMA concentration in the copolymer increases. It is clear that the rate of activation energies are in the same order as the stabilities.

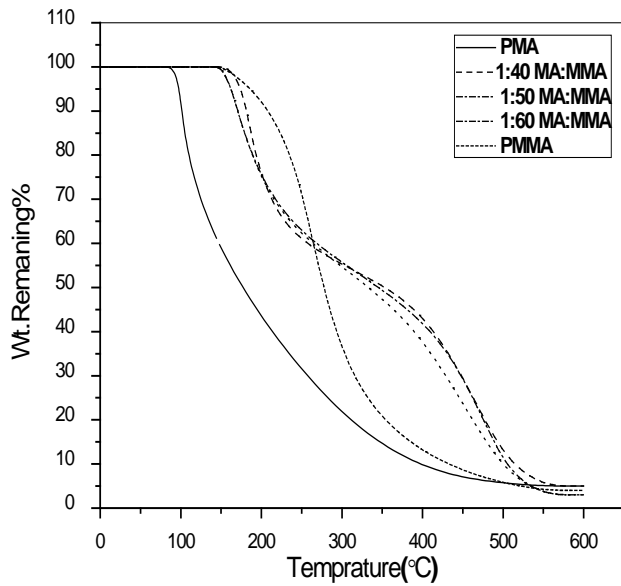


Fig. 6. TG curves for PMA and PMMA homopolymers and MA-MMA copolymers.

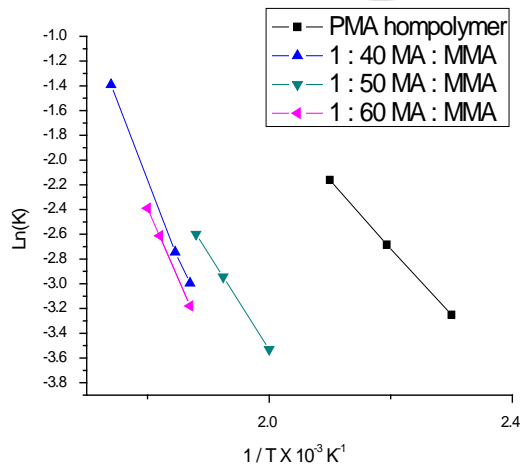


Fig. 7. Arrhenius plots of the rate constants of degradation of PMA homopolymer and MA-MMA copolymers.

Table (1): Weight loss % of PMA and PMMA homopolymers and MA-MMA copolymers.

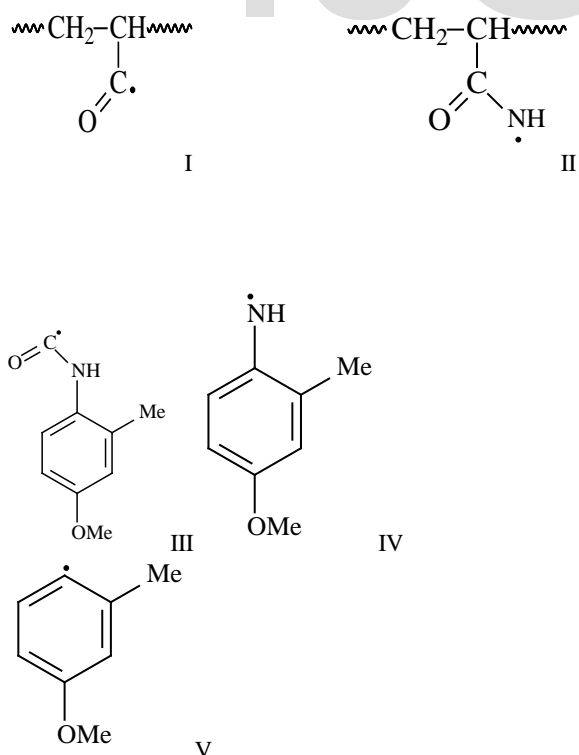
Polymer mole MA:MMA	Volatilization Temperature, °C	First stage		Second stage		Third stage		Remaining wt % after 500°C
		T _{max} °C	Wt loss, %	T _{max} °C	Wt Loss, %	T _{max} °C	Wt Loss, %	
PMA	110	148	6	326	89	-	-	4.8
1:40	204	347	42	412	49	442	4	5
1:50	206	311	37	396	54	423	5	3
1:60	207	344	38	436	56	472	3	3
PMMA	250	350	53	500	41	-	-	6

Table (2): Activation energies of the thermal degradation of PMA and PMMA homopolymers and MA-MMA copolymers.

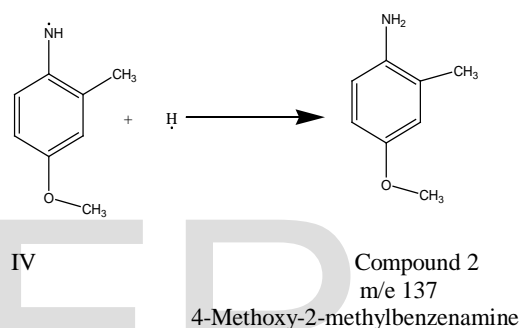
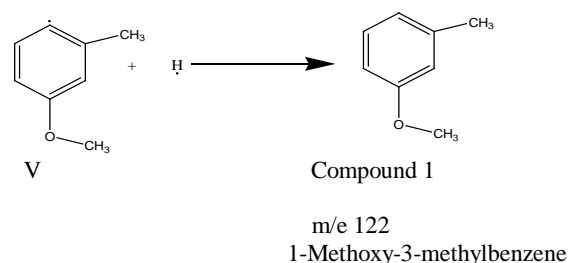
Polymer mole MA:MMA	Activation energy (E _a) KJ/mol
PMA	45.7
1:40	102.3
1:50	166.3
1:60	241
PMMA	249.42

3.4. Thermal degradation of PMA homopolymer

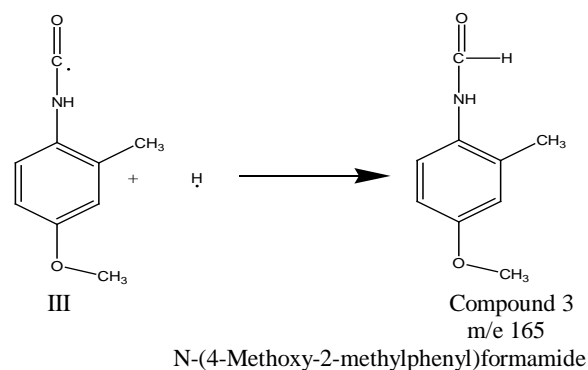
50 mg of PMA homopolymer was heated under vacuum from ambient temperature to 500 °C. The volatile products of degradation were collected in a small gas cell for identification by IR spectroscopy. Benzene, aniline and ammonia were among the degradation products of PMA homopolymer. The liquid fractions from the degradation of the homopolymer were injected into the GC-MS apparatus. Fig. (8) shows the GC trace for the liquid products of degradation of PMA homopolymer at 500 °C. Table (3) gives the results of the degradation which were identified by mass spectroscopy. The various degradation products of PMA homopolymer indicate that the mechanism of degradation is characterized by the elimination of low molecular weight radicals rather than monomer formation in the early stage of degradation, followed by random scission mechanism along the backbone chain. It seems that the breakdown of PMA homopolymer occurs mainly in the C-N bond producing the radicals:



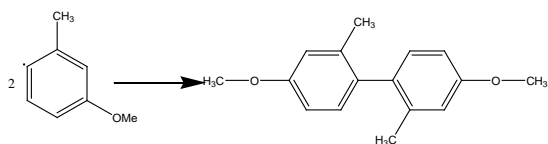
Compounds 1 and 2 in the GC curve listed in Table 3 could be formed by abstraction of H by the radicals V and IV and produce 4-methoxybenzenamine and 4-methoxy-2-methylbenzenamine.



Compound 3 could be formed by abstraction of H by the radical III.



The suggested structure of compound 4 is formed by the reaction between two radicals V.



V
Compound 4
m/e 242
1,1'-Dimethyl-3,3'-dimethoxydiphenyl

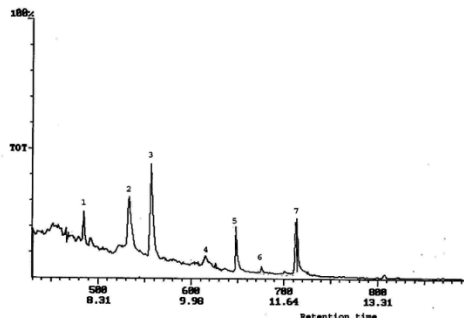
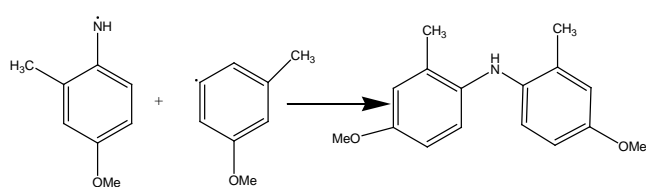


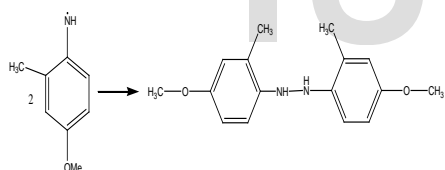
Fig. 8. GC curve of the liquid fraction of degradation of PMA homopolymer

The mass spectrum of compound 5 is a termination reaction of the radicals IV and V.



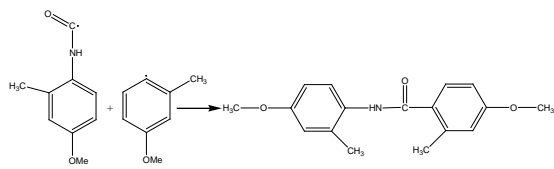
IV
V
Compound 5
m/e 257
Bis(4-methoxy-2-methylphenyl)amine

Compound 6 is formed by the dimerization of the radical IV.



IV
Compound 6
m/e 272
1,2-Bis(4-methoxy-2-methylphenyl)hydrazine

The suggested structure of compound 7 is formed by the reaction between the radicals III and V.



III
V
Compound 7
m/e 285
4-Methoxy-N-(4-methoxy-2-methylphenyl)-2-methylbenzamide

Table (3): GC-MS data of the liquid fraction of the degradation of PMA homopolymer

Compound no.	Retention time, min.	Major MS fragment	Suggested structure
1	8.1	122,105,47	1-Methoxy-3-methylbenzene
2	8.85	137,115,75,61,47	4-Methoxy-2-methylbenzenamine
3	9.3	165,123,105,47	N-(4-Methoxy-2-methylphenyl)formamide
4	10.25	242,214,180,126,111,47	1,1'-Dimethyl-3,3'-dimethoxydiphenyl
5	10.8	257,227,186,126,111,47	Bis(4-methoxy-2-methylphenyl)amine
6	11.3	272,241,171,135,115,61,47	1,2-Bis(4-methoxy-2-methylphenyl)hydrazine
7	11.9	285,241,171,126,111,47	4-Methoxy-N-(4-methoxy-2-methylphenyl)-2-methylbenzamide

3.4. Conclusion

Different composition of copolymers of N-(4-Methoxy-2-methylphenyl)acrylamide and methyl methacrylate (MA-MMA) were prepared and the reactivity ratios were determined using microanalysis method. Thermal degradation of poly(N-(4-methoxy-2-methylphenyl)acrylamide) (PMA) was studied and the products of degradation were identified by GC-MS techniques. 1-Methoxy-3-methylbenzene, 4-Methoxy-2-methylbenzenamine, ammonia, N-(4-Methoxy-2-methylphenyl)formamide, 1,1'-Dimethyl-3,3'-dimethoxydiphenyl, Bis(4-methoxy-2-methylphenyl)amine, 1,2-Bis(4-methoxy-2-methylphenyl)hydrazine and 4-Methoxy-N-(4-methoxy-2-methylphenyl)-2-methylbenzamide were the main degradation products. Accordingly, it seems that the mechanism of degradation of PMA is characterized by breaking down in the C-N bond producing low-molecular radicals. Combination of these radicals and random scission mechanism along the backbone chain are the main source of the degradation products.

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