THERMAL STABILITY OF POLY (2-ACRYLAMIDO-4- ANTIPYRINYL) THIAZOLE HOMOPOLYMER AND COPOLYMER OF 2-ACRYLAMIDO-4- ANTIPYRINYL THIAZOLE WITH METHYL METHACRYLATE

الثبات الحرارى لهوموبوليمرات انتى بايرين اكريلاميدو ثيازول وكوبوليمرات انتى بايرين اكريلاميدو ثيازول مع الميثيل ميثا اكريلات

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ملخص

فى هذا البحث تم تحضير تركيزات مختلفة من كوبوليميرات (٢-اكريلاميدو-٤- انتى بايرينايل) ثيازول مع الميثيل ميثا أكريلات وقياس نسبة نشاطية المونمر فى الكوبوليمير باستخدام طيف الرنين النووى المغناطيسى. كذلك استخدمت اجهزة التحليل الحرارى فى التعرف على ثباتية الكوبولمرات المحضرة وتم قياس طاقة تنشيط تكسير هذة البوليمرات باستخدام معادلة ارهينيوس.

ABSTRACT

Different concentrations of copolymer of (2-acrylamido-4-antipyrinyl) thiazole with methyl methacrylate were prepared and the reactivity ratio values of copolymerization were calculated using ^{1}H-NMR technique. Thermal analysis of the copolymers showed that the thermal stability are intermediate between poly (2-acrylamido-4-antipyrinyl) thiazole and poly methyl methacrylate homopolymers.The activation energies of the thermal degradation of the copolymers were calculated using Arrhenius relationship.
Keywords: Thermal stability,(2-acrylamido-4-antipyrinyl) thiazole ,Reactivity ratios.

1. INTRODUCTION

Thermal analysis of polymers is very important in determining their utility under various environmental conditions, high temperature applications, in understanding molecular architecture, decomposition and mechanisms. Thermogravimetric analysis not only furnishes data on weight loss as a function of temperature but also provides a means to estimate kinetic parameters or thermal decomposition reactions. It is also possible to establish a pyrolysis mechanism and a rapid comparison of thermal stabilities and decomposition temperatures of different polymers. Polymers are usable over a certain range of temperatures. The working range can

be increased by copolymerization, using additives and stabilizers. Thermally stable and heat resistant polymers are in great demand as insulators and enamels. DTA and DSC are very sensitive and provide information on glass transition, heat of fusion and melting temperature. Thermal degradation causes a rupture of chemical bonds, which gives an endothermic peak. Simultaneous DTA and TGA studies are very useful to differentiate an endothermic melting peak from that of a peak due to thermal degradation. The ability to be cured rapidly or slowly by conventional processing, absence of volatiles during cure, accurate reproduction, excellent adhesion to almost any substrate,

outstanding toughness, electrical insulation, excellent chemical resistance and an ability to accept a wide range of fillers and pigments are some characteristic features of epoxy systems which undoubtedly induce interest in their users. Because of the wide range of resins, curing agents and modifying agents, it is possible to tailor the epoxy systems to yield products with desired properties over a temperature range of 0–200 °C [1]. In this paper, homopolymes of 2-acrylamido-4-antipyrinyl thiazole (PAAT) and methyl methacrylate (PMMA) and four different composition of copolymers of 2-acrylamido-4-antipyrinyl thiazole and methyl meth-acrylate (AAT-MMA) were prepared, so that the reactivity ratios might be determined using ^{1}H-NMR method. The thermal stability of the homopolymers and copolymers were examined. 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 [2]. 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. All other chemicals and solvents were purified by standard procedures.

2-2. Preparation of amine
2-amino-4-antipyrinyl thiazole was prepared by the reaction of equimolar amounts of chloroacetylantipyrine(1) and thiourea(2) in water and reflux for four hours , cool and neutralization with potassium hydroxide, filter the product and wash with water and dried in a vacuum oven at 40oC for several days .The compound was obtained(3) in 80% crystallization from ethanol as colourless needle with m.p.230oC
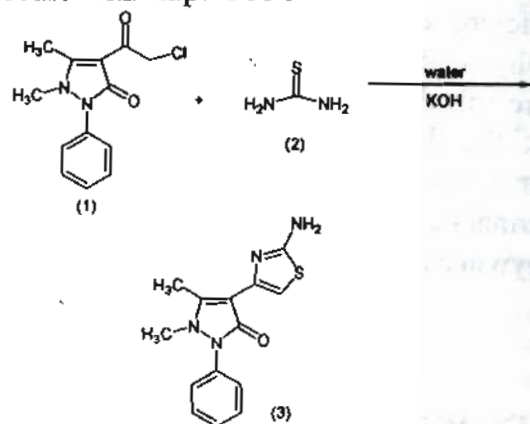
2-amino-4-antipyrinyl thiazole

2-3. Preparation of monomer and polymers

(2-acrylamido-4-antipyrinyl) thiazole (AAT) monomer was performed by the reaction of equimolar amounts of AC and 2-amino-4-antipyrinyl thiazole in dry DMF until the evolution of hydrogen chloride ceased forming a white powder of AAT monomer. Poly (2-acrylamido-4-antipyrinyl) thiazole (PAAT) homopolymer was prepared by free radical initiation of AAT using 0.1 w/v% AIBN as initiator and DMF as solvent ,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 ^{0}C. Copolymers of AAT with MMA were prepared using 0.2 w/v. % AIBN as free radical initiator and 50/50 (v/v) DMF as solvent. Four different copolymer compositions of AAT-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.

3. Analytical techniques
3-1. Infrared spectroscopy (IR)
Spectra were recorded on Pye Unicam SP 2000 spectrometry, for the homopolymers and copolymers.
3-2. Nuclear magnetic resonance spectroscopy (NMR)
^{1}H-NMR spectra were obtained using a Varian EM 390 90 MHz spectrometer with integration and 20 mg samples. The integral values obtained for each value sample was used for determination of the polymer compositions.
3-3. 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.

4. RESULTS AND DISCUSSION
4-1. Characterization of PAAT homopolymer and AAT-MMA copolymers
The IR spectrum of PAAT homopolymer shows a band at 1680 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 v(C-H), v(C=C) and v(C-C) bands, respectively [3]. 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 AAT-MMA copolymer show bands at 1680 and 1730 cm^{-1} assigned to antisymmetric stretching vibration of the amidic carbonyl group of AAT and carbonyl group of MMA in the copolymers, respectively [4]. The bands at 1600, 1545 and 1440 cm^{-1} are due to v(C-H), v(C=C) and v(C-C) bonds [5], respectively.

4-2. Determination of reactivity ratios of AAT-MMA copolymers
Four different copolymers of AAT-MMA with 10:1, 20:1, 30:1 and 40:1 mole of MMA:AAT covering the entire composition range between PAAT and PMMA homopolymers were prepared, so the reactivity ratios might been be determined using ^{1}H-NMR method. This method has already used for the determination of reactivity ratios for styrene-MMA [6] , methacrylate-acrylate copolymer [7] and recentely for copolymers of 4-nitro-3-methylphenylmethacrylate and N-(4-bromophenyl)-2-methacrylamide with glycidyl methacrylate, respectively [8,9] . Figure 1 shows the ^{1}H-NMR spectrum of AAT-MMA copolymers. The bands at ∂

2.26 and 2.78-2.86 ppm are due to CH_2 and CH protons of AAT and MMA in the copolymers [10], The band at δ 7.89 ppm is due to −NH proton of AAT in the copolymer [11].
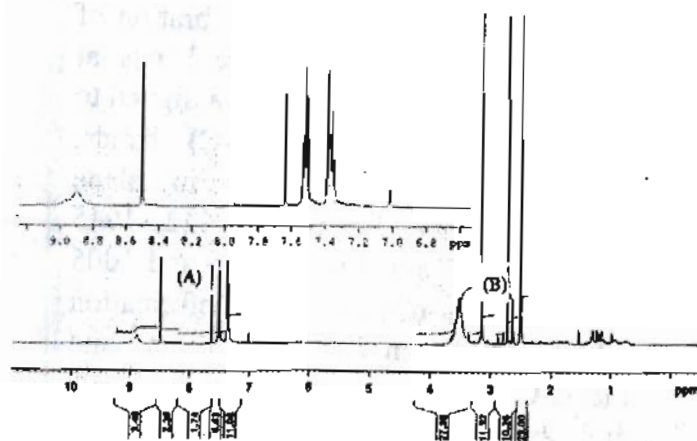

Fig. (1): ^{1}H-NMR spectrum of AAT-MMA copolymers

The peak (A) at δ 7.35 ppm due to phenyl protons of AAT in the copolymer, Peak (B) at 3.52 ppm is due to −OCH$_3$ protons of MMA units in the copolymers. Dividing peak A by five and peak B by three, the monomer composition of the copolymer can be calculated. 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 [12].

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

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

of MMA (M_1) in copolymers,

$f_1 = \dfrac{n_1}{n_1+n_2}$ is the mole fraction of M_1 in

feed and r_1 and r_2 are the reactivity ratios of MMA and AAT, respectively. Figure 2

is a plot of $\dfrac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$ versus $\dfrac{f_1(1-2F_1)}{(1-f_1)F_1}$.

From the slope and intercept in Figure 2 reactivity ratio values for AAT-MMA copolymer are:

$r_1(MMA) = 19.14$ and $r_2(AAT) = 0.056$

4-2. Thermogravimetry (TG)

TG curves of PAAT and PMMA homopolymers and AAT-MMA copolymers are shown in Figure 3. PAAT homopolymer degrade in two stages. The first starts at ~140°C with a weight loss ~ 71.1%. The second stage srarts at ~250°C with a weight loss of ~ 17.8%.
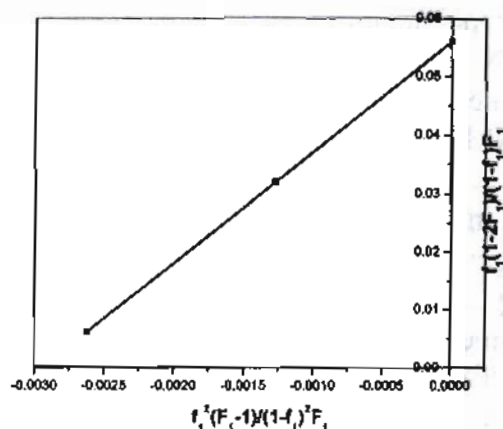

Fig. (2): Graph of $\dfrac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$ versus

$\dfrac{f_1(1-2F_1)}{(1-f_1)F_1}$ for AAT-MMA copolymers.

PMMA homopolymer shows two TG decomposition stages. The first starts at ~250°C with a weight loss ~ 53.2%. The second stage srarts at ~375°C with a weight loss of ~ 41.1%. There are three TG degradation stages for all the AAT-MMA copolymers. The degradation temperature started at ~ 110, 120, 140 and 150 °C for the copolymers 10:1, 20:1, 30:1 and 40:1 mole of MMA:AAT. Table 1 represents the weight loss
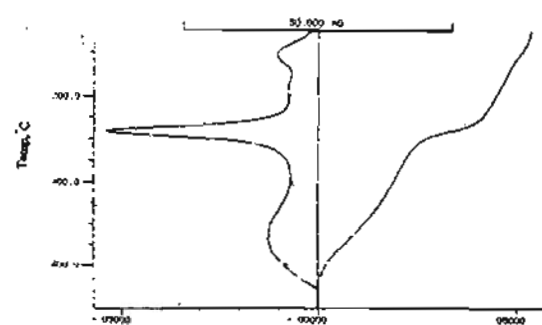
percentage and the maximum rate of weight loss shown by derivative TG apparatus. TG curves of the copolymers reveal that the stability of copolymers are intermediate between PAAT and PMMA homopolymers.
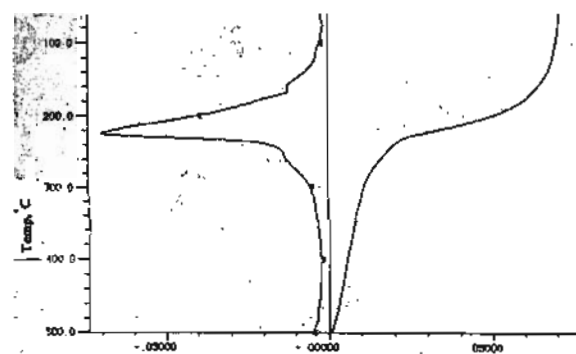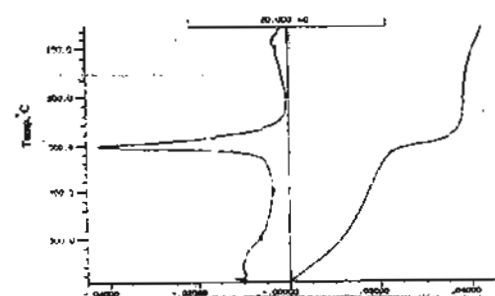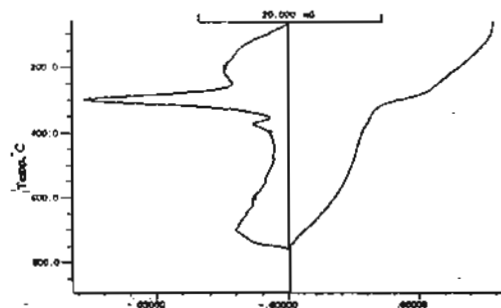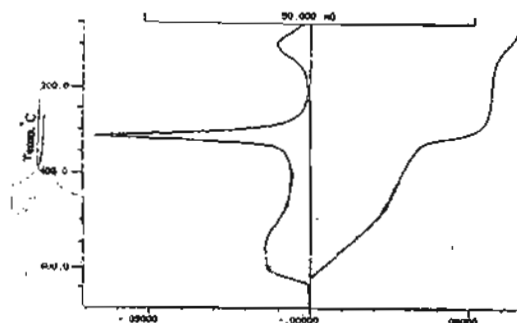
(a)
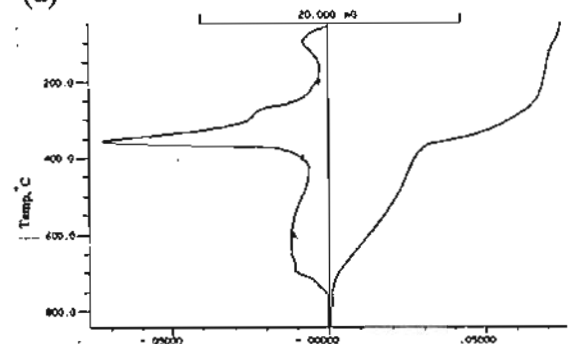
(b)

(c)

(d)

(e)

(f)

Fig. (3): TG curves for PAAT and PMMA homopolymers and AAT-MMA copolymers (a) PAAT & (b) PMMA & (c) 10:1 & (d) 20:1 & (e) 30:1 and (f) 40:1 MMA:AAT copolymers.

The most clearly result is the increase of the thermal stability of PAAT homopolymer and AAT-MMA copolymers towards PMMA homopolymer. The effective activation energies for the thermal degradation of PAAT and PMMA homopolymers and AAT-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 (Figure 4). Table 2 lists the activation energies of the homopolymers and copolymers, from which the values of activation energy of the copolymers increasing from 51.27 to 249.42 KJ/mol were obtained as the MMA concentration in the copolymer increases. It is clear

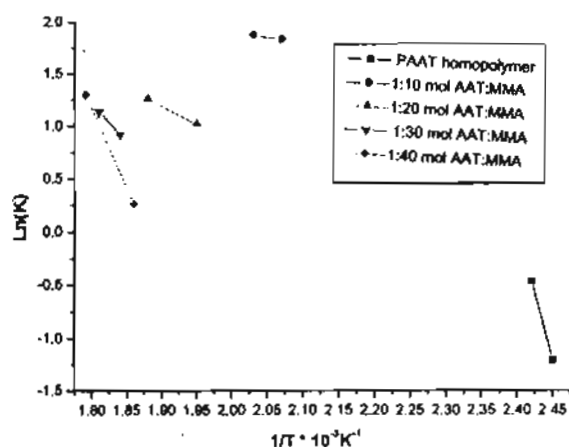that the rate of activation energies are in the same order as the stabilities.

Fig. (4): Arrhenius plots of the rate constants of degradation of PAAT homopolymer and AAT-MMA copolymers.

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

Polymer mole MMA:AAT	Volatilization Temperature, °C	First stage		Second stage		Thirde stage		Remaining wt% after 700°C
		T_{max} °C	Wt loss, %	T_{max} °C	Wt Loss, %	T_{max} °C	Wt Loss, %	
PAAT	100	220	71.1	480	17.8	-	-	11.1
10:1	110	282	16.8	393	33.6	500	47.4	2.3
20:1	120	305	7.5	400	38.7	540	22.4	31.5
30:1	140	310	30.7	402	29.1	700	38.3	1.9
40:1	150	314	5.2	405	35.8	640	56.3	2.8
PMMA	250	350	53.2	700	41.1	-	-	5.8

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

Polymer mole MMA:AAT	Activation energy (E_a) KJ/mol
PAAT	51.27
20:1	-----
30:1	60.97
40:1	123.52
PMMA	249.42