

**THERMAL STABILITY OF POLY (N-[3-(5-AMINO- 1,2,4-
TRIAZOLO)] ACRYLAMIDE) HOMOPOLYMER AND
COPOLYMER OF N-[3-(5-AMINO- 1,2,4- TRIAZOLO)]
ACRYLAMIDE WITH METHYL ACRYLATE**

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(Received: 17 / 4 / 2008)

ABSTRACT

Different concentrations of copolymer of N-[3-(5-amino-1,2,4- triazolo)] acrylamide with methyl acrylate were prepared and the reactivity ratio values of copolymerization were calculated using ¹H-NMR technique. Thermal analysis of the copolymers showed that the thermal 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.

INTRODUCTION

There are two general approaches to the stabilization of polymers. 1) by modification of molecular structure such as copolymerization and 2) by the use of additives. Dependent on the mode of degradation, either, or both of these techniques may be employed. When the initiation rate is low, additives can be effective and radical traps or chain terminators may be useful under these conditions [**Load & Winslow (1972); Grassie et al. (1987) and El-Sonbati et, al. (2002)**]. At high initiation rates, additives are less effective, and stabilization by structure modification may be the only practical approach. Additives would be overwhelmed by the large number of radicals formed during initiation.

In this paper, homopolymers of N-[3-(5-amino-1,2,4- triazolo)] acrylamide (PATA) and methyl acrylate (PMA) and five different compositions of copolymers of N-[3-(5-amino-1,2,4- triazolo)] acrylamide and methyl acrylate (ATA-MA) were prepared, so that the

reactivity ratios might be determined using $^1\text{H-NMR}$ 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.

EXPERIMENTAL

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 [Khairou & Diab (1994)]. The solution was left to cool. The pure material then being collected by filtration and dried.

3,5-Diamino-1,2,4-triazole (Aldrich Chemical Co., Inc.) was purified by recrystallization from hot ethanol and filtering forming yellow crystal, m.p. 102°C .

Methyl acrylate (MA) (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.

Preparation of monomer and polymers:

N-[3-(5-amino-1,2,4-triazolo)] acrylamide (ATA) monomer was performed by the reaction of equimolar amounts of AC and 3,5-diamino-1,2,4 triazole in dry benzene until the evolution of hydrogen chloride ceased forming a yellow powder of ATA monomer (M.W.153). Microanalysis, Found C, 39.51; H, 4.70; N, 45.8%. Calcd. For $\text{C}_5\text{H}_7\text{ON}_5$, C, 39.22; H, 4.58; N, 45.75%.

Poly(N-[3-(5-amino-1,2,4-triazolo)]acrylamide (PATA) homopolymer was prepared by free radical initiation of ATA using 0.1 w/v% AIBN as initiator and DHF as solvent at 60°C 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 ATA with MA were prepared using 0.2 w/v.% AIBN as free radical initiator and 50/50 (v/v) DFM as solvent. Five different copolymer compositions of ATA-MA were prepared, so that the reactivity ratios might be determined. Polymerization was carried out at 60 °C 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.

Analytical techniques:

Infrared spectroscopy (IR):

Spectra were recorded on Pye Unicam SP2000 spectrometry, for the homopolymers and copolymers.

Nuclear magnetic resonance spectroscopy (NMR):

¹H-NMR spectra were obtained using a Varian EM 390 90 MHz spectrometer with integration and 20 mg samples. The polymers were dissolved in 1 ml of CDCl₃. The integral obtained for each sample was used for determination of the polymer compositions.

Microanalysis:

Nitrogen content determination were performed by the Microanalytical Unit at King Abdel Azzez University.

Thermal methods of analysis:

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.

RESULTS AND DISCUSSION

Characterization of PMA and PATA homopolymers and ATA-MA copolymers:

3290 and 3441 cm^{-1} assigned to symmetric and asymmetric stretching vibrations of the amino group. The 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 $\nu(\text{C-H})$, $\nu(\text{C-C})$ and $\nu(\text{C-C})$ bands, respectively [El-Sonbati et al.(1991)]. 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 ATA-MA copolymer shows two medium broad bands at 3280 and 3420 cm^{-1} assigned to symmetric and asymmetric stretching vibrations of the amino group. The bands at 1860 and 1730 cm^{-1} are assigned to antisymmetric stretching vibration of the amidic carbonyl group of ATA and carbonyl group of MA in the copolymers, respectively [Diab et al.(1990)]. The bands at 1600, 1545 and 1440 cm^{-1} are due to $\nu(\text{C-H})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C-C})$ bonds [El-Sonbati et al.(1989)], respectively.

Determination of reactivity ratios of ATA-MA copolymers:

Five different copolymers of ATA with 45, 27, 19, 13 and 11 mole% of ATA units covering the entire composition range between PATA and PMA homopolymers were prepared, so the reactivity ratios might be determined using $^1\text{H-NMR}$ method. This method has already used for the determination of reactivity ratios for styrene-MMA [Kato et al. (1964)] and methacrylate-acrylate copolymer [Grassie et al. (1965)]. Figure 1 shows the $^1\text{H-NMR}$ spectrum of ATA-MA copolymers. The bands at δ 2.26 and 2.78-2.86 ppm are due to CH_2 and CH protons of ATA and MA in the copolymers [Williams & Fleming (1966)]. The peak (A) at δ 7.89 ppm is due to the amino group which was disappeared on addition of D_2O , due to $-\text{NH}$ proton of ATA in the copolymer [Mochel (1967)]. Peak (B) at 3.52 ppm is due to $-\text{OCH}_3$ protons of MA units in the copolymers. Dividing peak A by one 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 [El-Sonbati (1990)]:

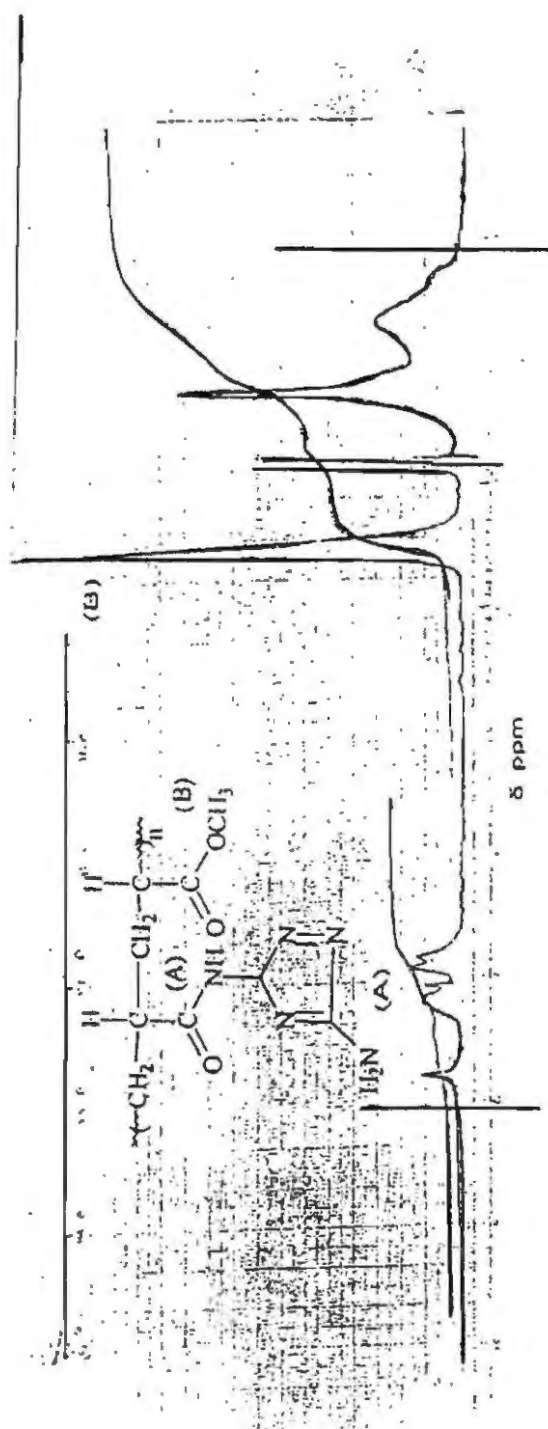


Figure 1: ¹H-NMR spectrum of ATA-MA copolymer.

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

Where $F_1 = \frac{M_1/M_2}{M_1/M_2+1}$ is the mole fraction of ATA (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 ATA and MA, respectively.

Figure 2 is a plot of $\frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$ and Figure 3 is a plot of $\frac{f_2^2(F_2-1)}{(1-f_2)^2 F_2}$ 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 copolymers and $f_2 = \frac{n_2}{n_1+n_2}$ is the mole fraction of M_2 in feed.

From the slopes and intercepts in Figures 2 and 3 reactivity ratio values for ATA-MA copolymer are

$$r_1(\text{ATA}) = 0.58 \pm 0.1 \text{ and } r_2(\text{MA}) = 1.52 \pm 0.1.$$

Thermal methods of analysis:

Thermogravimetry (TG):

TG curves of PATA and PMA homopolymers and ATA-MA copolymers are shown in Figure 4. PATA homopolymer degrade in two stages. The first starts at $\sim 117^\circ\text{C}$ with a weight loss $\sim 45\%$. The second stage starts at $\sim 333^\circ\text{C}$ with a weight loss of $\sim 44\%$. PMA homopolymer showing one decomposition stage with weight loss of $\sim 90\%$. This is similar to the results obtained in the thermal degradation of poly(vinyl bromide) and blends of poly(vinyl bromide) with poly(methyl acrylate) [Diab (1990)]. There are two TG degradation stages for all the ATA-MA copolymers. The degradation temperature started at $\sim 200, 225, 255, 275$ and 258°C for the copolymers 45, 27, 19, 13 and 11 mole% ATA units, respectively. 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 is intermediate between PATA and PMA homopolymers.

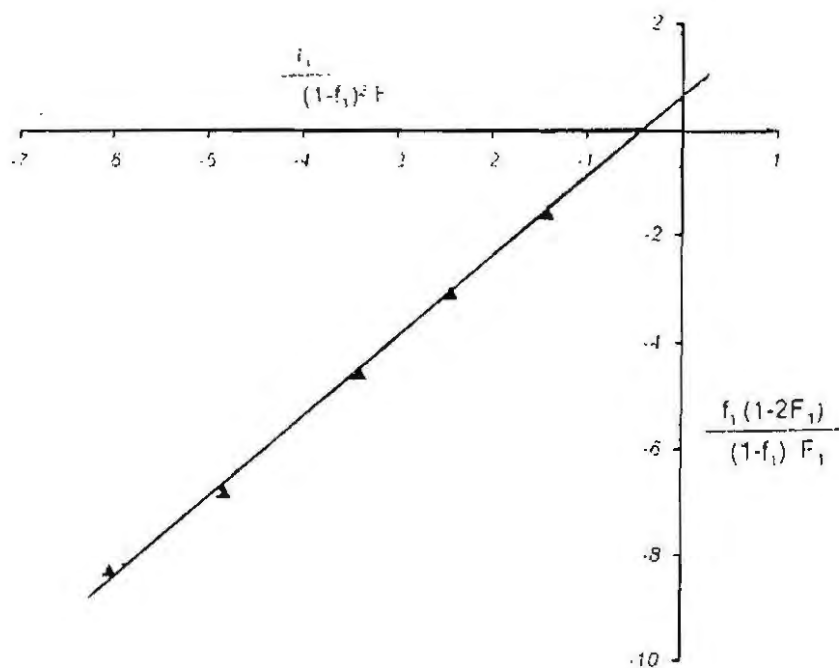


Figure 2. Graph of $\frac{f_1^2(F_1 - 1)}{(1 - f_1)^2 F_1}$ versus $\frac{f_1(1 - 2F_1)}{(1 - f_1)F_1}$ for ATA-MA copolymers.

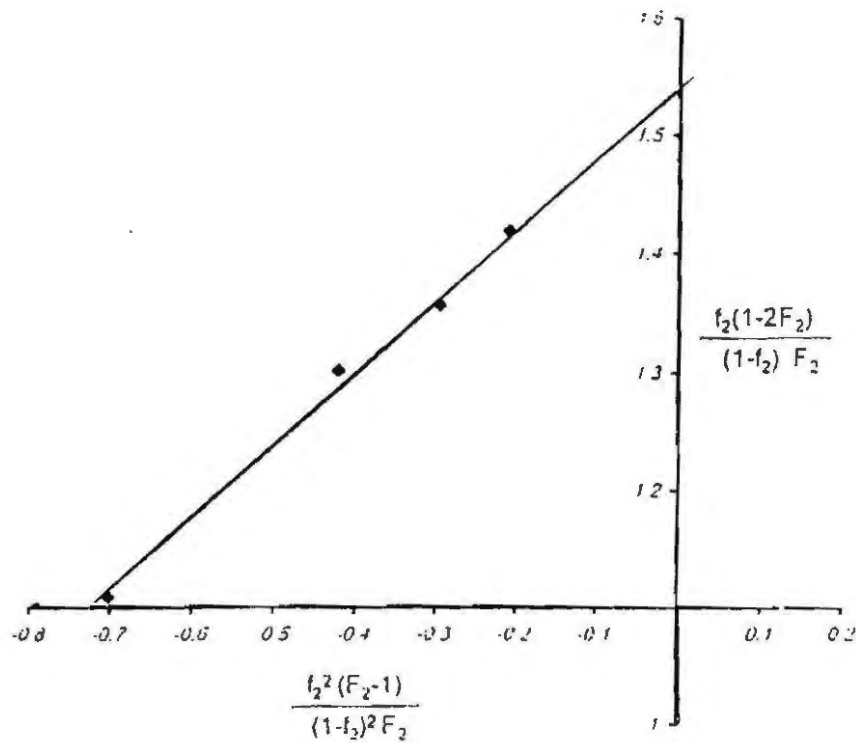


Figure 3 : Graph of $\frac{f_2^2(F_2 - 1)}{(1 - f_2)^2 F_2}$ versus $\frac{f_2(1 - 2f_2)}{(1 - f_2)F_2}$ for ATA-MA copoly mers.

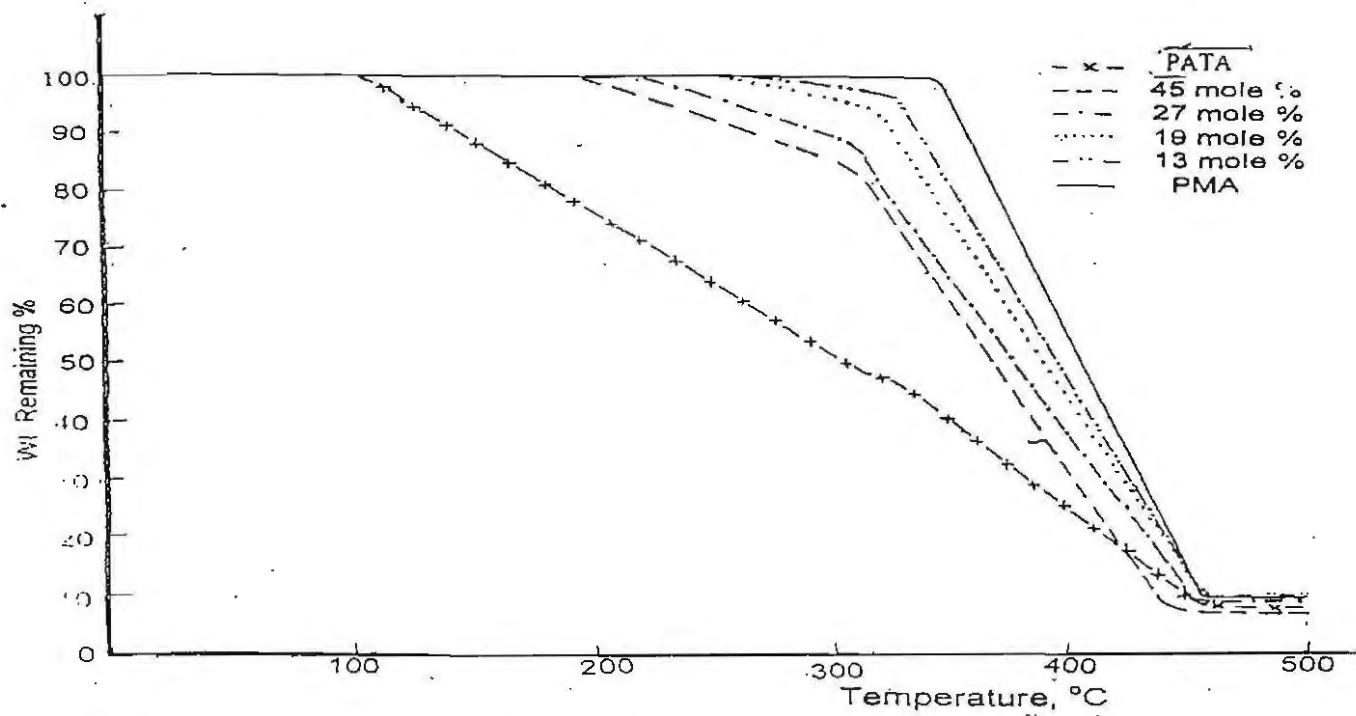


Figure 4 : TG curves of PATA and PMA homopolymers and ATA-MA copolymers.

Table (1): Weight loss percentage of PATA and PMA homopolymers and ATA-MA copolymers.

Polymer mol% ATA	Volatilization Temperature, °C	First stage		Second stage		Remaining wt% after 500°C
		T _{max} °C	Wt loss. %	T _{max} °C	Wt Loss, %	
PATA	112	250	47	370	44	9
45	200	260	18	390	74	8
27	225	270	13	395	79	8
19	255	277	8	400	84	8
13	275	289	6	405	85	9
11	285	300	5	415	87	8
PMA	350	420	90	--	--	10

The initial stages of degradation of the homopolymers and copolymers were studied to give a clear picture of relative stability for the entire composition range. The smooth change in stability with composition is well demonstrated in Figure 5, in which the weight loss percentage at 360 °C in the programmed degradation using the data in Figure 4 is plotted against composition. The most clearly result is the increase of the thermal stability of PATA homopolymer and ATA-MA copolymer towards PMA homopolymer.

The effective activation energies for the thermal degradation of PATA and PMA homopolymers and ATA-MA 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 6). Table 2 lists the activation energies of the homopolymers and copolymers, from which the values of activation energy of the copolymers increasing from 113.5 to 138.5 KJ/mol were obtained as the MA concentration in the copolymer increases. It is clear that the rate of activation energies are in the same order as the stabilities.

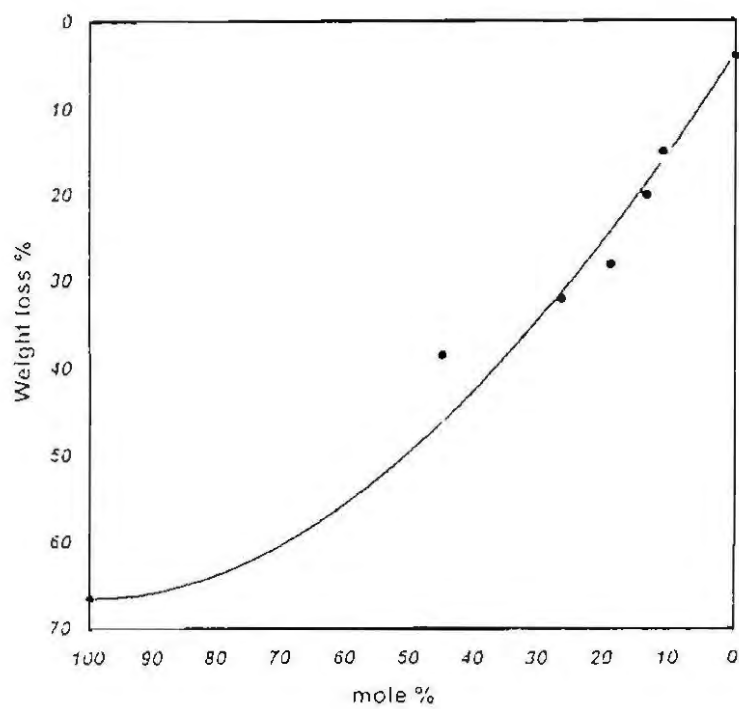


Figure 5 Comparison of weight loss percentage at 360°C for AEA-MA copolymers at different compositions.

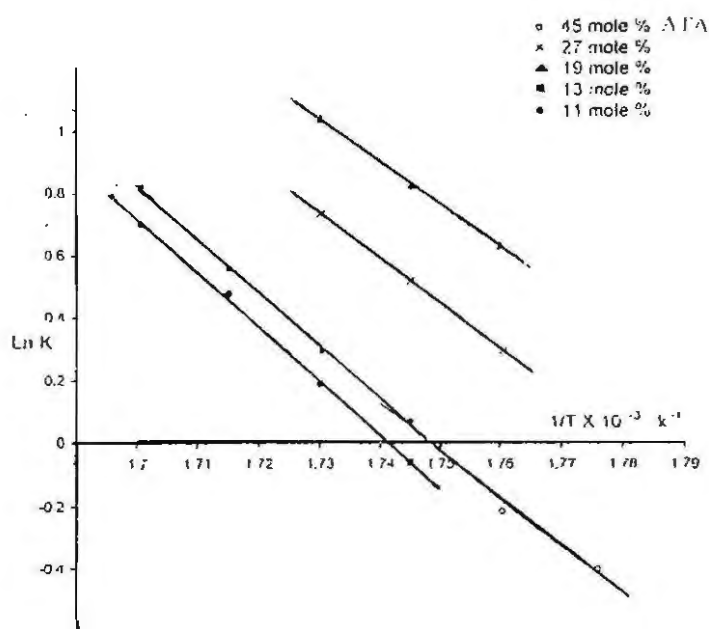


Figure 6 : Arrhenius plots of the rate constants of degradation of ATA-MA copolymers.

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

Polymer mole % ATA	Activation energy (E_a) KJ/mol
PATA	43.6
45	113.3
27	121.9
19	127.9
13	130.6
11	138.5
PMA	145.2

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الملخص العربي

في ذلك البحث تم تحضير تركيزات مختلفة من كوبوليميرات ن-(3-O - أمينو- $1\text{و}2\text{و}4$ تراى أزولو) أكريلاميد مع الميثيل أكريلات وقياس نسبة نشاطية المونمر في الكوبوليمير باستخدام طيف الرنين النووي المغناطيسي. كذلك استخدمت أجهزة التحليل الحرارى في التعرف على ثباتية الكوبوليمرات المحضرة وتم قياس طاقة تنشيط تكسير هذه البوليمرات باستخدام معادلة ارهينيوس