

**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 METHACRYLATE**

Fahd A.A. Tirkistani

Department of Chemistry, Faculty of Applied Sciences, Umm Al-Qura
University, Makkah Al Mukkaramah, P.O. Box 7655 Saudi Arabia

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ABSTRACT

Copolymers of (N-[3-(5-amino-1,2,4-triazolo)] acrylamide with methyle methacrylate were prepared and characterized using microanalysis and IR spectroscopy. The reactivity ratio values of the copolymerization were calculated using ¹H-NMR technique. Thermal analyses of the copolymers showed that the stability are intermediate between poly(N-[3-(5-amino-1,2,4-triazolo)]acrylamide) and poly (methyl methacrylate) homopolymers.

INTRODUCTION

It is well known that the thermal stability of polymers has been improved by copolymerization of primary monomer with traces of a comonomer [Khairou & Diab (1994) and Diab(1990)]. The poor thermal stability of nitrogenated and brominated polymers, due to the weak character of the C-N and C-Br bonds, respectevity, has received much attention [El-Agamey & Diab (1986) and Grassie et al . (1981)].

In this paper, homopolymers of N-[3-(5-amino-1,2,4-triazolo)] acrylamide (PATA) and methyl methacrylate (PMMA) and five different compositions of polymers of N-[3-(5-amino-1,2,4- triazolo)]acrylamide and methyl methacrylate (ATA-MMA) were prepared, so that the reactivity ratio might be determined using ¹H-NMR method and the application of Fineman-Ross plots [Fineman & Ross (1950)]. The thermal stability of the homopolymers and copolymers were examined. The activation energies of 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-stopper flask.

2,2'-Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co., Inc.) was used as initiator for all polymerizations. It was purified by dissolving in hot ethanol and filtration [Diab (1983)]. 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 the formed yellow crystals, m.p. 102°C .

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.

Preparation of monomer and polymers:

N-[3-(5-amino-1,2,4-triazolo)]acrylamide (ATA) monomer was prepared 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, 45.80%. and . for $\text{C}_5\text{H}_7\text{ON}_5$, C, 39.22, H, 4.85, 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 DMF as solvent at 60°C for 6h. 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 MMA were prepared using 0.2 w/v% AIBN as free radical initiator and 50/50 (v/v) DMF as solvent. Five different copolymer compositions of ATA-MMA were prepared, so that the reactivity ratios were 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 SP 2000 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 polymer compositions.

Microanalysis:

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

Thermal methods of analysis:

a) 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, 10mm × 5mm × 2.5mm 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.

b) Differential scanning calorimetry (DSC):

DSC curves were obtained using a Mettler TA 3000 DSC. The samples were heated at 10°/min from ambient temperature up to 500°C.

RESULTS AND DISCUSSION

Characterization of PATA homopolymer and ATA-MMA copolymer:

N-[3-(5-amino-1,2,4-triazolo)]acrylamide (ATA) monomer was prepared by the reaction of equimolar amounts of AC and 3,5-diamino-1,2,4-triazole in dry benzene.

PATA homopolymer was prepared by free radical initiation of ATA using 0.1 W/V% AIBN as initiator to ~ 10% conversion. The IR spectrum of PATA homopolymer shows two medium broad bands at 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 the $\nu(\text{C-H})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C-C})$ bonds, 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-plane C-H deformation vibration between 775 and 750 cm^{-1} and the C-C out-of-plane deformation at 500 cm^{-1} are assigned.

The IR spectrum for ATA-MMA copolymers exhibits a characteristic strong band at 1731 cm^{-1} assigned to the antisymmetric stretching vibration of carbonyl group of MMA. There is no change in the position of the bands of amino group of ATA units in the copolymers.

Determination of reactivity ratios of ATA-MMA copolymers:

Five different compositions of the ATA-MMA copolymers with 57, 34, 24, 17 and 14 mole% ATA units were prepared by free radical initiation using 0.2 w/v % AIBN and DMF (50/50 v/v) as solvent. The polymerizations were carried out at 60 $^{\circ}\text{C}$ to about 10% conversion.

The integration of $^1\text{H-NMR}$ spectrum for each sample of the copolymers was used for the calculation of copolymer composition. The monomer composition of the copolymer can be calculated from the ratio of these integrals which are proportional to the number of protons that contribute to the peaks. This method was already used for the determination of reactivity ratios for styrene – MMA [Kato et al (1964)], and methacrylate – acrylate copolymers [Grassie et al .91965)]. Figure 1 shows the $^1\text{H-NMR}$ spectrum of ATA-MMA copolymers. There are three characteristic peaks at 0.85-1.05, 1.88-1.94 and 2.77-2.89 ppm for CH_3 , CH_2 and CH protons respectively [El-Sonbati (1990)]. The amino proton at δ 7.85 ppm (peak A) disappeared on addition of D_2O , due to $-\text{NH}$

proton of ATA in the copolymer [Mochel (1967)]. Peak B at 3.65 ppm is due to $-\text{OCH}_3$ protons of the MMA unit. Dividing the integral values due 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 the means of the following equation: [Billmeyer(1971)]

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

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 MMA, 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 MMA (M_2) in the copolymer 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 - MMA copolymer are $r_1(\text{ATA}) = 0.2 \pm 0.01$ and $r_2(\text{MMA}) = 2.0 \pm 0.2$.

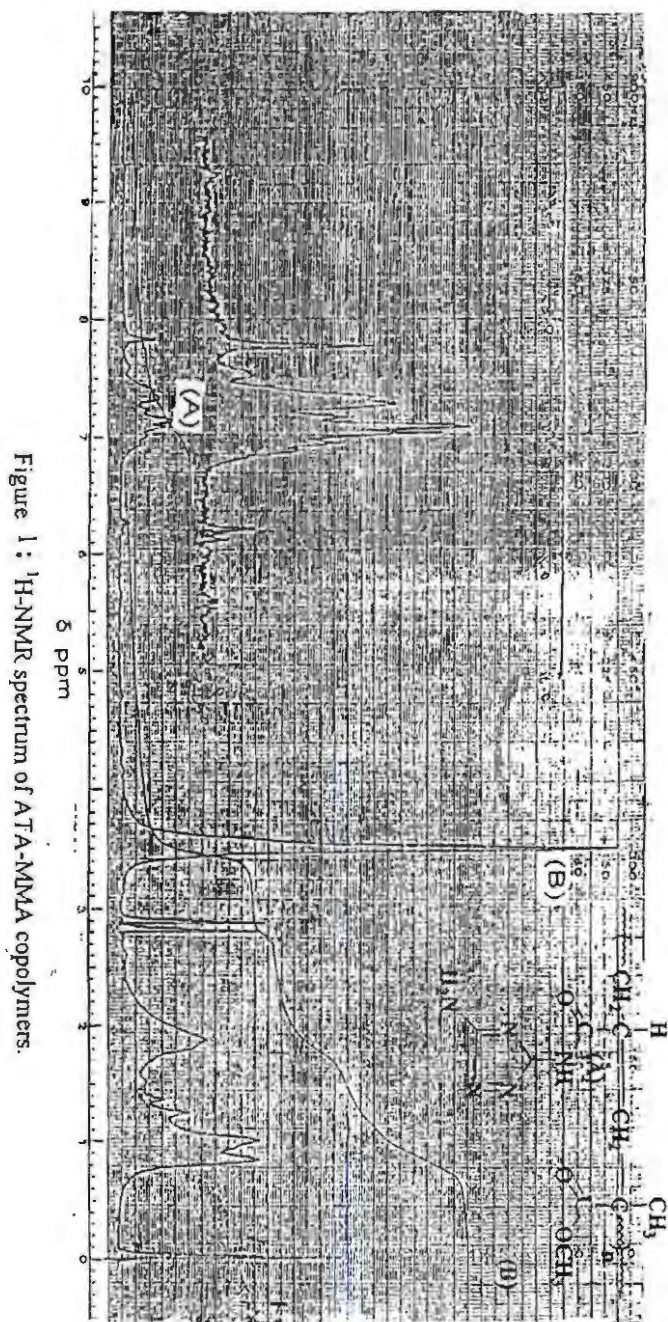


Figure 1 : ¹H-NMR spectrum of ATA-MMA copolymers.

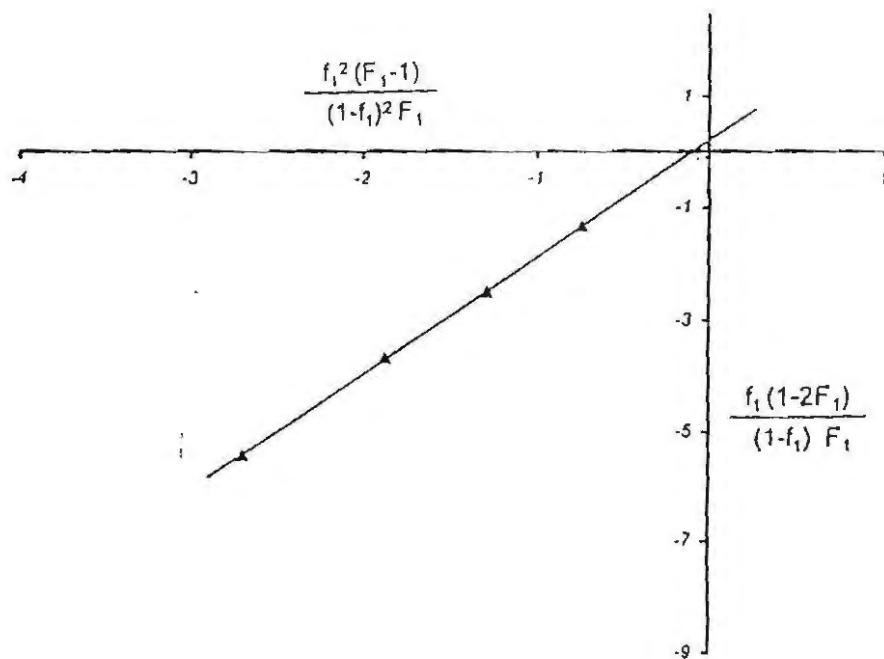


Figure 2 : Graph of $\frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1(1-2F_1)}{(1-f_1) F_1}$ for ATA-MMA copolymers.

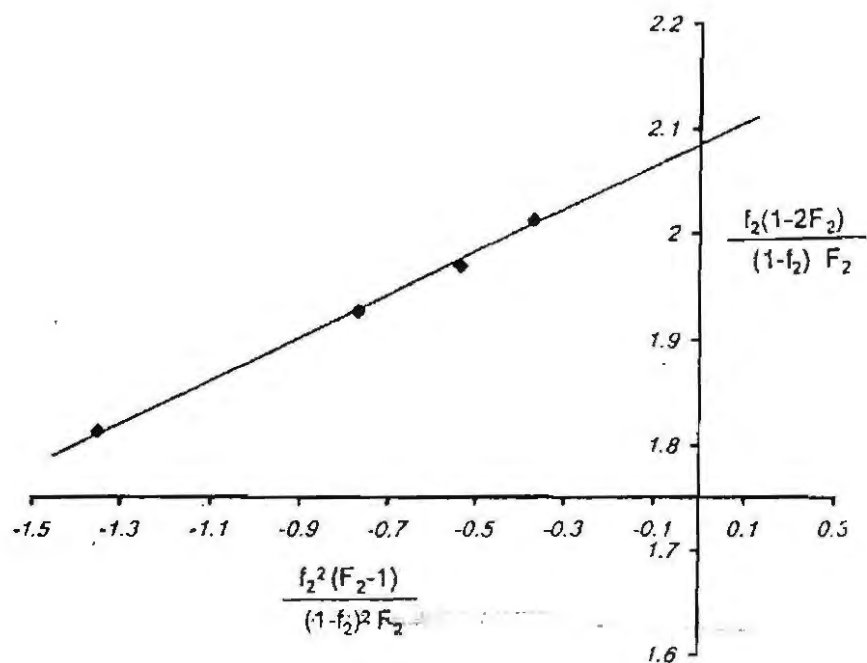


Figure 3: Graph of $\frac{f_2^2(F_2-1)}{(1-f_2)^2 F_2}$ versus $\frac{f_2(1-2F_2)}{(1-f_2) F_2}$ for ATAc-MMA copolymers.

Thermal methods of analysis:**Thermogravimetry (TG):**

TG curves of PATA and PMMA homopolymers and copolymers of ATA-MMA are shown in Figure 4. PATA homopolymer degrades in two stages. The first starts at $\sim 117^{\circ}\text{C}$ with a weight loss $\sim 45\%$. The second stage starts at 333°C with a weight loss of 44% . PMMA homopolymer degrades in two stages. The first step starts at 260°C with a weight loss percentage of 38% . The second degradation stage starts at 350°C with a weight loss of $\sim 56\%$. There are three TG degradation stages for all the ATA-MMA copolymers. The volatilization temperature starts at $\sim 188, 212, 240$ and 247°C for the copolymers 57, 34, 24 and 14 mole% ATA units, respectively. Table 1 lists the percentage weight losses and the maximum rate of weight loss shown in the derivative thermogravimetry DTG. The TG curves show that the stabilities of the copolymers are intermediate between those of the homopolymers.

Table (1): Weight loss of PATA and PMMA homopolymers and ATA-MMA copolymers.

Polymer Mol% ATA	Volatilization temp. $^{\circ}\text{C}$	First stage		Second stage		Third stage		Remaining wt. % after 500°C
		T_{max} $^{\circ}\text{C}$	Wt. loss %	T_{max} $^{\circ}\text{C}$	Wt. loss %	T_{max} $^{\circ}\text{C}$	Wt. loss %	
PATA	117	293	45	380	44	--	--	11
57	188	242	6	267	15	390	73	6
34	212	245	5	285	20	390	70	5
24	240	250	4	310	25	400	67	4
14	247	263	3	340	30	405	64	3
PMMA	260	297	38	350	56	--	--	6

To illustrate the initial stages of breakdown more clearly, a comparison study of weight loss percentage at definite temperature with copolymer composition give a clear picture on the relative stability of the entire composition range. Smooth changes in stability with composition is well shown in Figure 5, in which the weight loss percentage at a selected temperature (250°C) using the data in Figure 4 is plotted against composition. The most clearly defined features of the reaction is the increase of stability towards PMMA homopolymer. This is not the case in the thermal stabilities of vinyl bromide-methyl acrylate and β -

bromostyrene-methyl acrylate copolymers [Diab (1982) and Diab & El-Sonbati (1987)], which have thermally stable copolymers at definite compositions.

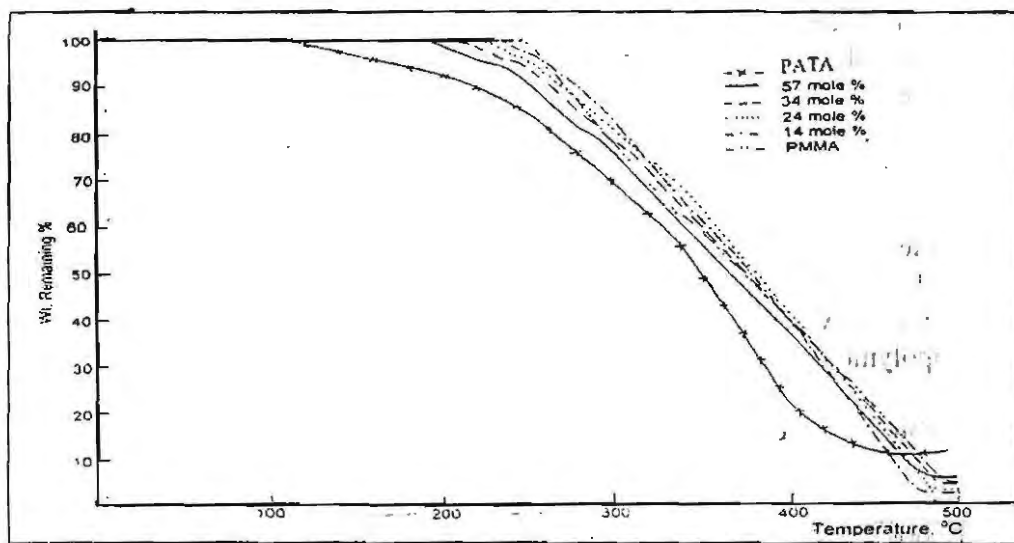


Figure 4: TG curves for PATA and PMMA homopolymers and AFA-MMA copolymers.

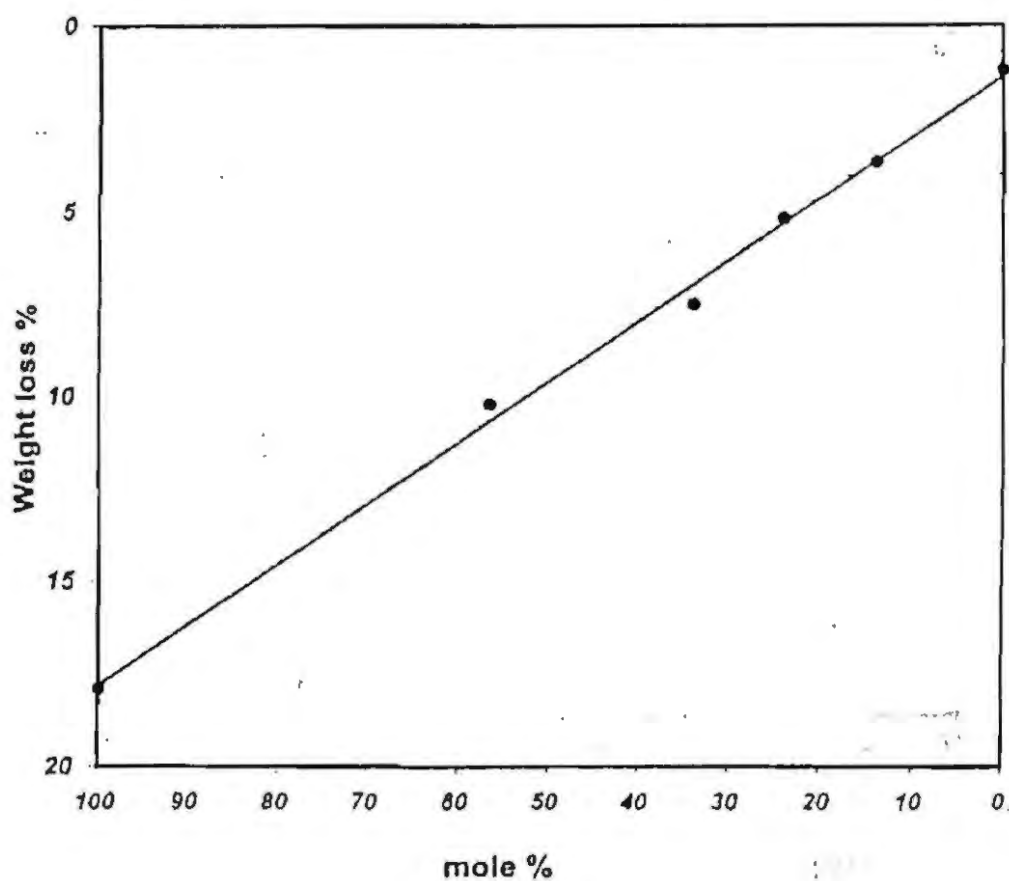


Figure 5: Comparison of weight loss percentage at 250°C for ATA-MMA copolymers at different compositions.

The effective activation energies of the thermal degradation of PATA and PMMA homopolymers and ATA-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 6). Table 2 lists the activation energies of PATA and PMMA homopolymers and ATA-MMA copolymers. The activation energy of PATA homopolymer is smaller than that of the

copolymers and PMMA homopolymers. Therefore PATA homopolymer will undergo decomposition more readily than ATA-MMA copolymers and PMMA homopolymer.

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

Polymer ATA mole %	Activation Energy (E_a) KJ mol ⁻¹
PATA	71.2
57	--
34	83.1
24	98.2
17	108.7
14	111.7
PMMA	116.4

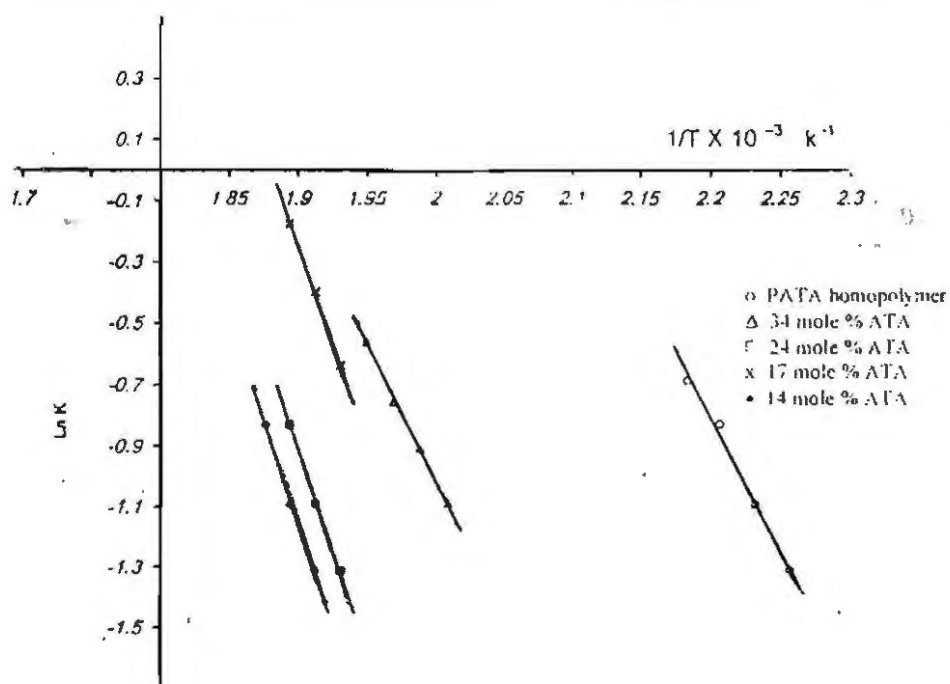


Figure 6: Arrhenius plots of the rate constants of degradation of PATA homopolymer and ATA-MMA copolymers.

3.3.2. Differential scanning calorimetry (DSC):

DSC apparatus was used for the determination of glass transition (T_g) of PATA and PMMA homopolymers and ATA-MMA copolymers. Figure 7 represents the DSC curve of 34% mole ATA units of ATA-MMA copolymer and PMMA homopolymer. The T_g of PATA and PMMA homopolymers and ATA-MMA copolymers are shown in Table 3. It seems that the values of T_g increase with increasing the mole percentage of MMA in the copolymers.

Table (3): Glass transition temperature (T_g) of PATA and PMMA homopolymers and ATA-MMA copolymers.

Polymer mole. % ATA	T_g . °C
PATA	73
57	78
34	80
24	85
17	103
14	107
PMMA	111

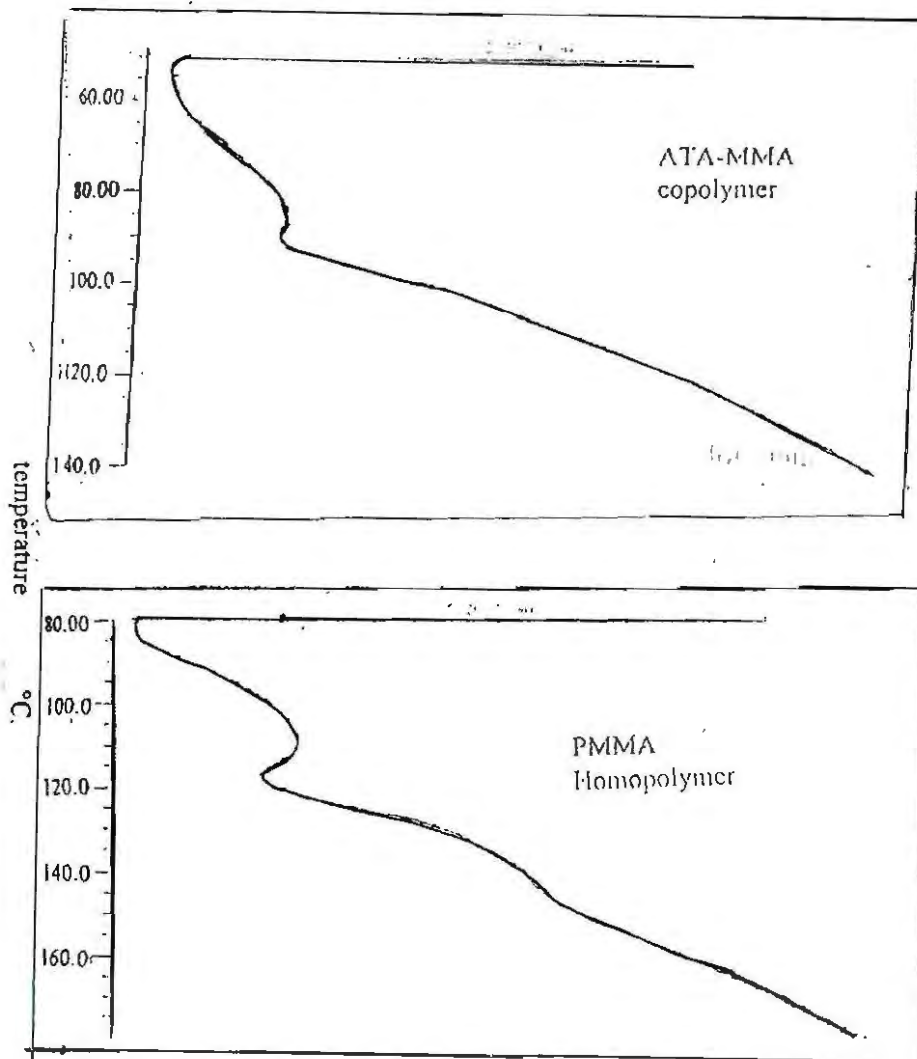


Figure 7 : DSC curve of ATA-MMA copolymer (34 mole% ATA unit) and PMMA homopolymer.

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الملخص العربي

يتضمن هذا البحث تحضير كوبوليمرات ن(٣و٥-أمينو-١و٢و٤-تراى أزلو) أكريلاميد مع الميثيل ميثا أكريلات وأثبت التركيب البنائى لها باستخدام التحليل الدقيق وطيف الأشعة تحت الحمراء كذلك تم تعيين نسبة نشاطية المونمرات فى الكوبولمر باستخدام طيف الرنين النووى المغناطيسى واستخدمت قياسات التحليل الحرارى لدراسة ثباتية البولمرات المحضرة ومقارنتها بالهوموبوليمرات المقابلة.

