

**THERMAL STABILITY OF COPOLYMERS OF  
P-BROMOPHENYL ACRYLAMIDE-METHYL  
METHACRYLATE**

**Fahd A. A. Trikistani**

Department of Chemistry, Faculty of Applied Science, Umm Al-Qura  
University, Makkah Al-Mokkaramah, B.O.Box 7650, Saudi Arabia

(Received: 10 / 8 / 2008)

**ABSTRACT**

Copolymers of p-bromophenyl acrylamide with methyl methacrylate were prepared and characterized using microanalysis and IR spectroscopy. The reactivity ratio values of the copolymerization were calculated using <sup>1</sup>H-NMR technique. Thermal analyses of the copolymers showed that the stability are intermediate between poly(p-bromophenyl acrylamide) and poly(methyl methacrylate) homopolymers.

**INTRODUCTION**

It is well known that the thermal stability of polymers has been improved by copolymerization of the primary monomer with traces of a comonomer [Al-Mazroai (2000); Tirkistani (2008) and Tirkistani (2008)]. The poor thermal stability of brominated polymers, due to the weak character of the C-Br bond, has received much attention [El-Agamey & Diab (1986) and Grassie et al. (1981)]. In this paper, homopolymers of poly(p-bromophenyl acrylamide) (PBPA) and poly(methyl methacrylate) (PMMA) and five different compositions of copolymer of p-bromophenyl acrylamide and methyl methacrylate (BPA-MMA) were prepared, so that the reactivity ratios might be determined using <sup>1</sup>H-NMR method. The thermal stability of the homopolymers and copolymers were examined.

## EXPERIMENTAL

**Materials:**

Methyl methacrylate (MMA) (BDH Chemical Ltd.), stabilized with 0.1% by hydroquinone was washed with a small amount of sodium hydroxide solution, separated with a separated funnel, distilled in a vacuum line, dried over anhydrous sodium sulphate and stored below  $-18^{\circ}\text{C}$ .

Acryloyl chloride (AC) (Aldrich Chemical Co., Inc.) was used without further purification. It was stored below  $-18^{\circ}\text{C}$  in a tightly glass-stoppered flask.

2,2'-Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co., Inc.) was used as initiator for polymerization. It was purified by dissolving in hot ethanol and filtering [Diab (1983)]. The solution was left to cool, the pure material then being collected by filtration and dried under vacuum.

*p*-Bromoaniline (BA) (BDH Chemical Ltd.), was purified by distillation under atmospheric pressure [Wei & Hsueh (1968)].

**Preparation of monomers and polymers:**

*p*-Bromophenyl acrylamide (BPA) monomer was prepared by the reaction of equimolecular amounts of AC and BA using dry benzene as solvent in an ice bath. This process is similar to the one reported of the preparation of acryloyl hydrazine, *N*-(*B*-ethyl-amino)acrylamide and *N*-2(6-aminopyridine)acrylamide [Takrony (2000)].

Poly(*p*-bromophenyl acrylamide) (PBPA) and poly(methyl methacrylate) (PMMA) homopolymers were prepared by refluxing BA or MMA monomers with dimethylformamide (DMF) (50/50 v/v) as solvent and 0.2 w/v % AIBN as initiator for two hours. The polymer products were precipitated by pouring in distilled water and dried in a vacuum oven for several days at  $40^{\circ}\text{C}$ .

Copolymers of BPA-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 BPA-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  $40^{\circ}\text{C}$  for several days.

## ANALYTICAL TECHNIQUES

### **Infrared spectroscopy (IR)**

Spectrum were recorded on Pye Unicam SP 2000 spectroscopy, for the homopolymers and copolymers.

Nuclear magnetic resonance spectroscopy (NMR):

<sup>1</sup>H-NMR spectra were obtained using a Varian EM 390 90 MHZ spectrophotometer with integration and 20 mg samples. The polymers were dissolved in 1 ml of CDCl<sub>3</sub>. 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 aziz University, Saudi Arabia.

### **Thermal method 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 boot-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 Arrhenius equation.

## RESULTS AND DISCUSSION

### **Characterization of PBPA homopolymers and BPA-MMA copolymer:**

BPA monomer was prepared by the reaction of equimolar amounts of AC and *p*-bromophenol in dry benzene until the evolution of hydrogen chloride ceased forming a brown powder of BPA monomer (M.W. 226). (Microanalysis, found N, 6.2% calcd. for C<sub>9</sub>H<sub>8</sub>ONBr, N 6.19%).

PBPA homopolymers was prepared by free radical initiation of BPA using 0.2 w/v % AIBN as initiator to (~ 10 %) conversion. The IR spectrum of PBPA homopolymers shows two medium broad bands at

3290 and 3441  $\text{cm}^{-1}$  assigned to symmetric and asymmetric stretching vibrations of the amino group. The band at 1680  $\text{cm}^{-1}$  is assigned to the antisymmetric stretching vibration of amidic carbonyl group. The bands at 1600, 1545 and 1440  $\text{cm}^{-1}$  are assigned to the  $\nu(\text{C-H})$ ,  $\nu(\text{C=C})$  and  $\nu(\text{C-C})$  bonds, respectively [El-Sonbati et al (1991)]. The C-H in plane deformation in the region 1225-1045  $\text{cm}^{-1}$ , the ring breathing at 995 and 1005  $\text{cm}^{-1}$  the out-of-plane C-H deformation vibration between 775 and 750  $\text{cm}^{-1}$  and the C-C out-of-plane deformation at 500  $\text{cm}^{-1}$  are assigned.

The IR spectrum of BPA-MMA copolymer exhibits a characteristic strong band at 1730  $\text{cm}^{-1}$  assigned to the antisymmetric stretching vibration of carbonyl group of MMA. There is no change in the position of the bonds of amino group of BPA units in the copolymers.

#### Determination of reactivity ratios of BPA-MMA copolymers:

Five different compositions of the BPA-MMA copolymers with 67, 52, 43, 29 and 13 mole % BPA units prepared by free radical initiation using 0.2 w/v % AIBN and DMF (50/50 v/v) as solvent. The polymerization were carried out at 60°C to about 10% conversion.

The integration of  $^1\text{H-NMR}$  spectrum from each sample of the copolymer 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 different copolymers [Grassie et al. (1986) and Grassie et al. (1965)]. Figure 1 shows the  $^1\text{H-NMR}$  spectrum of BPA-MMA copolymers. There are three characteristic peaks at  $\delta$  0.85-1.05, 1.88-1.94 and 2.77-2.86 ppm for  $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{CH}$  protons, respectively [El-Sonbati (1990)]. The amino proton at  $\delta$  7.85 ppm was disappeared on addition of  $\text{D}_2\text{O}$ . Peak A at  $\delta$  7.15 and 7.38 ppm which is a composite peak, due to two protons in the ortho-position and two protons in meta-position of the benzene ring of BPA in the copolymer, respectively [Mochel (1967)]. Peak B at  $\delta$  3.65 ppm is due to  $-\text{OCH}_3$  protons of the MMA unit. Dividing the integral values due to peak A by four 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 means of the following equation [Billmeyer (1971)].

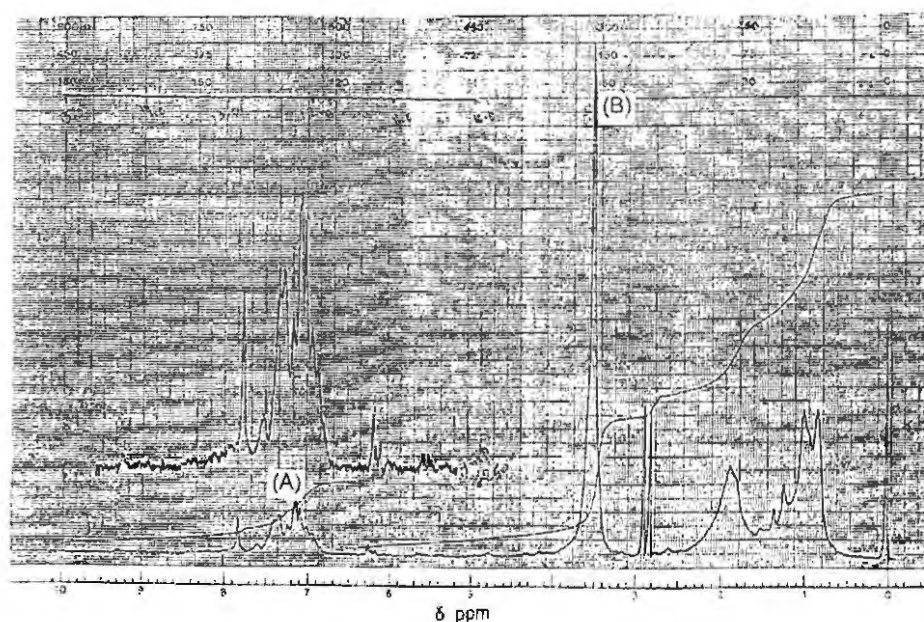


Fig (1):  $^1\text{H-NMR}$  spectrum of BPA-MMA copolymers.

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

where  $F_1 = \frac{M_1/M_2}{M_1/M_2 + 1}$  is the mole fraction of BPA ( $M_1$ ) in copolymer,

$f_1 = \frac{n_1}{n_1 + n_2}$  is the mole fraction of  $M_1$  in feed,  $r_1$  and  $r_2$  are the reactivity

ratios of BPA 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 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 Figure 2 and 3 reactivity ratio values for BPA-MMA copolymer are  $r_1(\text{BPA}) = 0.27 \pm 0.01$  and  $r_2(\text{MMA}) = 1.8 \pm 0.2$ .

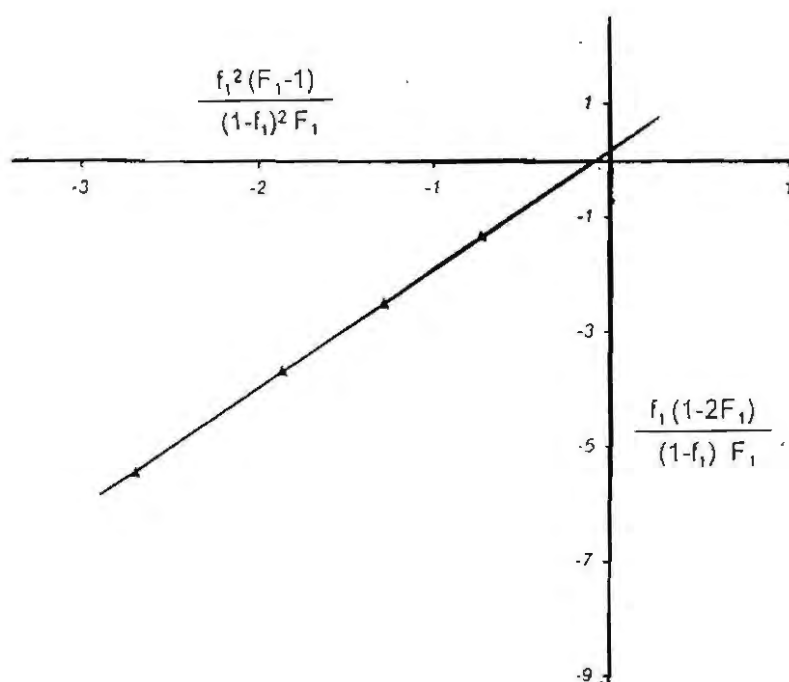


Fig (2):  $\frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$  Versus  $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$  for BPA-MMA copolymers.  
Plots of

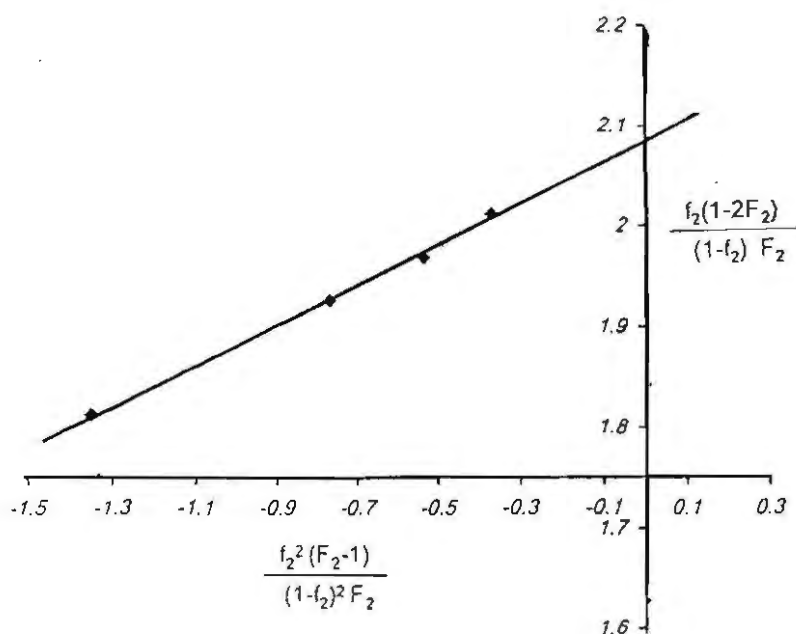


Fig (3): Plots of  $\frac{f_2^2(F_2-1)}{(1-f_2)^2 F_2}$  Versus  $\frac{f_2(1-2F_2)}{(1-f_2) F_2}$   
for BPA-MMA copolymers.

#### Thermal methods of analysis:

##### Thermogravimetry (TG):

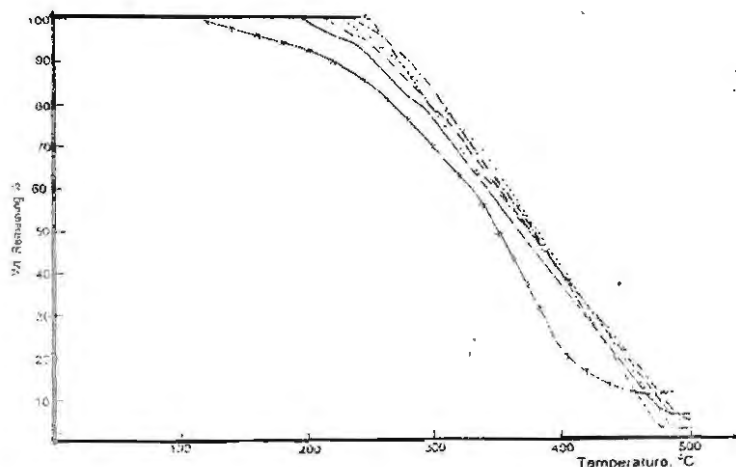
TG curves of PBPA and PMMA homopolymers and copolymers BPA-MMA are shown in Figure 4. There are two degradation stages of PBPA homopolymer, the first starts at  $\sim 110^\circ\text{C}$  with a weight loss of  $\sim 52\%$ . The second stage starts at  $\sim 310^\circ\text{C}$  with a weight loss of  $\sim 40\%$ . PMMA homopolymers degrades in two stages. The first step starts at  $\sim 260^\circ\text{C}$  with a weight loss percentage of  $\sim 38\%$ . The second degradation stage starts at  $\sim 350^\circ\text{C}$  with a weight loss percentage of  $56\%$ . There are three TG degradation stages for all the BPA-MMA copolymers. The volatilization temperature starts at  $\sim 160, 182, 198, 215$  and  $256^\circ\text{C}$  for the copolymers 67, 52, 43, 29 and 13 mole % BPA units, respectively.

Table I: Weight loss percentage of PBPA and PMMA homopolymers and BPA-MMA copolymers.

Polymer Mole % BPA	Volatilization Temperature, °C	First stage		Second stage		Third stage		Remaining wt. % after 500°C
		T <sub>max</sub> , °C, Wt.loss%		T <sub>max</sub> , °C, Wt.loss%		T <sub>max</sub> , °C, Wt.loss%		
PBPA	110	280	52	310	40	-	-	8
67	182	237	6	261	13	381	72	9
52	211	244	6	286	21	390	63	10
43	240	251	5	311	25	390	60	10
29	246	262	4	341	30	397	57	9
13	237	267	4	337	31	403	55	40
PMMA	260	297	38	350	56	-	-	6



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.



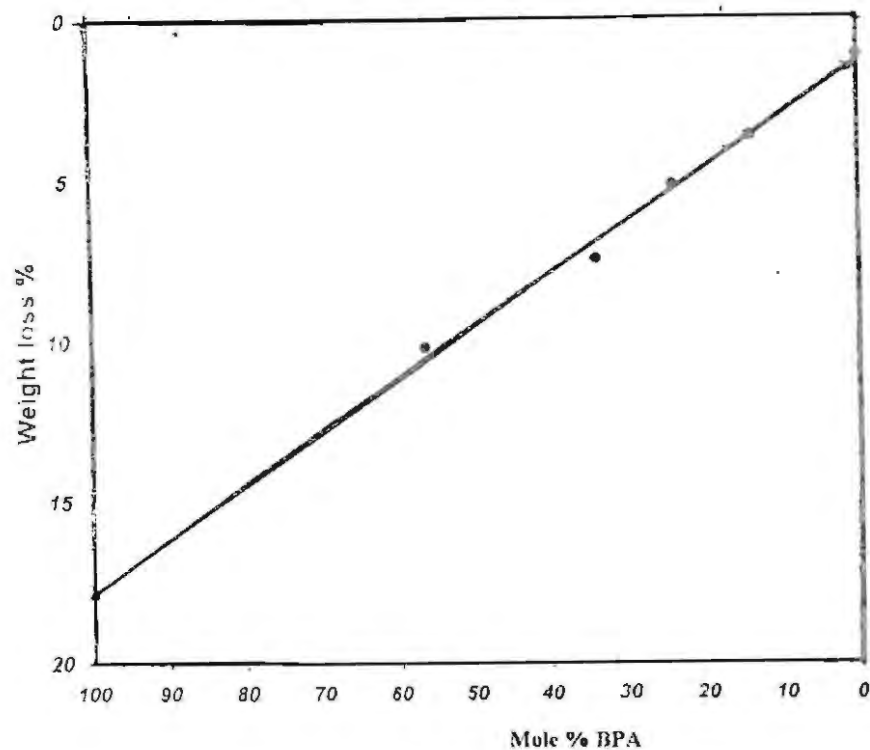
(-x-) PBPA homopolymer, (--) 67 mole % BPA, (- - -) 52 mole % BPA, (.....) 29 mole % BPA, (-.-) 13 mole % BPA, (-.-) PMMA homopolymer

**Fig (4):** TG curves for PBPA and PMMA homopolymers and BPA-MMA copolymers.

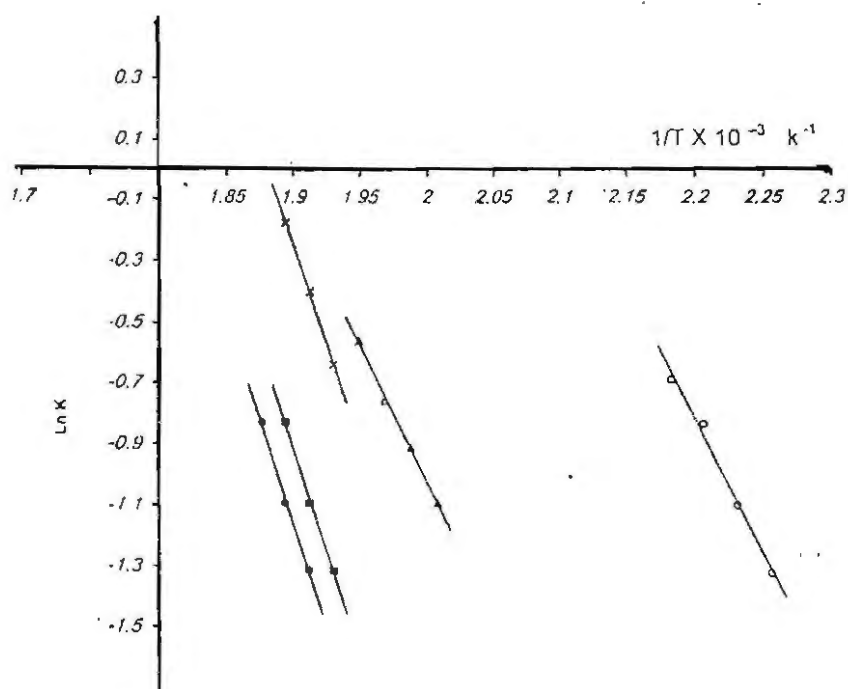
To illustrate the initial stages of breakdown more clearly, a comparison study of weight loss percentage at definite temperature with copolymer composition give a clear picture on the relative stability of the entire composition range. Smooth changes in stability with composition is well demonstrated in Figure 5 is plotted against composition. The most clearly defined feature of the reaction is the increase of stability towards PMMA homopolymer.

The effective activation energies of the thermal degradation of PBPA and PMMA homopolymers and BPA-MMA copolymers were determined from the temperature dependence of the chain rupture rate. The rate constant of the thermal degradation was plotted according to Arrhenius relationship (Figure 6). Table 2 lists the activation energies of PBPA and PMMA homopolymers and BPA-MMA copolymers. The

activation energy of PBPA homopolymers is smaller than of the copolymers and PMMA homopolymers. Therefore PBPA homopolymers will undergo decomposition more readily than BPA-MMA copolymers and PMMA homopolymers.



**Fig (5):** Comparison of weight loss percentage at 250°C for BPA-MMA copolymers at different compositions.



O PBPA homopolymer,  $\Delta$  67 mole % BPA,  $\blacksquare$  52 mole % BPA,  $\times$  29 mole % BPA,  $\bullet$  13 mole % BPA.

Fig (6): Arrhenius plots of the rate constants of degradation of PBPA homopolymer and BPA-MMA copolymers.

Table (2): Activation energies of the thermal degradation of PBPA and PMMA homopolymers and BPA-MMA copolymers:

Polymer BPA mole %	Activation energy ( $E_a$ ) kJ/mol
PBPA	69.1
67	72.7
52	78.2
43	84.8
29	89.3
13	96.1
PMMA	116.4

## REFERENCES

- Al-Mazroai, L. S. (2000). Stability and degradation of Some Copolymers, M. Sc. Thesis, Umm Al-Qura University.
- Billmeyer, F. W. Jr. (1971). Textbook of Polymer Science, New York, Wiley Interscience, Chap 11, 328 – 354.
- Diab, M.A. (1983). Thermal Stability of Poly(vinyl bromide) and Vinyl bromide-methyl acrylate copolymer, J. Polym. Sci., Polym. Chem. Ed. 21, 3249 – 3253.
- El-Agamey, A. A. and Diab, M. A. (1986). Thermal Stability of Poly(B-bromostyrene) and copolymer of B-bromostyrene with methyl methacrylate, J. Thermal Anal., 31, 239 – 245.
- El-Sonbati, A. Z. (1990). Synthesis and properties of 7-formyl-8-hydroxyquinoline and its transition metal complexes. Transition Met. Chem., 15, 222 – 229.
- El-Sonbati, A. Z., Kotb, M. A. and Killa, H. A. (1991). Structural chemistry of Poly(2-acrylamido-1,2-diaminobenzene) complexes. Bull. Soc. Chim. Fr., 128, 623 -636.
- Takrony, K. M. (2000). Physico-chemical studies on some polymer complexes, M.Sc. Thesis, Umm Al-Qura University.
- Grassie, N., Torrance, B. J. D.; Fortune, J. D. and Gemmel, J. D. (1965). Stability and degradation of methyl methacrylate-methyl acrylate copolymers, Polymer, 6, 653 – 659.
- Grassie, N.; Jhonstone, A. and Scotony, A. (1981). Thermal degradation of bromine containing polymers, Eur. Polym. J., 17, 589 – 599.
- Grassie, N.; Diab, M. A. and Scotony, A. (1986). Thermal degradation of bromine containing polymers, Polym. Deg. And Stab., 16, 361 – 369.
- Mochel, V. (1967). Presented at a meeting of the division of rubber chemistry, Amer. Chem. Soc., Montreal, Canada.

Tirkistani, F. A. A. (2008). 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, Mans. J. Chem., 35, 177 – 193.

Tirkistani, F. A. A. (2008). Thermal stability of Poly(N-[3-(5-amino-1,2,4-triazolo]acrylamido and copolymer of N-[3-(5-amino-1,2,4-triazolo]acrylamido with methyl acrylate, Mans. J. Chem., 35, 195 – 208.

### الملخص العربي

يتضمن هذا البحث تحضير كوبوليمرات بارا-بروموفينيل اكريلاميد مع الميثيل ميثا أكريلات واثبات التركيب البنائي لها باستخدام التحليل الدقيق وطيف الأشعة تحت الحمراء. كذلك تم تعيين نسبة نشاطية المونمرات في الكوبوليمر باستخدام طيف الرنين النووي المغناطيسي. وإستخدام قياسات التحليل الحراري لدراسة ثباتية البوليمرات المحضرة وقياس طاقة تنشيط التكسير الحراري باستخدام معادلة أرهينوس.