Mansoura Journal of Chemistry Vol. 35 (2), December, 2008.

THERMAL STABILITY AND DEGRADATION OF HOMOPOLYMER OF *P*-BROMOPHENYL ACRYLAMIDE

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(Received: 10 / 8 / 2008)

ABSTRACT

Poly (*p*-bromophenyl acrylamide) (PBPA) homopolymer was prepared and characterized. Thermal degradation products of the polymer were identified by GC-MS technique. It seems that the mechanism of degradation of PBPA homopolymer is characterized by free radical formation followed by recombination along the backbone chain. The activation energy of thermal degradation of the homopolymer was calculated using Arrhenius equation.

INTRODUCTION

The non-flammability properties of halogenated polymeric materials has given a great deal of attention in the last few years, their thermal decomposition and thermal stability properties were of particular interest [**Grassie et al. (1987); Khairou & Diab (1994) and Khairou & Diab (1994)**].

There are various mechanisms of fire retardance in polymeric materials [**Lyons (1970) and Jolles (1966)**].

i . A heat barrier may be formed by physically covering the polymer with a reflecting intumescent coating which reduces heat transfer from the heat source to the polymer so that polymer degradation is inhibited.

ii. The concentration of combustible gases may be diluted by the production of inert gases such as carbon dioxide and nitrogen.

iii. A dust may be produced which acts as a heterogeneous catalyst in deactivating the radicals involved in flame propagation.

iv. The proportion of volatile inflammable products may be reduced and the proportion of involatile char increased.

v. The degradation and decomposition reactions may be modified to

produce non-flammable volatiles (usually halogenated species). The last of these is perhaps the most important of the flame retardant mechanisms because of the relatively small proportion of flame retardant required for a significant effect. Unlike inert gases, halogens or halogen derivatives strongly affect the flame velocity in concentrations of less than one per cent. The flame propagation cycle involves radical species such as H· and OH· radicals. Halogen compounds react with these radicals in the following way:

$$RX + H\cdot \longrightarrow HX + R\cdot$$

The radical R· will be less reactive than the H· radical which replaces so this substitution results in flame inhibition.

In this paper, thermal stability of poly (*p*-bromophenyl acrylamide) (PBPA) homopolymer was reported by thermogravimetric analysis. Thermal degradation of the polymer was studied using GC-MS apparatus.

EXPERIMENTAL

Materials

Acryloyl chloride (AC) (Aldrich Chemical Co., Inc.) was degassed, twice distilled on a vacuum line, stored over anhydrous Na_2SO_4 and kept below -18°C in a tightly stoppered flask.

2,2`-Azobisisobutyronitrile (AIBN) ((Aldrich Chemical Co., Inc.) was used as initiator for polymerization. It was purified by dissolving in hot ethanol. The solution was left to cool, the pure material then being collected by filtration and dried under vacuum [**Issa et al. (2002)**].

p-Bromoaniline (BA)(BDH Chemical Ltd.), was purified by distillation under atmospheric pressure [**Al-Mazroai (2002)**].

Preparation of monomer and polymer

p-Bromophenyl acrylamide (BPA) monomer was prepared by the reaction of equimolar amounts of AC and BA using dry benzene as solvent in an ice bath. This process is similar to that reported for the preparation of acryloyl hydrazine, N-(β-ethyl amino) acryloyl and N-[2,(6-aminopyridino)] acrylamide [**Takrony (2002)**].

Poly (*p*-bromophenyl acrylamide)(PBPA) homopolymer was prepared by refluxing the formed BPA monomer with

dimethylformamide (DMF)(50/50 v/v) as solvent and 0.2 w/v % AIBN as initiator for two hours. The polymer product was precipitated by pouring in distilled water. PBPA homopolymer was washed with water and dried in a vacuum oven at 40°C for several days.

Analytical Techniques:

Infrared Spectroscopy (IR):

IR spectra of the polymer was recorded on a Pye Unicam SP 2000 spectrometry using KBr discs.

Microanalysis:

Elemental analysis of the polymer was performed by Microanalytical Unit at King Abd El Aziz University.

Thermal Gravimetric Analysis (TG):

TG measurements were made with a Mettler TG 3000 apparatus. Finely powdered (~ 10 mg) samples were heated at 10°C/min in a dynamic nitrogen atmosphere.

Thermal Degradation of the Polymer:

Sample of ~ 50 mg was 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 a fused quartz capillary column of 30 m x 0.25 mm coated with methylsilicon, under programmed heating condition from 60 to 200°C was used for their identification of the condensable degradation products. The GC is interfaced with a Varian mass spectrometer.

RESULTS AND DISCUSSION

Characterization of PBPA homopolymer:

The IR spectrum of PBPA homopolymer (Figure 1) 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 ν(C-H), ν(C=C) and ν(C-C) bands, respectively [**El-Sonbati (1990)**]. The C-H in plane deformation in the region 1225-1025 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.

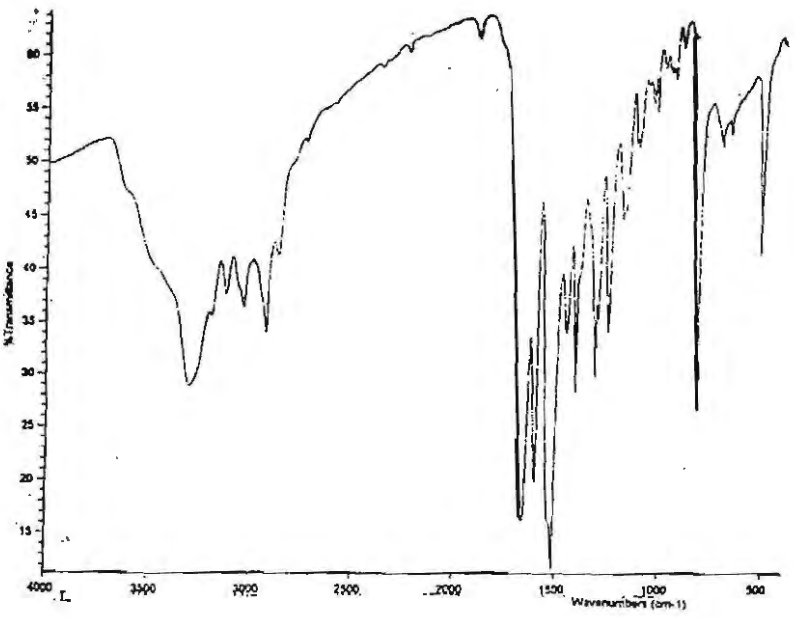


Fig (1): IR spectrum of PBPA homopolymer.

Thermal methods of analysis:

Thermogravimetry (TG):

TG curve of PBPA homopolymer is shown in (Figure 2). There are two degradation stages, the first starts at ~ 110°C with a weight loss - 52%. The second stage starts at ~ 310°C with a weight loss of ~ 40%. The effective activation energy of the thermal degradation of PBPA homopolymer was 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 3). The activation energy of the homopolymer was found to be 69 KJ/mole. This value is smaller than the value obtained for poly(8-quinolyl acrylate) and poly(acrylamidophenol) homopolymers [**El-Sonbati & Diab (1988) and Diab et al. (1988)**]. Therefore, PBPA homopolymer will undergo decomposition more readily than these homopolymers.

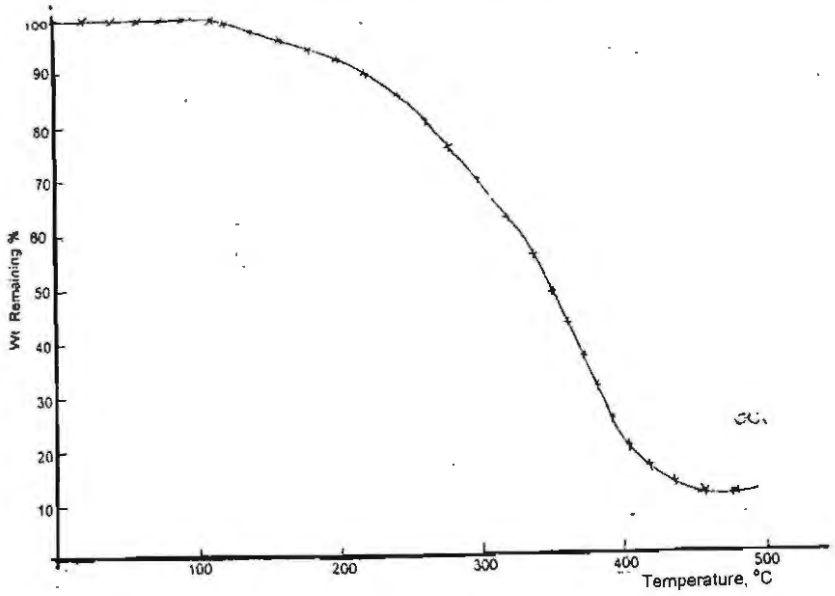


Fig (2): TG curve of PBPA homopolymer.

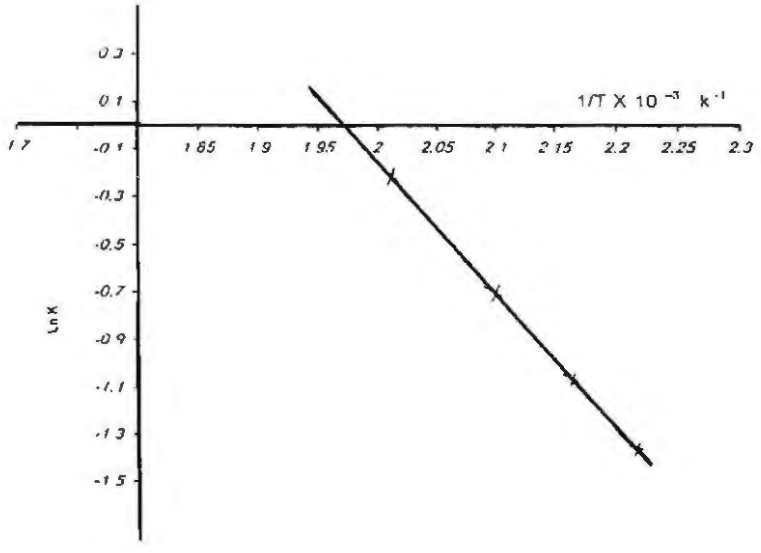


Fig (3): Arrhenius plot of the rate constant of degradation of PBPA homopolymer.

Thermal degradation of PBPA homopolymer:

50 mg of PBPA homopolymer was heated under vacuum from ambient temperature to 500°C. The volatile product of degradation was collected in a small gas cell for identification by IR spectroscopy. HBr, benzene, bromobenzene, aniline, *p*-bromoaniline and ammonia were among the degradation products of PBPA homopolymer. The liquid fractions from the degradation of the homopolymer were injected into the GC-MS apparatus. (Figure 4) shows the GC trace for the liquid products of degradation of PBPA homopolymer at 500°C. (Table 1) gives the results of degradation products which were identified by mass spectroscopy. Some of the peaks could not be identified due to the lack of reference materials or due to the uncleared mass spectra. The numerous degradation products of PBPA homopolymer indicate that the mechanism of degradation is characterized by the elimination of low-molecular weight radicals, rather than monomer formation in the early stages of degradation, followed by random scission mechanism along the backbone chain. It seems that the break down of PBPA homopolymer occurs mainly in the C-N bond producing the radicals

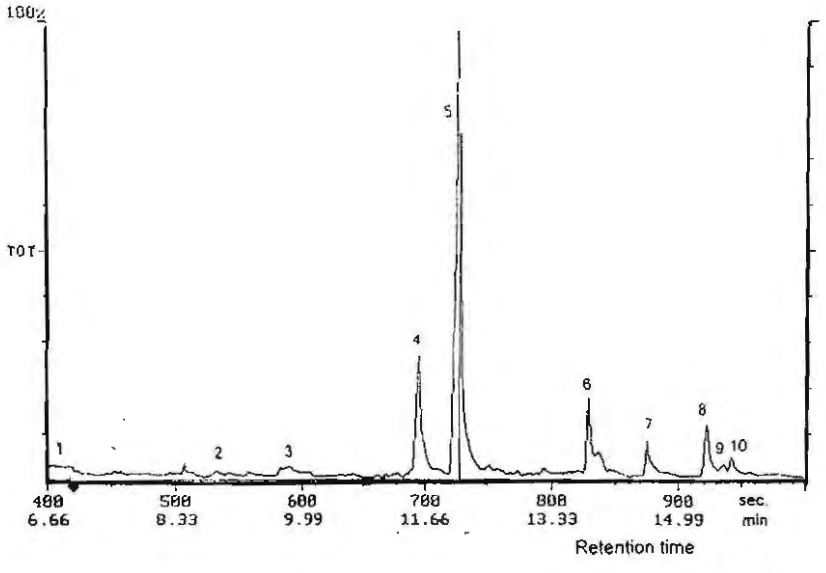
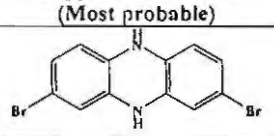
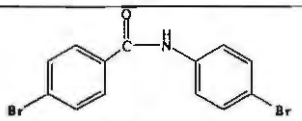
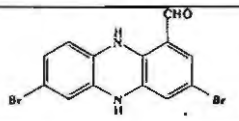
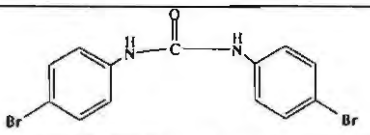
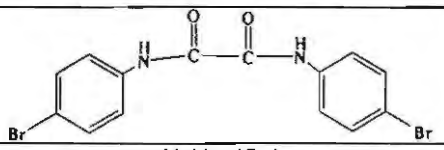
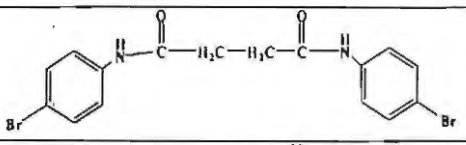
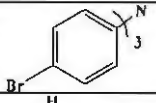
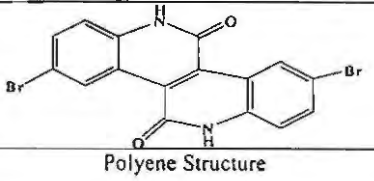
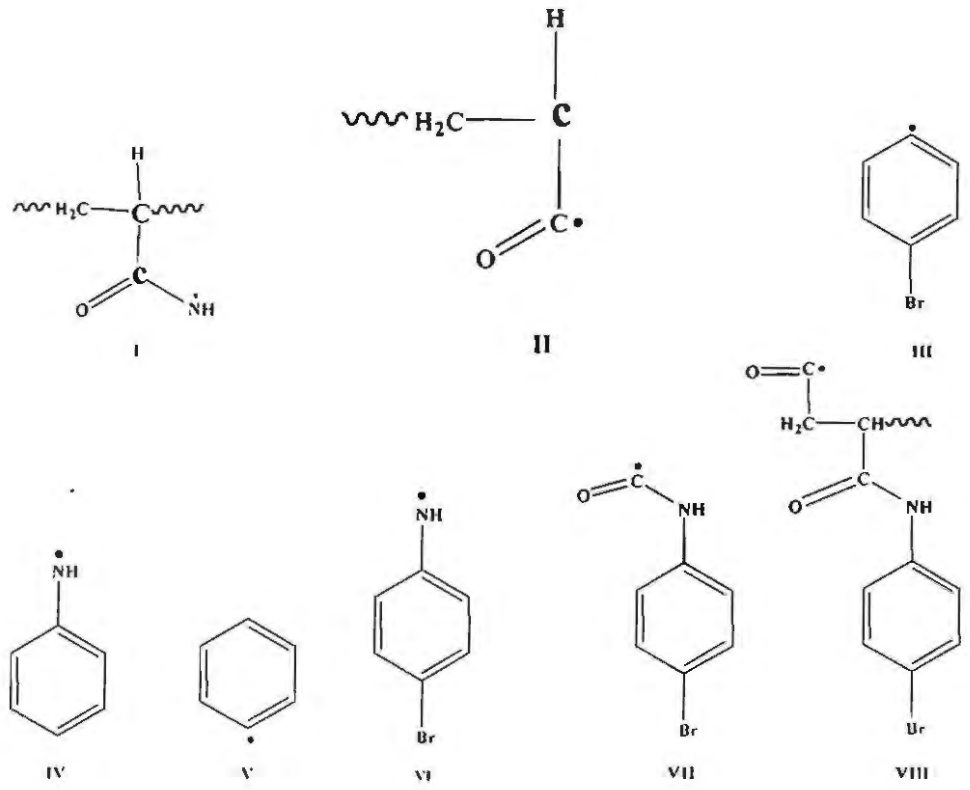


Fig (4): GC curve of the liquid fraction of the degradation of PBPA homopolymer.

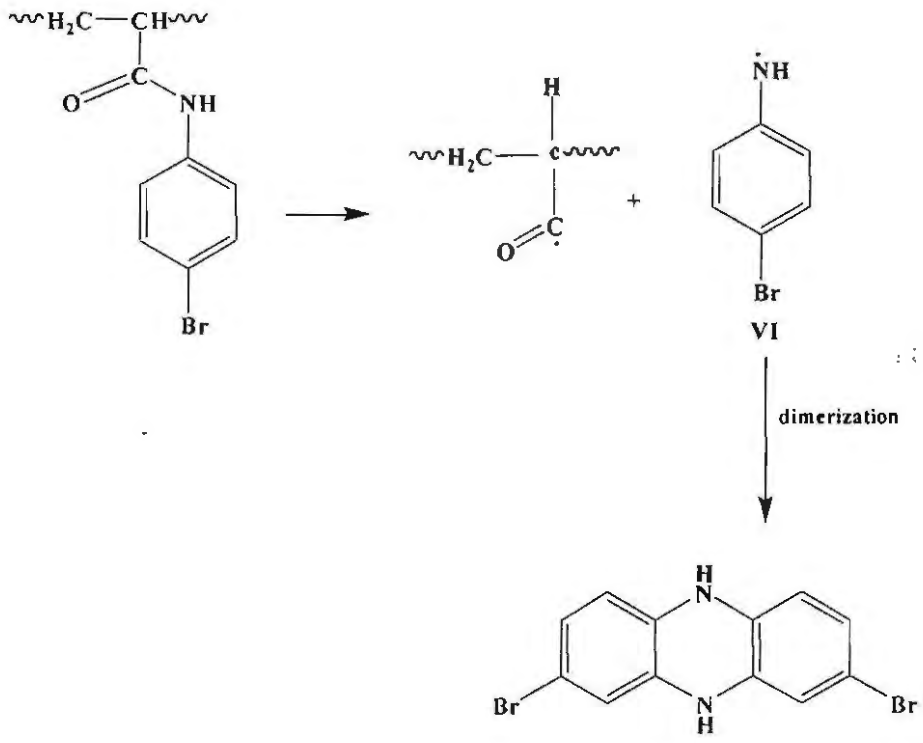
Table 1: GC-MS data of the liquid fraction of the thermal degradation of PBPA homopolymer

Compound No.	Retention time, min	Major MS fragments	Suggested Structure (Most probable)
1	6.84	(342,340,338), (261,259,182,168,152, 140,129,104,75,61,47	
2	8.96	(357,355,353), (274,272),198,166,141, 115,87,75,61,48	
3	9.91	(370,368,366), (287,285),213,167,150, 139,129,107,91,75,61	
4	11.52	(372,370,368), (289,287),215,187,155, 127,100,85,67,55	
5	12.35	(400,398,396), (317,315),241,227,213,195, 182,141,75,61,55	
6	13.92	(405,403,401), (372,370),357,291,258,241, 227,213,193,141,75,61,48	Unidentified
7	14.67	(428,426,424), (345,343),266,259,241,227, 216,188,160,151,129,101,61	
8	15.26	(509,507,505,503), (424,422,420),(345,343),244,216 ,204,175,160,132,107,91,65,55	
9	16.73	(424,422,420), (341,339),262,246,230,218, 204,160,143,129,120,84,61	
10	17.84	301,283,259,257,241,209, 183,129,101,61,48	Polyene Structure



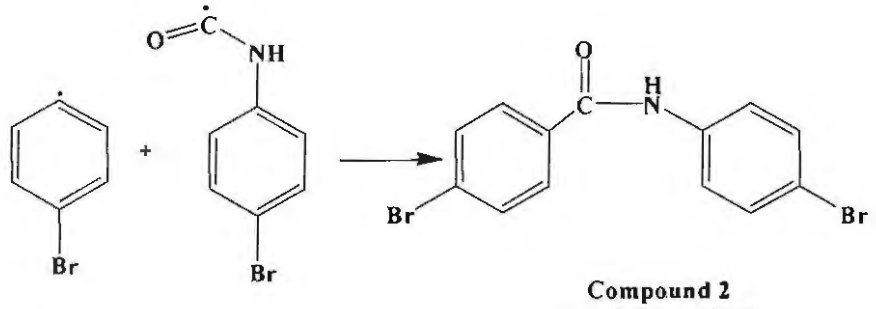
These radicals abstract H- and produce HBr, benzene, bromobenzene, aniline, *p*-bromoaniline and ammonia as major products.

Compound 1 in the GC curve listed in Table 1 could be found by a dimerization reaction of VI



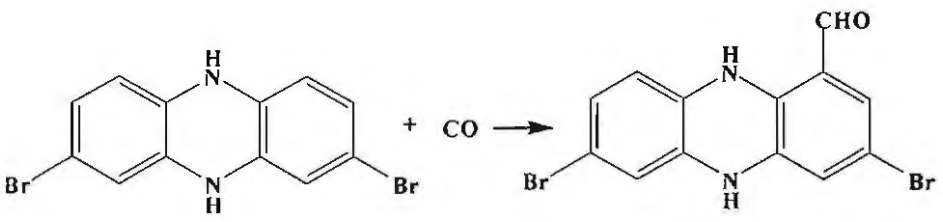
Compound 1
m/e (342,340,338)

The mass spectrum of the assignment of structure 2 is a termination reaction of the radicals III and VII



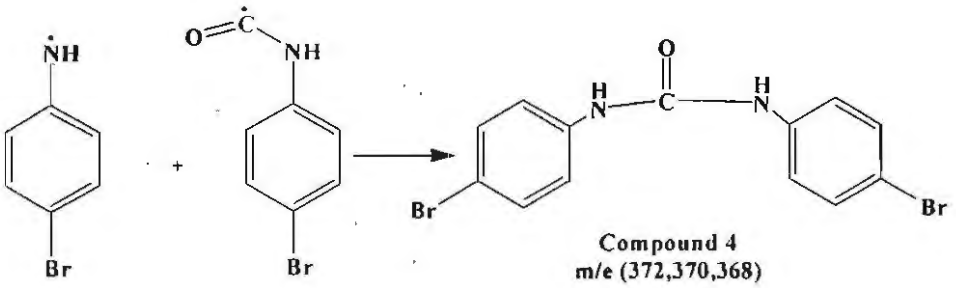
Compound 2
m/e (357,355,353)

The suggested structure of compound 3 is a reaction of the assignment structure of compound 1 and carbon monoxide.



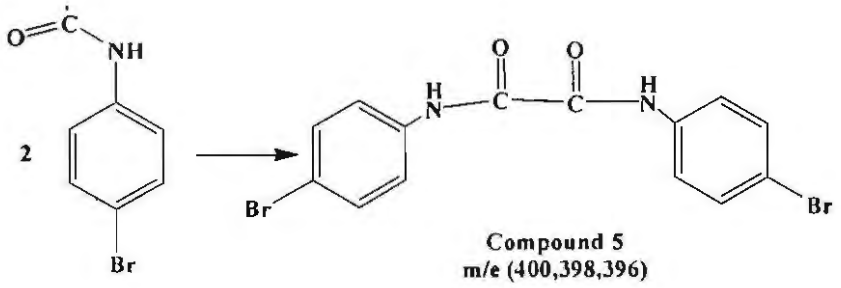
Compound 3
m/e (370,368,366)

It seems that compound 4 is formed by a reaction between the radicals VI and VII.



Compound 4
m/e (372,370,368)

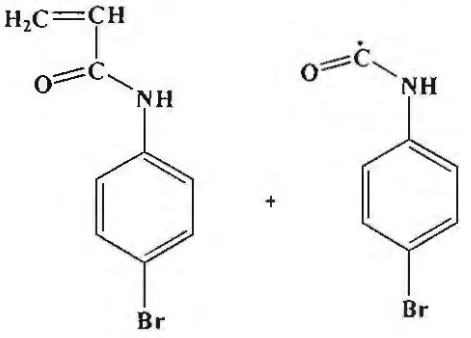
The assignment of structure 5 is a diamerization reaction of VI.

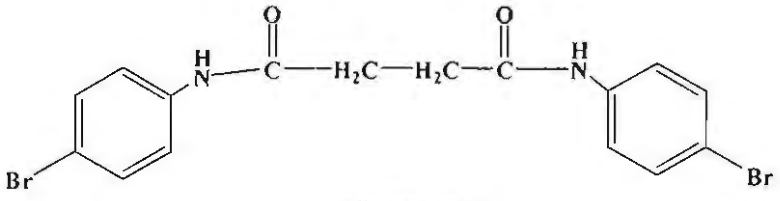


Compound 5
m/e (400,398,396)

The mass spectrum of the degradation product of PBA homopolymer (compound 6) was unidentified.

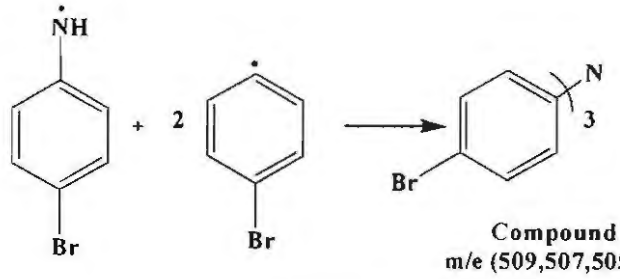
Compound 7 could be formed from the reaction of BPA monomer and the radical VII.





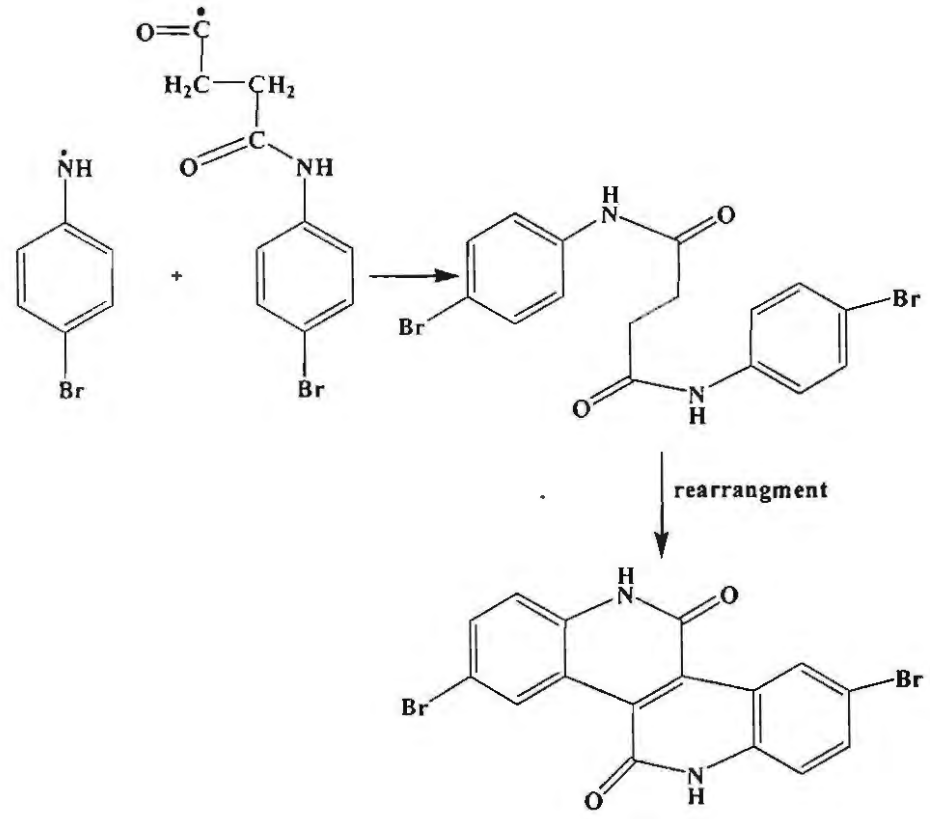
Compound 7
m/e (428,426,424)

Compound 8 is a termination of IV and two radical of III.



Compound 8
m/e (509,507,505,503)

The mass spectrum of the assignment structure 9 is a termination reaction of the radicals VI and VIII followed by rearrangement to give the compound 9.



Compound 9
m/e (424,422,420)

The major mass fragment of compound 10 gives a loss of mass either 14 or 13 indicating that it is a chain polyene fragment. The degradation behaviour of polyene is like polyolefin degradation [**Loan & Winslow (1976) and Chien & Kiang (1978)**] which produced chain fragments between C_6-C_{60}.

According to the degradation products, it seems that the mechanism of degradation of PBPA homopolymer is characterized by free radical formation followed by random scission or combination of these radical along the backbone chain are the main source of the degradation products.

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الملخص العربى

يتضمن هذا البحث تحضير بولى (بارا- برومو فينول اكريلاميد) ودراسة الثبات الحرارى له باستخدام التحليل الحرارى الوزنى، كذلك يشتمل هذا البحث التعرف على نواتج التكسير الحرارى للبوليمر المحضر باستخدام مطياف الكتله المتصل بالكروماتوجراف الغازى. وضحت ميكانيكية التكسير الحرارى. كذلك تم قياس طاقه التنشيط للتكسير الحرارى للبوليمر باستخدام معادلة أرهينيوس.