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Thermal stability and degradation ofpoly(N-*p*-tolylacrylamide)homopolymer and copolymer of N-*p*-tolylacrylamide with methyl methacrylate

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**Abstracted from her M.Sc. Thesis*

Abstract

Different concentrations of copolymer of N-*p*-tolylacrylamide(TAA)with methyl methacrylate (MMA) 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(N-*p*-tolylacrylamide) (PTAA)and poly(methyl methacrylate) (PMMA)homopolymers. Thermal degradation products of the PTAA were identified by GC-MS techniques. It seems that the mechanism of degradation of PTAAhomopolymer is characterized by free radical formation followed by recombination along the backbone chain. The activation energies of the thermal degradation of the copolymers were calculated using Arrhenius relationship.

*Key words:*N-*p*-Tolylacrylamide, Thermal stability and degradation, 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 [1,2]. 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 [3].To calculate the polymerization rate or polymer productivity and copolymer composition, monomer reactivity ratios must be known. The method which is used most often nowadays for estimating monomer reactivity ratios is to perform a low conversion copolymerization at various initial monomers feed compositions[4,5]. Subsequently, the copolymer composition is determined for each reaction [4]. Reactivity ratio values may be evaluated by various procedures: linear procedures, nonlinear procedures, and other copolymer composition equations [7–10].

A monomer, acryloxyethylphenoxyphosphorodiethylamidate (AEPPA), was synthesized and characterizedusing Fourier transform infrared (FTIR), ^{1}H-Nuclear magnetic resonance spectroscopy (^{1}H NMR)and^{31}P NMR. The copolymer with various amounts of styrene (St) was obtained by the free radical bulkpolymerization between AEPPA and St, and characterized using ^{1}H NMR. The thermal properties of thecopolymers were investigated with thermogravimetric analysis [11].

In this paper, homopolymers of poly(N-*p*-tolylacrylamide)(PTAA)and poly(methyl methacrylate) (PMMA) and four different composition of copolymers N-*p*-tolylacrylamide(TAA) and methyl methacrylate (TAA-MMA) were prepared, so that the reactivity ratios might be determined using ^{1}H-NMR method. The thermal stability of the homopolymesr and copolymers were examined. Thermal degradation of the PTAAhomopolymer was studied using GC-MS apparatus and the activation energies of the thermal degradation of the homopolymers and copolymers were calculated using Arrhenius relationship.

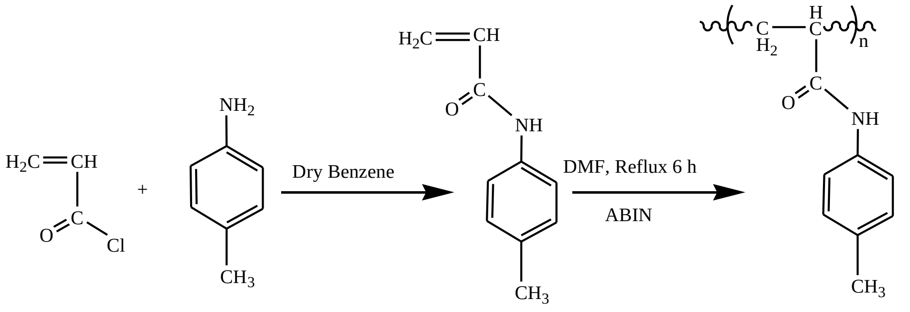
2. Experimental

2.1. Materials

Acryloyl chloride (AC) (Aldrich Chemical Co., Inc.) was used without further purification. It was stored below -18^{o}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 then recrystallization[12]. The solution was left to cool and the pure material 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^{o}C.4-Methylaniline(Aldrich Chemical Co., Inc.)was used without further purification.All other chemicals and solvents were purified by standardprocedures.

2.2. Preparation of monomer and polymers

N-*p*-tolylacrylamide(TAA)monomer was performed by the reaction of equimolar amounts of AC and *p*-methylaniline in dry benzeneuntil the evolution of hydrogen chloride ceased forming a white powder of TAA monomer. Poly (N-*p*-tolylacrylamide) homopolymer(PTAA) was prepared by free radical initiation of TAA using 0.1 w/v% AIBN as initiator and DMF as solvent andrefluxfor 6 hrs. The polymer product (~65%) was precipitated by pouring in distilled water and dried in a vacuum oven for several days at 40 ^{o}C.



N-*p*-tolylacrylamide
(TAA)

Poly(*N*-*p*-tolylacrylamide)
(PTAA)

Copolymers ofTAA with MMA were prepared using 0.2 w/v % AIBN as free radical initiator and 50/50 (v/v) DMF as solvent. Different copolymer compositions ofTAA-MMA were prepared, so that the reactivity ratios might be determined. Polymerization was carried out to about 10% conversion. It can be controlled byweighing the resultant copolymers. The copolymers were precipitated by pouring into a large excess of distilled water, filtered and dried in a vacuum oven at 40^{o}C for five days.

2.3. Analytical techniques

2.3.1. Infrared spectroscopy (IR)

Spectra were recorded on PyeUnicam SP 2000 spectrometry, for the homopolymers and copolymers in the form of KBr discs(4000-400 cm^{-1}).IR spectra of the degradation gas products were performed in a small gas cell.

2.3.2. 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.

2.3.3. Thermogravimetry (TG)

TG measurements were made with a Mettler TG 3000 apparatus. Finely powdered (~10 mg) samples were heated at 10^{o}/min in a dynamic nitrogen atmosphere (30 ml/min); the sample holder was boat-shaped, 10 mm×5 mm×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.

2.3.4. Thermal degradation of the PTAAhomopolymer

Samples of ~ 50 mg were heated under vacuum from ambient temperature to 500 ^{o}C. The volatile degradation productswerecollected for qualitative analysis by GC-MS technique. A Saturn GC 3400 with fused quartz capillary column of 30m × 0.25mm coated methyl silicon under programmed heating condition from 60 to 200 ^{o}C was used for the identification of the condensable degradation products. The GC is interfaced with a Varian mass spectroscopy equipped with the standard electron impact (E1) or chemical ionization (CI) sources and a DS 55 data system scans from m/e 300 to 20 at a scan rate of 10 s/decade. Perflurokerosene (PFK) was used for computer calibration and the ion source was maintained at 200 ^{o}C. Accurate mass measurements of the CI mass spectra were performed at 1000 resolving power using PFK as internal reference and by a computer interpolation data system.

3. Results and discussion

3.1. Characterization of PTAAhomopolymer and TAA-MMA copolymers

The IR spectrum of PTAAhomopolymer 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 ν(C-H), ν(C=C) and ν(C-C) bands, respectively [13]. 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 TAA-MMA copolymersshow bands at 1680 and 1730 cm^{-1} assigned to antisymmetric stretching vibration of the amidic carbonyl group of TAA and carbonyl group of MMA in the copolymers, respectively [14]. The bands at 1600, 1545 and 1440 cm^{-1} are due to ν(C-H),ν(C=C) andν(C-C) bonds [15], respectively.

3.2. Determination of reactivity ratios of TAA-MMA copolymers

Four different copolymers of TAA-MMA with 1:1, 1:0.35, 1:0.53 and 1:0.2 mole of TAA-MMAcovering the entire composition range between PTAA 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 [16], methacrylate-acrylate copolymers [17,18] and recently for copolymers of 4-nitro-3-methylphenylmethacrylate and N-(4-bromophenyl)-2-methacrylamide with glycidyl methacrylate, respectively [19,20]. The ^{1}H-NMR spectrum of TAA-MMA copolymers. The peaks at δ2.490 and 2.696-2.856 ppm are due to CH_2 and CH protons of TAA and MMA in the copolymers [21], the signalband at δ7.880 ppm is due to –NH proton of TAA in the copolymer [22]. The peak at δ 7.096-7.267 ppm due to phenyl protons of TAAin the copolymer and peak at 3.594 ppm is due to $–OCH_3$ protons of MMA units in the copolymers. Dividing the peak at δ 7.096-7.267 ppmby four and the peak at 3.594 ppm by three, the monomer composition of the copolymer can be calculated.

By knowing the number of moles of the monomer mixture and the molarratio of the copolymer, reactivity ratios can be calculated by applying the following equation [23]:

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

Where, $F_1=\frac{M_1/M_2}{M_1/M_2+1}$ is the mole fraction of MMA (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 MMA and TAA, respectively.Figure 1 is a plot of $\frac{f_1^{\,2}(F_1-1)}{(1-f_1)^2F_1}$ versus $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$, and Figure 2 is a plot of $\frac{f_2^{\,2}(F_2-1)}{(1-f_2)^2F_2}$ 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 TAA (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 slope and intercept in Figs. 1 and 2 are the reactivity ratio values for TAA-MMA copolymer:
r_1(MMA) = 8±0.5 and r_2 (TAA) = 5±0.5.

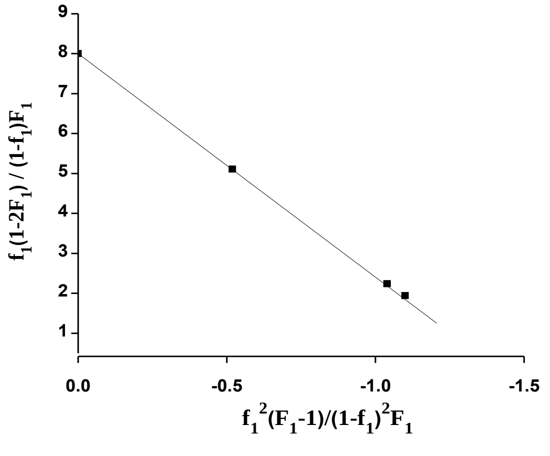


Figure 1: Graph of $\frac{f_1^{\,2}(F_1-1)}{(1-f_1)^2F_1}$ versus $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$ for TAA-MMA copolymers.

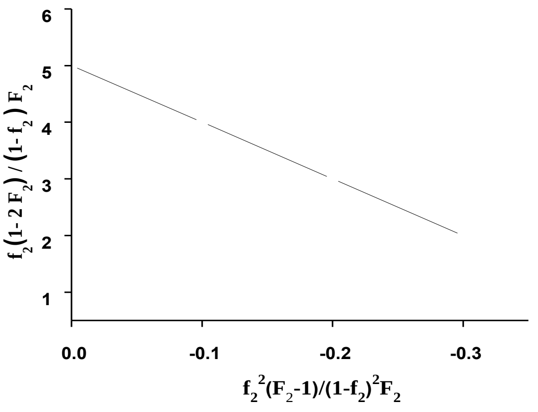
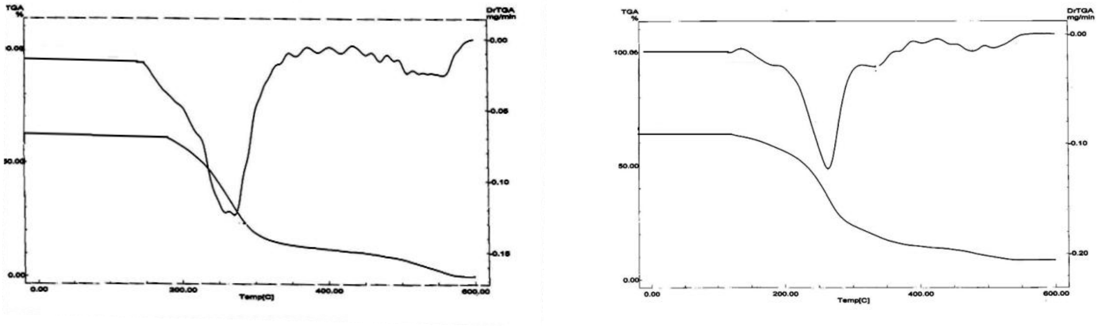


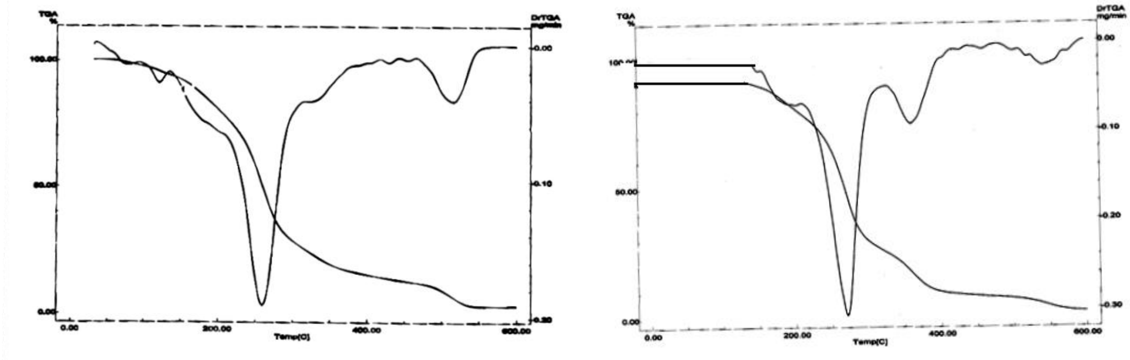
Figure 2: Graph of $\frac{f_2^{\,2}(F_2-1)}{(1-f_2)^2F_2}$ versus $\frac{f_2(1-2F_2)}{(1-f_2)F_2}$ for TAA-MMA copolymers.

3.3. Thermogravimetry (TG)

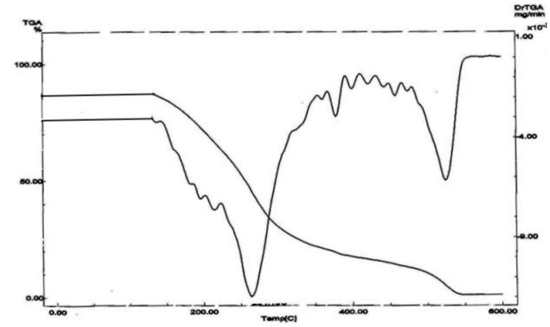
TG curves of PTAA and PMMAhomopolymers and TAA-MMA copolymers are shown in Fig.3. PTAAhomopolymer degrades in third stages. The first starts at ~52°Cwith a weight loss ~ 34%. The second stage starts at ~359°C with a weight loss of ~ 55%. The third stage starts at ~552°C with a weight loss of ~ 10%.



(a): TG curve for PTAAhomopolymer **(b)**: TG curve for TAA-MMA (1:1).



(c); TG curve for TAA-MMA (1:0.53). **(d)**: TG curve for TAA-MMA (1:0.35).



(e): TG curve for TAA-MMA (1:0.2).

Figure 3: TG curves for PTAA and PMMAhomopolymers and TAA-MMA copolymers.

PMMA homopolymer shows two TG decomposition stages. The first starts at ~210°C with a weight loss ~ 16%. The second stage starts at ~295°C with a weight loss of ~ 80% [24]. There are four TG degradation stages for all the TAA-MMA copolymers. The degradation temperature started at ~ 54,75,81and100°C for the copolymers 1:0.2, 1:0.35, 1:0.53 and 1:1 mole of TAA-MMA. 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 is intermediate between PTAA and PMMA homopolymers.

Table 1. Weight loss% of PTAA and PMMA homopolymersand PTAA-MMA copolymers.

Polymer mol TAA:MMA	Volatilization Temperature, °C	First stage		Second stage		Third stage		Remaining wt% after 700°C
		T_{max}, °C	Wt. Loss, %	T_{max}, °C	Wt. Loss, %	T_{ma}, °C	Wt. Loss, %	
PTAA(1:0)	52	114	34	359	55	552	10	2
1:0.2	54	125	41	301	43	599	11	5
1: 0.3	75	130	8	447	76	584	14	2
1:0.5	81	127	62	365	20	550	13	5
1:1	100	295	11	419	68	559	17	4
PMMA(0:1)	250	350	53	500	41	-	-	6

The most clearly result is the increase of the thermal stability of PTAAhomopolymer and TAA-MMA copolymers towards PMMA homopolymer. The effective activation energies for the thermal degradation of PTAA and PMMA homopolymers and TAA-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 (Fig. 4). Table 2 lists the activation energies of the homopolymers and copolymers, from which the values of activation energy of the copolymers increasing from 25 to 50 kJ/mol were obtained as the MMA concentration in the copolymer increases. It is clear that the increased of the value of activation energies the thermal stabilities are increased [25,26].

Table 2. Activation energies of the thermal degradation ofPTAA and PMMA homopolymers and TAA-MMA copolymers.

Polymer mole TAA-MMA	Activation energy (E_a) KJ/mol
PTAA (1:0)	25
1:0.2	29
1:0.35	33
1:0.53	34
1:1	50
PMMA(0:1)	249

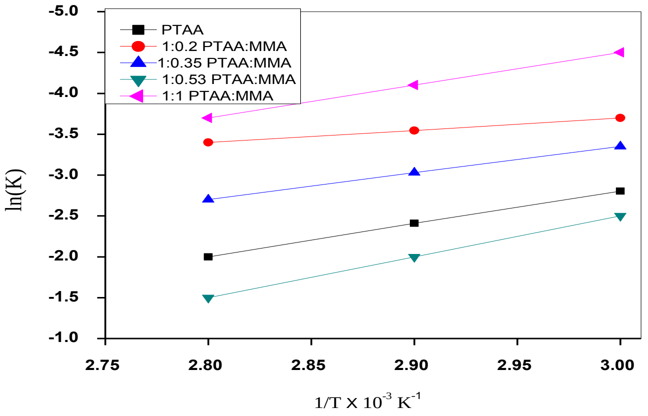


Figure 4: Arrhenius plots of the rate constants of degradation of PTAA homopolymer and AA-MMA copolymers.

3.4. Thermal degradation of PTAAhomopolymer

50 mg of PTAAhomopolymer was heated under vacuum from ambient temperature to 500 °C. The volatile products of degradation were collected in a small gas cell for identification by IR. There are characteristic IR bands due to benzene, aniline and ammonia were observed among the degradation products of PTAA homopolymer. Benzene, aniline and ammonia were among the degradation products of PTAA homopolymer. The liquid fractions from the degradation of the homopolymer were injected into the GC-MS apparatus. Figure 5 shows the GC trace for the liquid products of degradation of PTAA homopolymer at 500 °C. Table 3 gives the results of the degradation products which were identified by mass spectroscopy.

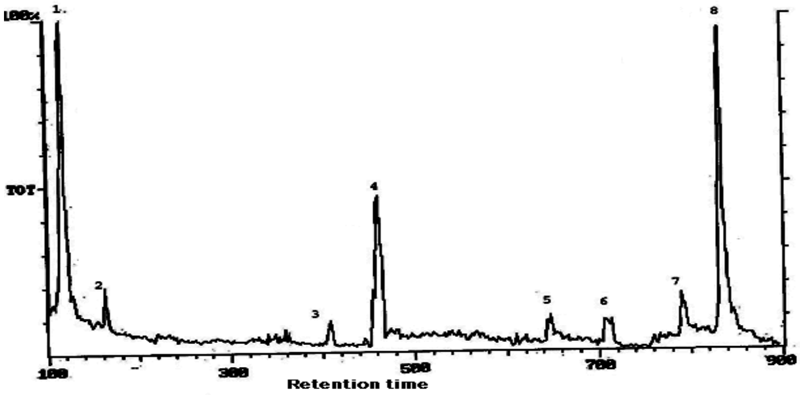
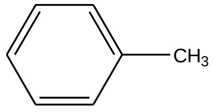
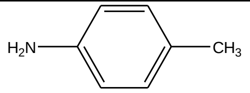
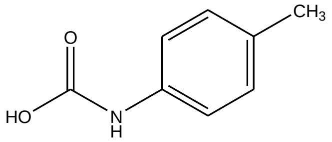
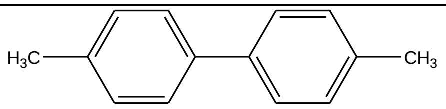
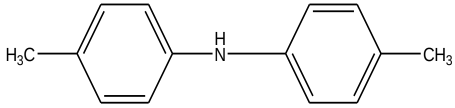
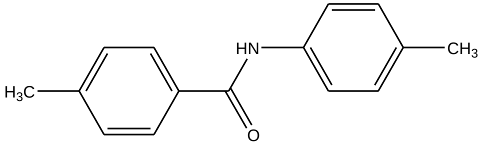
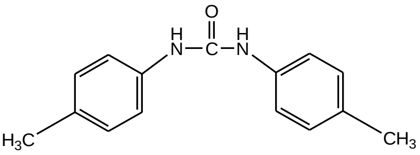
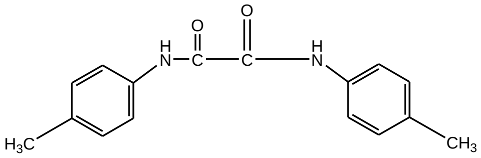
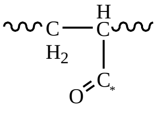


Figure 5: GC curve of the liquid fraction of degradation of PTAA homopolymer.

Table 3.GC-MS data of the liquid fraction of the degradation of PTAA homopolymer.

Comp.	Retention time, min.	Major MS fragment	Suggested structure
1	2	49,77,92	 Toluene
2	3	49,77,91,107	 *P*-Methylaniline
3	6.8	77,106,134,151	 *P*-Tolylcarbamic acid
4	8	77,92,182	 4,4'-Dimethylbiphenyl
5	10.8	77,92,107,197	 Dip-tolylamine
6	12	77,107,133,225	 4-Methyl-N-*P*-tolylbenzamide
7	13	77,107,133,152, 240	 1,3-Dip-tolylurea
8	14	119,135,163,178, 269	 N$_1$,N$_2$-Dip-tolyloxalamide

The various degradation products of PTAAhomopolymer indicate that the mechanism of degradation is characterized by the elimination of low molecular weight radicals rather than monomer formation in the early stage of degradation, followed by random scission mechanism along the backbone chain. It seems that the breakdown of PTAAhomopolymer occurs mainly in the C-N bond producing the radicals.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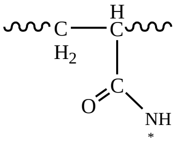
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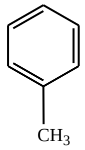
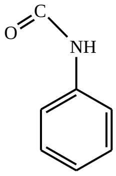
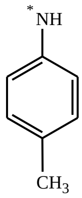
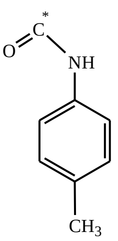
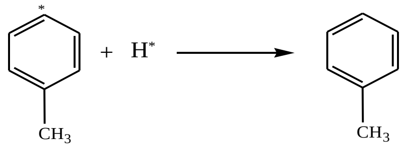

III


IV


V


VI

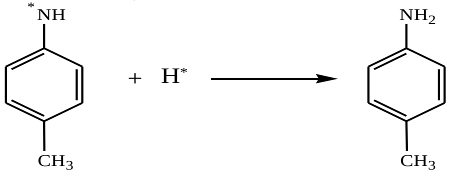
Theradical**III**abstract H and producetoluene (Compound **1**).Compound**1** in the GC curve listed in Table 3.



III

Compound 1
m/e 92
Toulene

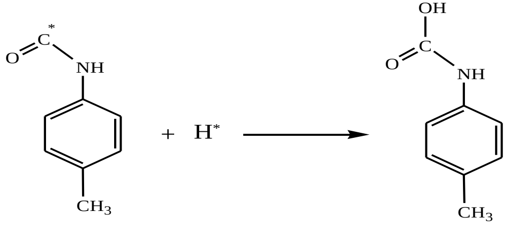
Compound **2** could be formed byabstraction of H by the radical **V**.



V

Compound 2
m/e 107
***P*-Methylaniline**

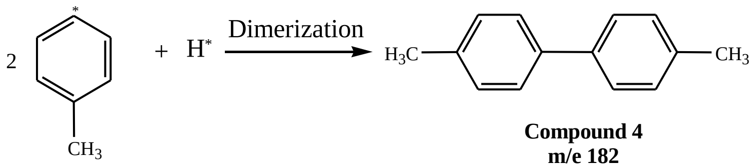
Compound **3** could be formedby abstraction of OH by the radical**IV**.



VI

Compound 3
m/e 151
***P*-tolylcarbamic acid**

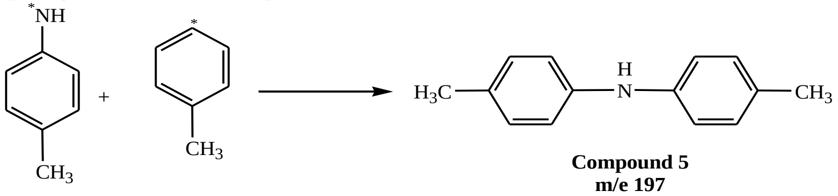
Compound **4** could be formed by a dimerization of**III**.



III

Compound 4
m/e 182
4,4'-Dimethylbiphenyl

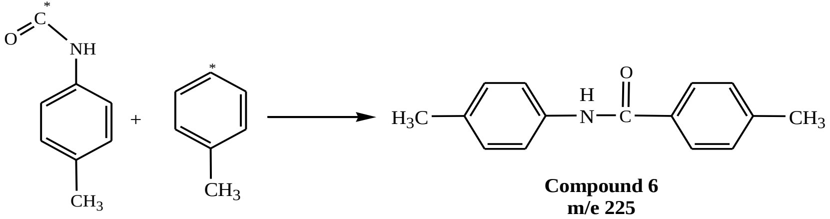
The mass spectrum ofN-phenylbenzamide (Compound **3**) is a termination reaction of the radicals **III** and **IV**.



V **III**

Compound 5
m/e 197
Dip-tolylamine

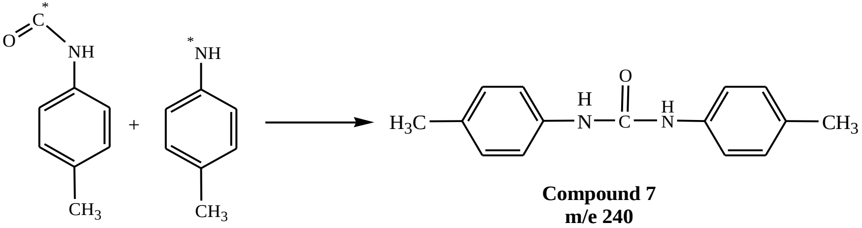
The suggested structure of compound **6** is formed by the reaction between the radicals **IV** and **III**.



VI **III**

Compound 6
m/e 225
4-Methyl-N-*P*-tolylbenzamide

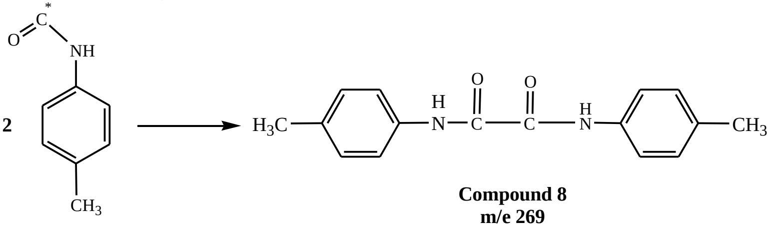
The assignment of structure **7** is formed by the reaction between the radicals VIand**V**.



VI **V**

Compound 7
m/e 240
1,3-Di*p*-tolylurea

The assignment of structure **8** is formed by the reaction between two radicals **VI**.



VI

Compound 8
m/e 269
N_1,N_2-Dip-tolyloxalamide

Conclusion

Four different compositions of copolymers of N-*p*-tolylacrylamideand methyl methacrylate (TAA-MMA) were prepared and the reactivity ratios were determined using ^{1}H-NMR method. Thermal degradation of poly (N-*p*-tolylacrylamide) (PTAA) was studied and the products of degradation were identified by GC-MS techniques. Toluene, *P*-methylaniline, *P*-tolylcarbamic acid, 4,4'-dimethylbiphenyl, dip-tolylamine, 4-methyl-N-*P*-tolylbenzamide, 1,3-dip-tolylurea and N_1,N_2-dip-tolyloxalamide were the main degradation products. Accordingly, it seems that the mechanism of degradation of PTAA is characterized by breaking down in the C-N bond producing low-molecular radicals. Combination of these radicals and random scission mechanism along the backbone chain are the main source of the degradation products.

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