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

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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 1H-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 PTAA homopolymer 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 characterized using Fourier transform infrared (FTIR), 1H-Nuclear magnetic resonance spectroscopy (1H NMR) and 31P NMR. The copolymer with various amounts of styrene (St) was obtained by the free radical bulk polymerization between AEPPA and St, and characterized using 1H NMR. The thermal properties of the copolymers 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 1H-NMR method. The thermal stability of the homopolymers and copolymers were examined. Thermal degradation of the PTAA homopolymer 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°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°C. 4-Methylaniline (Aldrich Chemical Co., Inc.) was used without further purification. All other chemicals and solvents were purified by standard procedures.

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 benzene until 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 and refluxing for 6 hrs. The polymer product (~65%) was precipitated by pouring in distilled water and dried in a vacuum oven for several days at 40°C.

\[
\begin{align*}
\text{H}_2\text{C}=\text{CH} & \text{O} \equiv \text{Cl} \quad \text{Dry Benzene} \\
\text{NH}_2 & \quad \text{CH}_3 \\
\text{O} \equiv \text{C} & \quad \text{O} \equiv \text{NH} \\
\text{NH} & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{DMF, Reflux 6 h} & \\
\text{AIBN} & \\
\text{N-p-tolylacrylamide} & \quad \text{Poly(N-p-tolylacrylamide)}
\end{align*}
\]

Copolymers of TAA 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 of TAA-MMA were prepared, so that the reactivity ratios might be determined. Polymerization was carried out to about 10% conversion. It can be controlled by weighing 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°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)
\(^1\text{H}-\text{NMR}\) 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°/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 PTAA homopolymer
Samples of ~ 50 mg were heated under vacuum from ambient temperature to 500°C. The volatile degradation products were collected 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°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 (EI) 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. Perfluorokerosene (PFK) was used for computer calibration and the ion source was maintained at 200°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 PTAA homopolymer and TAA-MMA copolymers

The IR spectrum of PTAA homopolymer shows a band at 1680 cm\(^{-1}\) assigned to the antisymmetric stretching vibration of amido carbonyl group. The bands at 1600, 1545 and 1440 cm\(^{-1}\) are assigned to \(v(\text{C-H})\), \(v(\text{C}=\text{C})\) and \(v(\text{C}-\text{C})\) 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-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 of TAA-MMA copolymers shows bands at 1680 and 1730 cm\(^{-1}\) assigned to antisymmetric stretching vibration of the amido 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 \(v(\text{C-H}), v(\text{C}=\text{C})\) and \(v(\text{C}-\text{C})\) 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-MMA covering the entire composition range between PTAA and PMMA homopolymers were prepared, so the reactivity ratios might been be determined using '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 'H-NMR spectrum of TAA-MMA copolymers. The peaks at \(\delta 2.490\) and \(2.696\) ppm are due to CH\(_2\) and CH protons of TAA and MMA in the copolymers [21], the signalband at 87.880 ppm is due to –NH proton of TAA in the copolymer [22]. The peak at \(\delta 7.096\) ppm due to phenyl protons of MMA copolymers. The peaks at \(\delta 2.490\) and \(2.696\) ppm due to \(\text{CH} - \text{CH}_2\) and MMA in the copolymers. Dividing the peak at \(\delta 7.096\) ppm by 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 molar ratios of the copolymer, reactivity ratios can be calculated by applying the following equation [23]:

\[
\frac{f_1(1-2F_1)}{(1-f_1)F_1} = \frac{f_2(1-F_2-1)}{(1-f_2)^2F_2} f_2 + r_2
\]

Where, \(F_1 = \frac{M_1/M_2 + 1}{M_1/M_2}\) 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 \(f_1^2(1-F_2)\) versus \(f_1(1-2F_1)\), and Figure 2 is a plot of \(f_2(1-F_2-1)\) versus \(f_2(1-2F_2)\) 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.
3.3. Thermogravimetry (TG)

TG curves of PTAA and PMMA homopolymers and TAA-MMA copolymers are shown in Fig.3. PTAA homopolymer degrades in third stages. The first starts at ~52°C with 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%.

![TG curve for PTAA homopolymer](image)

(a): TG curve for PTAA homopolymer

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, 81 and 100°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.

![TG curve for TAA-MMA](image)

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

![TG curve for TAA-MMA (1:0.53)](image)

(c): TG curve for TAA-MMA (1:0.53).

![TG curve for TAA-MMA (1:0.35)](image)

(d): TG curve for TAA-MMA (1:0.35).

![TG curve for TAA-MMA (1:0.2)](image)

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

**Figure 3:** TG curves for PTAA and PMMA homopolymers and TAA-MMA copolymers.

<table>
<thead>
<tr>
<th>Polymer mol TAA:MMA</th>
<th>Volatilization Temperature, °C</th>
<th>First stage</th>
<th>Second stage</th>
<th>Third stage</th>
<th>Remaining wt% after 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T&lt;sub&gt;max&lt;/sub&gt; °C</td>
<td>Wt. Loss, %</td>
<td>T&lt;sub&gt;max&lt;/sub&gt; °C</td>
<td>Wt. Loss, %</td>
<td>T&lt;sub&gt;max&lt;/sub&gt; °C</td>
</tr>
<tr>
<td>PTAA (1:0)</td>
<td>52</td>
<td>114</td>
<td>34</td>
<td>359</td>
<td>55</td>
</tr>
<tr>
<td>1:0.2</td>
<td>54</td>
<td>125</td>
<td>41</td>
<td>301</td>
<td>43</td>
</tr>
<tr>
<td>1:0.3</td>
<td>75</td>
<td>130</td>
<td>8</td>
<td>447</td>
<td>76</td>
</tr>
<tr>
<td>1:0.5</td>
<td>81</td>
<td>127</td>
<td>62</td>
<td>365</td>
<td>20</td>
</tr>
<tr>
<td>1:1</td>
<td>100</td>
<td>295</td>
<td>11</td>
<td>419</td>
<td>68</td>
</tr>
<tr>
<td>PMMA (0:1)</td>
<td>250</td>
<td>350</td>
<td>53</td>
<td>500</td>
<td>41</td>
</tr>
</tbody>
</table>

**Table 1:** Weight loss% of PTAA and PMMA homopolymers and TAA-MMA copolymers.
The most clearly result is the increase of the thermal stability of PTAA homopolymer 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 of PTAA and PMMA homopolymers and TAA-MMA copolymers.

<table>
<thead>
<tr>
<th>Polymer mole TAA-MMA</th>
<th>Activation energy (E_a) KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTAA (1:0)</td>
<td>25</td>
</tr>
<tr>
<td>1:0.2</td>
<td>29</td>
</tr>
<tr>
<td>1:0.35</td>
<td>33</td>
</tr>
<tr>
<td>1:0.53</td>
<td>34</td>
</tr>
<tr>
<td>1:1</td>
<td>50</td>
</tr>
<tr>
<td>PMMA(0:1)</td>
<td>249</td>
</tr>
</tbody>
</table>

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

### 3.4. Thermal degradation of PTAA homopolymer

50 mg of PTAA homopolymer 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.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Retention time, min.</th>
<th>Major MS fragment</th>
<th>Suggested structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>49,77,92</td>
<td>Toluene</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>49,77,91,107</td>
<td>P-Methylaniline</td>
</tr>
<tr>
<td>3</td>
<td>6.8</td>
<td>77,106,134,151</td>
<td>P-Tolylcarbamic acid</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>77,92,182</td>
<td>4,4’-Dimethylbiphenyl</td>
</tr>
<tr>
<td>5</td>
<td>10.8</td>
<td>77,92,107,197</td>
<td>Dip-tolylamine</td>
</tr>
<tr>
<td>6</td>
<td>12</td>
<td>77,107,133,225</td>
<td>4-Methyl-N-P-tolylbenzamide</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>77,107,133,152, 240</td>
<td>1,3-Dip-tolylurea</td>
</tr>
<tr>
<td>8</td>
<td>14</td>
<td>119,135,163,178, 269</td>
<td>N₁,N₂-Dip-tolyloxalamide</td>
</tr>
</tbody>
</table>

The various degradation products of PTAA homopolymer 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 PTAA homopolymer occurs mainly in the C-N bond producing the radicals.
Compound 2 could be formed by abstraction of H by the radical V.

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

Compound 4 could be formed by a dimerization of III.

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

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

The assignment of structure 7 is formed by the reaction between the radicals VI and V.
The assignment of structure 8 is formed by the reaction between two radicals VI.

Conclusion
Four different compositions of copolymers of N-p-tolylacrylamide and methyl methacrylate (TAA-MMA) were prepared and the reactivity ratios were determined using ¹H-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,N,N'-dip-tolylxalamide 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.

References