Synthesis of Polyimides derived from 2,6-diamino-4-methyl-1,3,5-triazine

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Received 30/9/2015
Accepted 20/12/2015

Abstract:
This work included synthesis of several new polymers of polyacryloyl chloride in two steps. The first step the included the reaction of N-(sub. or unsub. benzoyl and sub. or unsub. acetyl) amidyl sub. 2,6-diamino-4-methyl-1,3,5-triazine (1-5) by condensation of many substituted acid chlorides with 2,6-diamino-4-methyl-1,3,5-triazine. While the second step included the reaction of polyacryloyl chloride with the produced compounds (1-5) in step (1) in the presence amount triethyl amine (Et$_3$N) to obtain new polyimides (6-10). The prepared compounds were characterized by UV., FT-IR, and some of them by $^1$H-NMR and $^{13}$C-NMR spectroscopy.

Key words: 2,6-diamino-4-methyl-1,3,5-triazine, polyacryloyl chloride, polyimides derivatives.

Introduction:
Triazine derivatives are used in pharmaceutical industry as coupling agents for the synthesis of peptides and as side chain of antibiotics, as well as in formulating bactericides and fungicides[1-2]. 1,3,5-triazine are amongst the oldest known organic molecules; originally they were called the symmetric triazines usually abbreviated as s. or syn-triazines[3]. Some of the substituted 1,3,5-triazine have reported to possess interested biological activities[4]. Wide range of 1,3,5-triazines exhibit selective their bicalidal properties, such as anti-cancer, antiviral[5], bactericidal, fungicidal[6], antimalariol agents and antituberculosis[7]. One of the most important derivatives of 1,3,5-triazine is 2,4-diamino-6-methyl-1,3,5-triazine that has played an important role in organic chemistry[8]. It is used as an intermediate for pharmaceuticals and as a modifier and flexibizer of for maldehyde resins[9], which reacted with sub. or unsub. benzoyl and sub. or unsub. acetyl to give N-(sub. or unsub. benzoyl and sub. or unsub. acetyl amidyl sub. 2,4-diamino-6-methyl-1,3,5-triazine, which reacted with poly
acryloyl chloride to give new poly imides derivatives for 2,4-diamino-6-methyl-1,3,5-triazine. Polyimides (PIS) are classifided as a group of super-engineering plastics owing to their excellent thermal stability[10], and they are a class of high – performance representative and involving aromatic and hetero cyclic rings in the main chains that are well known as heat-resistant organic materials. Polymers have been widely used in flexible displays[11]. Like Polymer electronic memories, prevaporation, biofuels separation and many other fields of microelectronics[12], optics , a erospace industries and biomedical engineering [13]. However polyimide materials are usually difficult to be processed because of their insufibility at high temperature and insolubility in most organis solvent[14], inorder to improve the solubility and melting ability of polyimides, many studies have been focused on introducing the fluorocontaining groups, or flexible group into the polymer backbone[15].

Materials and Methods:

All chemicals used in this work from BDH , Merk and Fluka were used without further determination.

Melting points were determined in Gallen kammpelting point apparatus and were uncorrected. UV-visible spectra were recorded on shimadzu T60u spectrophotometer using ethanol as a solvent, FT-IR – 8400 Fourier transform infrared spectrophotometer as KBr disc. Softing points were determined by using Reichert Thermovar with Reichert Jung Temperature Controller , 1H-NMR and 13C- NMR spectra were recorded on Bruker specrospin Ultra shield magnets 300MHz in strument using tetra methyl silane (TMS) as an internal standard and DMSO.d6 as solvent in Al-Albate University in Jordan.

Genaral procedure preparation of [(subs. Aryl or acetyl ) subs. 2,6 – diamino-6- methyl- 1,3,5-Triazine[14] (1-5):

mixture of 2,6 – diamino-6-methyl- 1,3,5-Triazine (0.02 mol) , sub. benzoyl chloride (0.04 mol) and triethyl amine Et3N (4-5 drops) with DMF as a solvent in (100 ml) round bottom flask were refluxed for (4 hrs.). After that, the solvent was removed and recrystallized from ethanol . All physical properties for products compounds are listed in Table (1).

Genaral procedure preparation of poly (N-acryl-N-sub. or unsub. acetyl of benzoyl) Imidyl substituted 2,6 – diamino-6- methyl- 1,3,5-Triazine[14] (6-10):

Dissolved (0.02) of N-subamidyl – sub. 2,6 – diamino-6- methyl- 1,3,5-Triazine in (25 ml) THF and mixing with poly acryloyl chloride (0.02 mol) and add (1 ml) triethyl amine( Et3N ) in (100 ml) round bottom flask . The mixture was refluxed for (6-8 hr.). After cooling, the solvent was removed. The separated sold was filtered and purified by dissolving in DMF and reprecipitating from water or acetone. This procedure was applied on compounds as shown in Table (2). All physical properties are listed in Table (2).
Scheme (1): The general pathway of the reaction.
**Table (1): The physical properties for [(sub. Aryl or actyl ) sub.(trimethoprim)] Amide**

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>Name</th>
<th>Colour</th>
<th>Melting Point</th>
<th>% Conversion</th>
<th>Solvent used in react.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><img src="structure1.png" alt="Structure" /></td>
<td>N,N-(6-methyl-1,3,5-triazine-2,4-diyldiacetamide)</td>
<td>Yellow</td>
<td>Oily</td>
<td>86</td>
<td>DMF</td>
</tr>
<tr>
<td>2.</td>
<td><img src="structure2.png" alt="Structure" /></td>
<td>N,N-(6-methyl-1,3,5-triazine-2,4-diyl)bis(2-chloroacetamide)</td>
<td>Blake</td>
<td>Oily</td>
<td>78</td>
<td>DMF</td>
</tr>
<tr>
<td>3.</td>
<td><img src="structure3.png" alt="Structure" /></td>
<td>N,N-(6-methyl-1,3,5-triazine-2,4-diyl)dibenzamide</td>
<td>White</td>
<td>160-163</td>
<td>90</td>
<td>DMF</td>
</tr>
<tr>
<td>4.</td>
<td><img src="structure4.png" alt="Structure" /></td>
<td>N,N-(6-methyl-1,3,5-triazine-2,4-diyl)bis(2-chlorobenzamide)</td>
<td>Brown</td>
<td>Oily</td>
<td>80</td>
<td>DMF</td>
</tr>
<tr>
<td>5.</td>
<td><img src="structure5.png" alt="Structure" /></td>
<td>N,N-(6-methyl-1,3,5-triazine-2,4-diyl)bis(4-nitrobenzamide)</td>
<td>White</td>
<td>181-182</td>
<td>73</td>
<td>DMF</td>
</tr>
</tbody>
</table>

**Table (2): The physical properties of polymers (6-10):**

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>Colour</th>
<th>Softing point</th>
<th>% Conversion</th>
<th>Solvent used in react.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.</td>
<td><img src="structure6.png" alt="Structure" /></td>
<td>Brown</td>
<td>102-108</td>
<td>90</td>
<td>THF</td>
</tr>
<tr>
<td>7.</td>
<td><img src="structure7.png" alt="Structure" /></td>
<td>Yellowish brown</td>
<td>132-136</td>
<td>86.66</td>
<td>THF</td>
</tr>
</tbody>
</table>
Table (3): FT-IR spectral data for all product compounds

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>v(C-H) cm(^{-1}) aromatic</th>
<th>v(C-H) cm(^{-1}) aliphatic</th>
<th>v(C=O) cm(^{-1})</th>
<th>v(N-H) cm(^{-1})</th>
<th>v(C-H) cm(^{-1}) and v(C=O) cm(^{-1})</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3039</td>
<td>2777-2993</td>
<td>1651</td>
<td>3363</td>
<td>1465 and 1539</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>3062</td>
<td>2777-2939</td>
<td>1701</td>
<td>3390</td>
<td>1469 and 1597</td>
<td>(C-Cl) 752</td>
</tr>
<tr>
<td>3.</td>
<td>3155</td>
<td>2738-2978</td>
<td>1685</td>
<td>3313</td>
<td>1473 and 1543</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>3008</td>
<td>2777-2989</td>
<td>1651</td>
<td>3417</td>
<td>1465 and 1543</td>
<td>(C-Cl) 1018</td>
</tr>
<tr>
<td>5.</td>
<td>3059-3113</td>
<td>2738-2978</td>
<td>1693</td>
<td>3448</td>
<td>1477 and 1543</td>
<td>(C-NO(_2)) 1350 and 1519</td>
</tr>
<tr>
<td>6.</td>
<td>3190</td>
<td>2938-2976</td>
<td>1701</td>
<td>-</td>
<td>1477 and 1539</td>
<td>-</td>
</tr>
<tr>
<td>7.</td>
<td>3050</td>
<td>2738-2939</td>
<td>1635</td>
<td>-</td>
<td>1435 and 1473</td>
<td>(C-Cl) 848</td>
</tr>
<tr>
<td>8.</td>
<td>3065</td>
<td>2730-2970</td>
<td>1697</td>
<td>-</td>
<td>1471 and 1627</td>
<td>(C-Cl) 1035</td>
</tr>
<tr>
<td>9.</td>
<td>3055</td>
<td>2939</td>
<td>1716</td>
<td>-</td>
<td>1471 and 1627</td>
<td>(C-Cl) 1035</td>
</tr>
<tr>
<td>10.</td>
<td>3111</td>
<td>2941-2978</td>
<td>1689</td>
<td>-</td>
<td>1465 and 1653</td>
<td>(C-NO(_2)) 1346 and 1521</td>
</tr>
</tbody>
</table>

Results and Discussion:
The present work involved two steps, The first step includes the preparation of new five amides (1-5) that were prepared by the reaction of 2,4-diamino-6-methyl-1,3,5-triazine with different substituted acid chlorides. The synthesis of these compounds was carried out lined in scheme (1).

The starting material for the synthetic polyimides is 2,4-diamino-6-methyl-1,3,5-triazine which condensed with different substituted acid chlorides through nucleophilic substitution of chloride with amino group lead to amides (1-5) (Scheme 2).

The FT-IR spectrum of compounds (4) and (5) showed the absence of (\(-NH_2\)) stretching together with appearance of band at 3355 cm\(^{-1}\) and 1693 cm\(^{-1}\) attributed to (N-H) stretching of amide, amide respectively, which indicated the substitution and formation of amides as shown in Table (3), Figure (4) and (5). Attributed UV. Spectrum of compounds (1) and (4) showed an absorption \(\lambda_{max}\) at (273) nm
and (294) nm which to (π-π). The absorption is listed in Figure (1) and (3).

The 'H-NMR of compounds (2) and (4) showed the signals at (2.116 - 3.600) ppm and was attributed to (CH₃) proton and multiple signals at (7.187 - 7.939) ppm due to aromatic protons and singlet at (9.218) ppm due to (N-H) protons for amide [17-18] as shown in Figure (9) and (11).

The ¹³C-NMR spectrum of compounds [2] and [4] showed the signal at (168-174) ppm for carbonyl group while the aromatic carbon appeared at (104-114) ppm as shown in Figure (10) and (12).

The second step: included the preparation new five polyimides (6-10) that were prepared by the reaction of amides (1-5) in the first step with polyacryloyl chloride subjected to another nucleophile substitution by treating with poly acryloyl chloride using triethyl amine (Et₃N) as catalyst. The mechanism of reaction involves a nucleophilic attach on the carbonyl as shown in Schemes (3) [14].

(i) DMF = Dimethylformamide , Et₃N = Triethylamine.
(ii) poly acryloyl chloride , THF , Et₃N.

R= -CH₃ , Cl-CH₂

Scheme (2): The products of the general reaction.
Scheme (3): The mechanism of reaction.

The FT-IR spectrum showed the disappearance of amide bands $\nu$(N-H), $\nu$(C=O), with appearance bands at (1716) cm$^{-1}$ attributed to (C=O) amide as shown in Table (3) Figure (6). Another evidence for compounds (7) and (9) its' ¹H-NMR spectrum that showed different signals, two multiplet at (1.799-1.976) ppm and (2.753-2.792) ppm as signals for ethylene (acryl) protons as shown in Figure (13) and (15).

The ¹³C-NMR spectrum of compounds (7) and (9) the ethylene carbon appeared at (39.707-42.697) ppm, and aromatic carbon at (127.4 - 131.9) ppm while the imide carbonyl appeared at (167.5) ppm as shown in Figure (14) and (16).
Fig. (1): UV. Spectrum of compounds (1)

Fig. (2): UV. Spectrum of compounds (6)

Fig. (3): UV. Spectrum of compounds (4)
Fig. (4): UV. Spectrum of compounds (9)

Fig. (5): FT-IR spectrum of compounds (4).

Fig. (6): FT-IR spectrum of compounds (5).
Fig. (7): FT-IR spectrum of compounds (9).

Fig. (8): FT-IR spectrum of compounds (10).

Fig. (9): $^1$H-NMR of compound (2).
Fig. (10): $^{13}$C-NMR spectrum of compounds (2).

Fig. (11): $^1$H-NMR of compound (4).

Fig. (12): $^{13}$C-NMR spectrum of compounds (4).
Fig. (13): $^1$H-NMR of compound (7).

Fig. (14): $^{13}$C-NMR spectrum of compounds (7).

Fig. (15) $^1$H-NMR of compound (9).
Fig. (16): $^{13}$C-NMR spectrum of compounds (9).

References:


تحضير بولي ايميدات جديدة مشتقة من 2، 6- داي امينو -4- ميثيل 1، 3، 5- ترايازين

رنا رافع حمزة

قسم الكيمياء / كلية العلوم للبنات / جامعة بغداد / العراق

الخلاصة:

يتضمن هذا البحث تحضير عدد بوليمرات جديدة ومختلفة لـ بولي اكريلول كلورايد، وفق الخطوتين. حيث تضمنت الخطوة الأولى تحضير N-(sub. Or unsub. Benzoyle and sub. Or unsub. Acetyl) amidyl sub. 2,6-diamino -4- methyl -1، 3، 5 – triazine (1-5) الحوامض المعوضة وغير المعوضة (اليفاتية، اروماتية) مع 2، 6- داي امينو -4- ميثيل 1، 3، 5- ترايازين. أما الخطوة الثانية تتضمن تفاعل بولي اكريلويل كلورايد مع الأميدات المحضرة في الخطوة الأولى (1-5) في مذيب مناسب وكمية مناسبة في ثلاثي اثيل امين (Et3N) مع التسخين ليعطي بولي ايميدات جديدة (6-10). وتم تحليل المركبات المحضره باستخدام أطياف الإشعاع فوق البنفسجي (FT-IR)، واطيف U. V. و 13C-NMR و 1H-NMR الرنين المغناطيسي بالإضافة إلى القياسات الفيزيائية المختلفة من درجات التنين ودرجات الانصهار والذوبانية.

الكلمات المفتاحية: 2، 6- داي امينو -4- ميثيل 1، 3، 5- ترايازين، بولي اكريلول كلورايد، مشتقات البولي ايميد