Synthesis of N-benzothiazole derivative imide on polymeric chain, have possible biological activity

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Abstract:
In this research Some new substituted and unsubstituted poly imides compounds were synthesized by reaction of acrylol chloride with different amides (aliphatic and aromatic) in a suitable solvent in the presence amount triethyl amine (Et₃N) with heating. The Structure confirmation of all polymers were confirmed using FT-IR,¹H-NMR,¹³C-NMR and UV spectroscopy. Thermal analysis (TG) for some polymers showed their thermal stabilities. Other physical properties including softening points, melting point and solubility of the polymers were also measured

Key word:2-aminobenzothiaizol,acrylol chloride.

Introduction
A heterocyclic compound is one which possesses a cyclic structure with at least two different kinds of hetero atoms in the ring. Nitrogen, oxygen and sulphur are the most common hetero atoms. Benzothiazole is a heterocyclic compound, weak base, having varied biological activities and still of great Scientific interest nowa days. They are widely found in bioorganic and medicinal chemistry with application in drug discovery[1]. Benzothiazole moieties are part of compounds showing numberings biological activities such as antimicrobial [2-6], anticancer [7-11], antilmintic and anti-diabetic activities. Polyimides have been widely used as high temperature insulators and dielectrics, coatings, adhesives and materials in a variety of advanced technologies related to microelectronics, where miniaturization and large-scal integration are important technical issues [13-14]. Then high thermal stability and balanced mechanical and electrical properties [15-17]. Polyimides are mainly used in the aerospace and electronics industries in the form of film and mouldings, but high melting point and insolubility in organic solvent limited their [18-20], application. furthermore,few successful attempts have been made to convert or modify some specific N-substituted imide to serve as ion exchange resins, such as cross linked poly[N-phenyl maleimide] which was prepared by free radical polymerization of the corresponding imide in benzene. The precipitated polyimides were hydrolyzed to obtain some pendant carboxylic groups on the polymeric chains. The last compounds were found to be useful cationic [21] exchange resins of good capacities.

Materials and Methods
General
1. Melting points were recorded by using Gallen Kamp MFB-600 capillary melting point apparatus.
2. FT-IR spectra were recorded using solid KBr discs by testing

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Shimadzu FT-IR 8000 series
Fourier transform, infrared
spectrophotometer.

3. Thermal analyses were performed
using thermal analysis system
consisting from TG50 Shimadzu,
Japan. Ibn Sina in Iraq.

4. \( ^1H \)-NMR and \( ^{13}C \)-NMR spectra.
Company Bruker, model ultra shield
300MHz, were made at the
Chemistry Department, Al-Albyt
University, Jordan.

1. Preparation of 2-
aminobenzothiazole Derivatives[22, 23]

In a 250 ml round bottomed
flask equipped with a magnetic bar
stirrer and dropping funnel, a solution
of bromine (1.2 ml) in glacial acetic
acid (75 ml) was allowed to run
during 30 min. To a mixture of Para
substituted aromatic amine (0.03 mol)
and ammonium thiocyanate (0.1 mol)
in 150 ml glacial acetic acid with
stirring. The mixture was stirred for 1
hr., then diluted with water and
neutralized with solid sodium
hydroxide. The precipitated substance
was filtered, triturated and
recrystallized from a suitable solvent to
obtain 2-amino benzothiazole
derivatives. The physical properties of
the synthesized compounds are given
in Table (1).

2. General Procedure Preparation of
2-[N-(sub or unsub benzyol and sub
or unsub acetyl)amidyl sub
benzothiazole]

In a round bottom flask
equipped with a magnetic bar stirrer
and reflux condenser was placed a
mixture of sub-benzyol chloride (0.06
mol) and (0.06 mol) 6-sub-2-
aminobenzothiazole with (3) drops of
triethyl amine (Et\(_3\)N) in (25 ml) of
suitable solvent (Benzen) and
refluxed (1-3 hrs) after the solvent was
removed and recrystallized
from ethanol.

3. General Procedure Preparation of
Poly 2-(N-acryl-N-sub or unsub
benzyol) imidyl Substituted
Benzothiazole

In a round bottom flask
equipped with a magnetic bar stirrer
was placed a mixture of poly
(acryloyl chloride) (0.06 mol) and
(0.06 mol) of 2-N-sub amidyl-sub
benzothiazole with (1 ml) of triethyl
amine (Et\(_3\)N) in (25 ml) of suitable
solvent (THF or DMF) and refluxed
for (5-7) hrs. after cooling and
removed the solvent. The solid
separated was filtered and purified by
dissolving at DMF or DMSO and re
precipitating from water or acetone.
This procedure was applied on
compounds as shown in Table (1). All
physical properties are listed in Table
(1).

Results and Discussion

Preparation of [2-(N-benzoyl) amidyl sub benzothiazole]
All poly [2-(N-acryl-N-benzoyl) imidyl substituted benzothiazole] were prepared by the reaction of poly (acryloyl chloride) with different amides, in presence of triethyl amine (Et₃N) as a catalyst [24]. All these compounds were characterised by (FTIR, UV, and softing point), Table (1).

The mechanism of reaction involves a nucleophilic attack on the carbonyl as shown below [25].

Structures confirmation of all prepared polymer proved using FT-IR, UV, ¹H-NMR, ¹³C-NMR, TG and physical properties including softening point, solubility, Tg and percent conversion of the polymers. FT-IR spectrum of compounds showed the same bands appearance. Stretching band at 1670 cm⁻¹ v(C=O), (2800-2920) cm⁻¹ v(C-H) aliphatic, (1590-1630) cm⁻¹ v(C=C) and (3010-3100) cm⁻¹ v(C-H) aromatic as shown Table (2). ¹H-NMR spectrum of polymers [3,4,5] showed the signals at δ(1.2) (t, 2H, δC), δ(3.1) (m, 1H, 1H, δC) while a signal at δ(7-8) (d or m, 1H, Ph-H) and δ1.02 (s, 3H, Ph-CH₃), as shown listed in Table (3).

The ¹³C-NMR spectrum of compound showed the signal at (170-180) ppm for carbonyl group (C=O) and appeared at (120-140) ppm and appeared at (20-50.48) ppm. UV spectrum of compounds absorption λ_max at 300 nm and 380 nm which attributed to (π→π*) and (n→π*) transitions. See Table (4). TG analysis provides a change in the mass of the polymer during heating. The thermal analysis was carried out at temperatures (200-400)°C with heating rate 20.0 °C/min. in N₂ atmosphere. Thermal stability of the product was estimated from TG and DTG thermograms. See Table (5), it was found that the prepared polymers high stability, resists to isomerization by...
heat, light or using acidic or basic solution[26,27].

**Table (1): Physical properties of the poly imide**

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>Conversion %</th>
<th>Softing point °C</th>
<th>Color</th>
<th>Solvent used in reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Compound Structure" /></td>
<td>75</td>
<td>120-135</td>
<td>Brownish yellow</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Compound Structure" /></td>
<td>80</td>
<td>120-135</td>
<td>Brownish yellow</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Compound Structure" /></td>
<td>82</td>
<td>125-140</td>
<td>Brownish yellow</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Compound Structure" /></td>
<td>78</td>
<td>112-125</td>
<td>Light yellow</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="Compound Structure" /></td>
<td>85</td>
<td>120-132</td>
<td>Light yellow</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Compound Structure" /></td>
<td>80</td>
<td>200-205</td>
<td>Light yellow</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>Comp. No.</td>
<td>Compound structure</td>
<td>Conversion %</td>
<td>Softing point °C</td>
<td>Color</td>
<td>Solvent used in reaction</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------</td>
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<td>------------------</td>
<td>-------</td>
<td>------------------------</td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="Chemical Structure" /> Poly [2-(N-acryl-N-acetyl) imidyl-4,6-di-chloro benzothiazole]</td>
<td>78</td>
<td>85-100</td>
<td>Light yellow</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>8</td>
<td><img src="image" alt="Chemical Structure" /> Poly [2-(N-acryl-N-acetyl) imidyl-2,4-di-chloro benzothiazole]</td>
<td>70</td>
<td>170-180</td>
<td>Light yellow</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>9</td>
<td><img src="image" alt="Chemical Structure" /> Poly [2-(N-acryl-N-benzoyl)imidyl -4-nitro-6-chloro benzothiazole]</td>
<td>85</td>
<td>95-105</td>
<td>Brown</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>10</td>
<td><img src="image" alt="Chemical Structure" /> Poly [2-(N-acryl-N-acetyl) imidyl-6-chloro benzothiazole]</td>
<td>87</td>
<td>125-142</td>
<td>Brown</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>11</td>
<td><img src="image" alt="Chemical Structure" /> Poly [2-(N-acryl-N-2-mercaptopbenzoyl) imidyl-6-chloro benzothiazole]</td>
<td>85</td>
<td>170-180</td>
<td>Brown</td>
<td>THF or DMF</td>
</tr>
<tr>
<td>12</td>
<td><img src="image" alt="Chemical Structure" /> Poly [2-(N-acryl-N-2-mercaptopbenzoyl) imidyl-6-methyl benzothiazole]</td>
<td>82</td>
<td>130-140</td>
<td>Light yellow</td>
<td>THF or DMF</td>
</tr>
</tbody>
</table>
Table (2): FT-IR spectra of the prepared heterocyclic polyimide

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>FTIR spectral data cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\nu(C=O)) imide</td>
</tr>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /></td>
<td>1697</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Image" /></td>
<td>1690</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Image" /></td>
<td>1685</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Image" /></td>
<td>1690</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Image" /></td>
<td>1682</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Image" /></td>
<td>1685</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Image" /></td>
<td>1699</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8.png" alt="Image" /></td>
<td>1716</td>
</tr>
<tr>
<td>9</td>
<td><img src="image9.png" alt="Image" /></td>
<td>1708</td>
</tr>
<tr>
<td>10</td>
<td><img src="image10.png" alt="Image" /></td>
<td>1695</td>
</tr>
<tr>
<td>11</td>
<td><img src="image11.png" alt="Image" /></td>
<td>1697</td>
</tr>
</tbody>
</table>
Table (3): The $^1$H-NMR chemical shifts of some of the prepared poly heterocyclic imides

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>Chemical shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td><img src="image" alt="Structure 3" /></td>
<td>$\delta$1.2 (t, $2H^2$, $\left{H_2C-CH\right}_n$); $\delta$3.01 (m, $1H^1$, $\left{H_2C-CH\right}_n$); $\delta$7-8 (m, HAr)</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Structure 4" /></td>
<td>$\delta$1.1 (s, $3H^3$); $\delta$1.1 (t, $2H^2$, $\left{H_2COCH\right}_n$); $\delta$3.1 (m, $1H^1$, $\left{H_2C-CH\right}_n$); $\delta$4.5 (s, $2H^7$); $\delta$7-8 (m, HAr)</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="Structure 5" /></td>
<td>$\delta$1.2 (s, $3H^3$); $\delta$1.2 (t, $2H^2$, $\left{H_2C-CH\right}_n$); $\delta$3 (m, $1H^1$, $\left{H_2C-CH\right}_n$); $\delta$7-8 (m, HAr)</td>
</tr>
</tbody>
</table>

Fig.(1): $^1$H-NMR for compound[3]
Fig. (2): $^1$H-NMR for compound[4]

Fig. (3): $^1$H-NMR for compound[5]
Table (4): UV spectra of the prepared heterocyclic polyimide

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{max}}$</td>
</tr>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>301</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>317, 459.5</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>370</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>303.5</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>317</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>435.5, 361.0</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Structure 7" /></td>
<td>315</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8.png" alt="Structure 8" /></td>
<td>303.5, 248</td>
</tr>
<tr>
<td>9</td>
<td><img src="image9.png" alt="Structure 9" /></td>
<td>409.5, 303</td>
</tr>
<tr>
<td>10</td>
<td><img src="image10.png" alt="Structure 10" /></td>
<td>305</td>
</tr>
<tr>
<td>11</td>
<td><img src="image11.png" alt="Structure 11" /></td>
<td>315.5, 454</td>
</tr>
<tr>
<td>12</td>
<td><img src="image12.png" alt="Structure 12" /></td>
<td>316, 449.5</td>
</tr>
</tbody>
</table>
### Table (5) : TG of some of the prepared poly heterocyclic imides

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>10% wt Loss temp ºC</th>
<th>50% wt Loss temp ºC</th>
<th>Peak 1 Temp ºC</th>
<th>Peak 2 Temp ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td><img src="image" alt="Compound 10" /></td>
<td>177.39</td>
<td>266.63</td>
<td>180.9</td>
<td>253 392</td>
</tr>
<tr>
<td>11</td>
<td><img src="image" alt="Compound 11" /></td>
<td>175.21</td>
<td>341.7</td>
<td>279.95</td>
<td>339 384.8</td>
</tr>
<tr>
<td>12</td>
<td><img src="image" alt="Compound 12" /></td>
<td>189.65</td>
<td>269</td>
<td>236</td>
<td>286.8 377.9</td>
</tr>
</tbody>
</table>

**Fig.(4): TG for compound[10]**
Fig. (5): TG for compound [11]

Fig. (6): TG for compound [12]


(تحضير مشتقات ن بنزوثيازول ا يمايد على السلسله البوليمريه ذات فعاليه بايولوجية متوقعة)

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كلية العلوم - قسم الكيمياء , كلية العلوم للبنات-قسم الكيمياء

الخلاصة:
في هذا البحث حضر بولي ايميدات جديدة معوضة وغير معوضة من تفاعل بولي كلوريد الاكريليل مع ايميدات مختلفة (اليفاتية , اروماتية) بوجود مذيب مناسب وكمية مناسبة من ثلاثي مثيل امين (Et3N) مع التسخين. وتم اثبات التراكيب الكيميائية للبوليمرات المحضره باستخدام الطرق الطيفيه، اطيفات اشعة تحت الحمراء FT-IR، اطيفات الرنين النووي المغناطيسي 1H-NMR، 13C-NMR، اطيفات النيون UV، كما تم التعرف على استقرارية بعض البوليمرات المحضره حرارياً عن طريق التحاليل الحرارية بالإضافة إلى القياسات الفيزيائية المختلفة من درجات التلين ودرجات الانصهار والمذوبانة.