Synthesis and Characterization of New Polyimide Contain Heterocyclic

Entesar O. Al-Tamimi* ***Thanaa M. Al-Mouamin****

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Abstract:

Novel heterocyclic polyimide 5(a,b) have been synthesized based on polyacrylic backbone. The synthetic route start with nucleophilic substitution of 2-amino, or 4-amino, pyridine 1(a,b) to the polyacryloyl chloride afforded poly substituted amide 2(a,b). Another nucleophilic substitution were carried with adipoyl chloride to form polyimide chloride 3(a,b). Treatment of 3(a,b) with hydrazine hydrate afforded acid hydrazide polyimide 4(a,b), which upon cyclocondensation with carbon disulfide gave the target heterocyclic polyimide. The synthesized compounds were identified by spectroscopic methods: FT-IR, ^{1}H-NMR and ^{13}C-NMR.

Key words: Polyimide, Heterocyclic polyimide.

Introduction:

Poly imides have garnered termendous interest across a range scientific and engineering disciplines. These polymers commonly exhibit high thermal stabilities [1-3] as well as good mechanical and electronic properties including non linear optical and semi conductive characteristics upon doping making good candidates for use in a variety of optoelectronic applications [4-6]. Since they can also coordinate to a variety of metal ion, polymer-metal ion interaction are a subject of interest for their analytical and technological applications in fields such as environmental science (removal of metal ion as pollutants) [7-9], industrial separation processes [10] and biological researches, (membrane bio reactive) [11-14]. On the other hand, the aromatic thiadiazole nucleolus is associated with a variety of pharmacological action such as fungicidal, controlling blood pressure and can affect central nervous system [15-18]. In this work, we synthesized a new polyimide bearing 1,3,4-thiadiazole which was prepared starting from the reaction of amino pyridine with acrylol chloride, with the hope that incorporating of thiadiazole in polyimide might enhance it to use in different application.

Materials and Methods:

Melting point were recorded using Gallen Khamp electro-thermal melting point apparatus. FT-IR spectra were recorded on SHIMADZU FT-IR8400 Fourier Transform Infrared spectrophotometer using KBr disc or thin films. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker spectrospin ultra shield magnet 300 MHz instrument using Me_4Si as the internal standard and DMSO-d_6 as solvent.

Synthesis of Poly Amide (2a and b) [19]

(23 mmol) of poly acryloyl chloride was added to a solution of amino

*Department of Chemistry, College of Science, Baghdad University

Pyridine (23 mmol) in (10 ml) of dimethylformamide (DMF) in the presence of (1 ml) of triethyl amine (Et_3N). The mixture were refluxed for (6 hrs). After cooling the solvent was removed to afford a very viscous solution. The resulted product was poured into chloroform to give (2a) as viscous polymer while (2b) as a light brown solid.

Poly N-(2-amino pyridinyl) acryl amide (2a)

85% of conversion, FT-IR (film); 3340 cm^{-1} (NH) amide, 3020 cm^{-1} (C-H) aromatic, 1600 cm^{-1} (C=C) aromatic, 1680 cm^{-1} (C=O) amide (band I), 1530 cm^{-1} (amide band II).

Poly N-(4-amino pyridinyl) acryl amide (2b)

88% of conversion, m.p. 165-167 ºC, FT-IR (film); 3254 cm^{-1} (NH) amide, 3025 cm^{-1} (C-H) aromatic, 2910 cm^{-1} (C-H) aliphatic, 1585 cm^{-1} (C=C) aromatic, 1660 cm^{-1} (C=O) amide (band I), 1540 cm^{-1} (amide band II).

Synthesis of Poly Imide (3a and b) [19]

To a solution of (2a or 2b) (20 mmol) in DMF (15 ml), equimolar of adipoyl chloride was added dropwise in the presence of Et_3N (1ml), then refluxed for (5 hrs). The solvent was removed then purified by using DMSO.

Poly N-[(2-amino pyridine) pentenoyl chloride] acryl imide (3a)

69% of conversion as a viscous polymer, FT-IR (film); 3035 cm^{-1} (C-H) aromatic, 2942 cm^{-1} (C-H) aliphatic, 1620 cm^{-1} (C=C) aromatic, 1708 cm^{-1} (C=O) Imide 1810 cm^{-1} (C=O) acid chloride.

Poly N-[(4-amino pyridine) pentenoyl chloride] acryl imide (3b)

72% of conversion as a brown fine crystal; m.p. 178-180 ºC; FT-IR (KBr) disk: 3031 cm^{-1} (C-H) aromatic, 2900 cm^{-1} (C-H) aliphatic, 1595 cm^{-1} (C=C) aromatic,1705 cm^{-1} (C=O) imide 1800 cm^{-1} (C=O) acid chloride.

Synthesis of Poly Imide hydrazide (4a and 4b)

To a solution of compound (3a or 3b) (10 mmol) in dry benzene (10 ml), hydrazine hydrate (10 mmol) was added. The mixture was refluxed for (4 hrs), the solvent was removed the product was washed and dried.

Poly N-[(2-amino pyridine) butenyl acid hydrazide] acryl imide (4a)

67.5% of conversion as a viscous polymer; FT-IR (film): 1670 cm^{-1} (C=O) amide (band I), 1520 cm^{-1} amide (band II), 1710 cm^{-1} (C=O) imide, 3310-3400 (NH_2 bands), 3420 (NH) amide.

Poly N-[(4-amino pyridine) butenyl acid hydrazide] acryl imide (4b)

70% of conversion as a brown crystal; m.p. 210-212ºC; FT-IR (KBr) disk: 1650 cm^{-1} (C=O) amide (band I), 1530 cm^{-1} amide (band II), 1700 cm^{-1} (C=O) imide, 3200-3300 (NH_2 bands), 3320 (NH) amide.

Synthesis of Heterocyclic Poly Imide (5a and 5b) [20]

A solution of (10 mmol) of potassium hydroxide in (15 ml) abs. ethanol was added to (10 mmol) of polyimide (4a or 4b) with stirring, carbon disulfide (20 mmol) was added slowly. The mixture was held at reflux for (8 hrs). After cooling the mixture was filtered, acidified with 10% HCl to yield the desired product.

Poly N-{[(2-amino pyridine)-2-thio-5-butenyl]-1,3,4-thiadiazole} acryl imide (5a)

65% of conversion as a viscous polymer; FT-IR (film): 1590 cm^{-1} (C=C) aromatic, 1700 cm^{-1} (C=O) imide, 2600 cm^{-1} (S-H), 1630 cm^{-1} (C=N), 669 cm^{-1} (C-S).

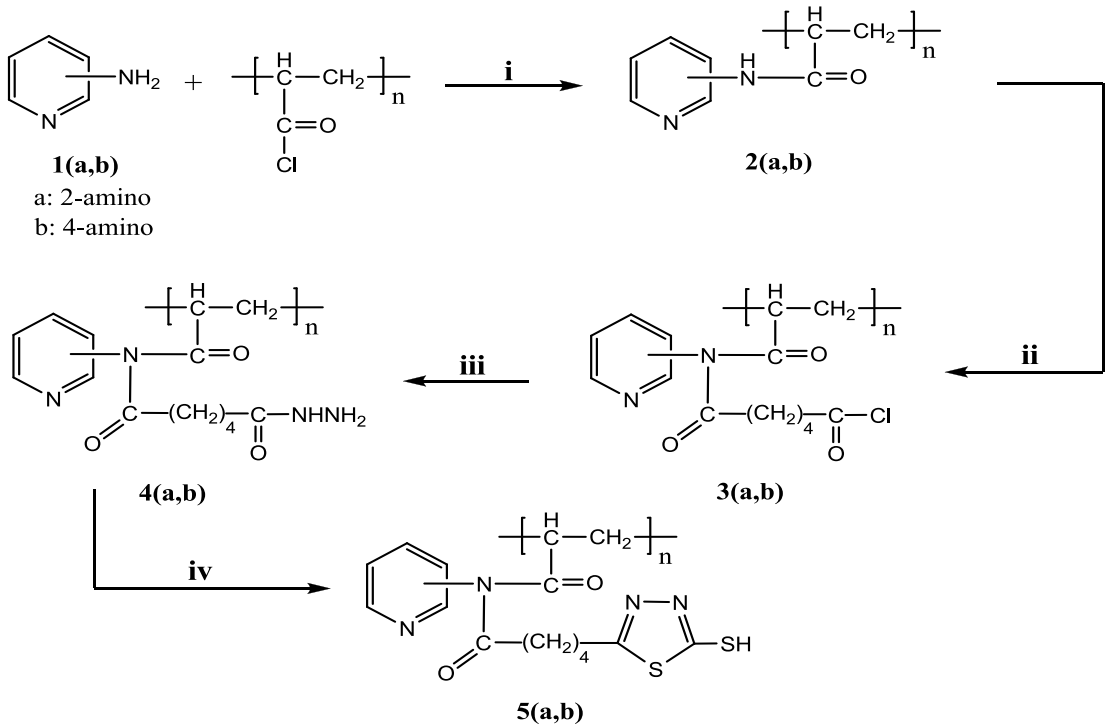
Poly N-{[(4-amino pyridine)-2-thio-5-butenyl]-1,3,4-thiadiazole} acryl imide (5b)

65% of conversion as a brownish violet large needle crystal; m.p. > 300ºC; FT-IR (KBr) film: 1705 cm^{-1} (C=O) imide,

2570 cm^{-1} (S-H), 1650 cm^{-1} (C=N), 660 cm^{-1} (C-S).

Results and Discussion:

New polyimide containing heterocyclic moiety was synthesized following the reaction sequence outlined in Scheme (1).



Reagents and conditions

(i): DMF, Et_3N, reflux;
(ii): adipoyl chloride, Et_3N, reflux;
(iii): dry benzene, hydrazine hydrate, reflux;
(iv): KOH, abs. EtOH, CS_2, reflux, 10% HCl.

Scheme (1)

The starting material for the synthetic polyimide is 2-amino or 4-amino pyridine which condensed with equimolar quantity of poly acryloyl chloride through nucleophilic substitution of chloride with amino group lead to polyamide (2a,b).

The FT-IR spectrum of (2a) showed an aliphatic (C-H) absorption at 3020 cm^{-1} and the absence of (-NH_2) stretching together with appearance of band at 3340 cm^{-1}, 1680 cm^{-1} and 1530 cm^{-1} attributed to (N-H) stretching of amide, amid (I) and amid (II) [21] respectively, which indicated the substitution and formation of polyamide. The ^{1}H-NMR of (2a) showed four different characteristic signals, two multiplet at 1.23 ppm and 2.6 ppm assigned for ethylene (acryl) protons and a signal at 7.4 ppm as a singlet was attributed to amid proton [22], while pyridine protons appeared as multiplet at 7.6 ppm Table (1).

In the ^{13}C-NMR spectrum of (2a) the ethylene carbons appeared at 27 ppm and 47 ppm and amide carbonyl at 171 ppm, while the pyridine's carbon appeared at 159, 128, 136.5, 123 and 147 ppm for C_2, C_3, C_4, C_5 and C_6 respectively(Table2).

In order to obtain polyimide

(3a,b) the polyamide (2a,b) were subjected to another nucleophilic substitution by treating with adipoyl chloride using triethyl amine (Et_3N) as a catalyst. The FT-IR spectrum showed the disappearance of amide bands (N-H)υ, (C=O)υ and (N-H)δ, with appearance bands at 1708 cm^{-1} and 1810 cm^{-1} attributed to (C=O) amide and (-CO-Cl-) respectively.

Another evidence for (3a) its ^{1}H-NMR spectrum showed different signals but the characteristic signals at 3.1 ppm and 3.8 ppm as triplet assigned to the two methylene groups that linked with (C=O) amide and (CO-Cl) respectively (Table 1).

The ^{13}C-NMR showed different pyridine's carbons and different aliphatic's carbons (Table 2), while the imide carbonyl appeared at 170 ppm and 173 ppm, another carbonyl at 179.1 ppm was due to (CO-Cl) group.

For synthesis the acid hydrazine polyimide (4a,b), the imide polymers (3a,b) were allowed to react with hydrazine hydrate in refluxing benzene. The resulting polymers are versatile key for synthesis of heterocyclic ring.

The FT-IR spectrum of (4a) showed two stretching bands at 3310-3400 cm^{-1} which assigned to the (NH_2) group. Beside this the absence of (CO-Cl) stretching band with appearance of bands at 1670 cm^{-1} (Amide I) and 1520 cm^{-1} (Amide II). On the other hand its ^{1}H-NMR spectrum showed a signal at 4.5 ppm as a singlet for (NH_2) protons and other singlet at 6.8 ppm assigned to the amide proton, and other characteristic signals for aliphatic and pyridine protons (Table 1). In the ^{13}C-NMR spectrum the amide carbonyl appeared at 169 ppm, while the imide carbonyl appeared at 171 ppm and 171.5 ppm. Other characteristic signals (Table 2) for aliphatic and pyridine carbons.

In order to obtain our synthetic target, the acid hydrazide polyimide (4a,b) were condensed with carbon disulfide in methanolic potassium hydroxide, afforded the heterocyclic polyimide (5a,b).

In FT-IR spectrum of (5a) the disappearance of amide and amine bands and the appearance of stretching bands at 2600 cm^{-1}, 1630 cm^{-1} and 669 cm^{-1} for (S-H), (C=N) and (C-S) respectively. The ^{1}H-NMR spectrum of (5a) showed different signals for aliphatic and aromatic protons (Table 1) and the characteristic signal at 4.1 ppm as singlet assigned for (S-H) proton [23]. The ^{13}C-NMR spectra showed many characteristic signals including 172 ppm and 172.5 ppm for two imide carbonyl groups and at 152.5 ppm and 158.2 ppm for thiadiazole carbons. The other aliphatic and pyridine carbons were listed in Table (2).

All spectroscopic data that mentioned above gave a good evidence that the 1,3,4-thiadiazol was created and verify that the heterocyclic polyimide will obtained. In the final, the compounds (2b, 3b, 4b and 5b) showed the same spectral data with simple shift either blue or red shift for FT-IR as mentioned in experimental part and for ^{1}H-NMR and ^{13}C-NMR mentioned in Table (1 and 2 In addition of that there physical state was different, (2a, 3a, 4a and 5a) formed as a viscous polymers, while (2b, 3b, 4b and 5b) formed as a brownish violet large needle crystal polymers.

Table (1): The ^{1}H-NMR chemical shifts of the prepared compounds

Comp. No.	Chemical shifts (ppm)
2a	1.23 (m, 2H, $-(HC(-Cl)-CH_2)_n-$); 2.6 (m, 1H, $-(HC(-Cl)-CH_2)_n-$); 7.4 (s, 1H, amide); 7.9 (m, 4H, Py. H).
2b	1.25 (m, 2H, $-(HC(-Cl)-CH_2)_n-$); 2.65 (m, 1H, $-(HC(-Cl)-CH_2)_n-$); 7.1(s, 1H, amide); 7.75 (m, 4H, Py. H).
3a	1.1 (m, 2H, $-(HC(-Cl)-CH_2)_n-$); 2.5 (m, 1H, $-(HC(-Cl)-CH_2)_n-$); 3.1(t, 2H, -CO-CH_2 ; 1.4 (m, 4H, 2CH_2). 3.8 (t, 2H, -CH_2-CO-Cl); 7.6 (m, 4H, Py. H).
3b	1.15 (m, 2H, $-(HC(-Cl)-CH_2)_n-$); 2.6 (m, 1H, $-(HC(-Cl)-CH_2)_n-$); 3.0 (t, 2H, -CO-CH_2); 1.35 (m, 4H, 2CH_2); 3.75 (t, 2H, -CH_2-CO-Cl); 7.45 (m, 4H, Py. H).
4a	1.26 (m, 2H, $-(HC(-Cl)-CH_2)_n-$); 2.64 (m, 1H, $-(HC(-Cl)-CH_2)_n-$); 3.4 (t, 2H, -CO-CH_2); 1.31 (m, 4H, 2CH_2); 3.65 (t, 2H, -CH_2-CO-NH); 6.8 (s, 1H, -CO-NH); 4.5 (s, 2H, NH_2); 7.7 (m, 4H, Py. H).
4b	1.24 (m, 2H, $-(HC(-Cl)-CH_2)_n-$); 2.69 (m, 1H, $-(HC(-Cl)-CH_2)_n-$); 3.4 (m, 2H, -CO-CH_2); 1.29 (m, 4H, 2CH_2); 3.69 (t, 2H, -CH_2-CO-NH); 6.6 (s, 1H, -CO-NH); 4.3 (s, 2H, NH_2); 7.68 (m, 4H, Py. H).
5a	1.5-2.1 (m, 7H, $-(HC(-Cl)-CH_2)_n-$ and 2CH_2); 3.3 (m, 4H, -CO-CH_2 and $H_2C=C<$); 4.1 (s, 1H, SH); 7.9 (m, 4H, Py. H).
5b	1.4-1.9 (m, 7H, $-(HC(-Cl)-CH_2)_n-$ and 2CH_2); 3.1 (t, 2H, -CO-CH_2); 2.9 (t, 2H, $H_2C=C<$); 4.0 (s, 1H, SH); 7.75 (m, 4H, Py. H).

Table (2): The ^{13}C-NMR chemical shifts of the prepared compounds

Comp. No.	Chemical shifts (ppm)
2a	27 ( ); 47 (); 171 (C=O amide); 159 (Py. C_2); 128 (Py. C_3); 136.5 (Py. C_4); 123 (Py. C_5); 147 (Py. C_6).
2b	26 ( ); 46.6 (); 170 (C=O amide); 150 (Py. C_2); 126 (Py. C_3); 155 (Py. C_4); 127 (Py.C_5); 150.5 (Py. C_6).
3a	28.2 ( ); 46.5 (); 48 (-CO-CH_2-); 25.2, 25.3 (-CH_2CH_2-); 50.2 (-CH_2-CO-Cl); 170, 173 (2 C=O Imide); 179.1 (-CO-Cl); 155 (Py. C_2); 127.8 (Py. C_3); 137 (Py. C_4); 122 (Py.C_5); 144 (Py. C_6).
3b	27.1 ( ); 45.3 (); 50 (-CO-CH_2-); 23.4, 23.6 (-CH_2CH_2-); 51.5 (-CH_2-CO-Cl); 171, 173.3 (2 C=O Imide); 180 (-CO-Cl); 149, 149.4 (Py. C_2, C_6); 124.1, 124.7 (Py. C_3, C_5); 160 (Py. C_4).
4a	26.5 ( ); 50.3 (); 50.9 (-CO-CH_2-); 26.1, 26.2 (-CH_2CH_2-); 51.2 (-CH_2-CO-NH); 169 (C=O amide); 171, 171.5 (2 C=O Imide); 160 (Py. C_2); 125 (Py. C_3); 141 (Py. C_4); 119 (Py.C_5); 148 (Py. C_6).
4b	29.2 ( ); 50.4 (); 48.3 (-CO-CH_2-); 25.2, 25.25 (-CH_2CH_2-); 50.9 (-CH_2-CO-NH); 170 (C=O amide); 175, 176 (2 C=O Imide); 147, 147.3 (Py. C_2, C_6); 122, 122.2 (Py. C_3, C_5); 158 (Py. C_4).
5a	29.8 ( ); 52 (); 50 (-CO-CH_2-); 25.7, 25.9 (-CH_2CH_2-); 48.2 (); 172, 172.5 (2 C=O Imide); 158 (Py. C_2); 122.2 (Py. C_3); 136.3 (Py. C_4); 117 (Py.C_5); 145.1 (Py. C_6); 152.5, 158.2 (thiadiazol 2C).
5b	28.1 ( ); 51.2 (); 49.6 (-CO-CH_2-); 25, 25.3 (-CH_2CH_2-); 48 (); 170, 171.7 (2 C=O Imide); 145.2 (Py. C_2); 120 (Py. C_3); 159 (Py. C_4); 120.8 (Py.C_5); 145.9 (Py. C_6); 155.4, 159.1 (thiadiazol 2C).

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تحضير وتشخيص بولي إيمايدات تحتوي على حلقة غير متجانسة جديدة

أنتصار عبيد التميمي* ***ثناء مهدي المؤمن****

* قسم الكيمياء - كلية العلوم - جامعة بغداد

الخلاصة:

يتضمن البحث تحضير بولي إيمايدات جديدة تحتوي على حلقة غير متجانسة، 5(b,a)، أساسها بولي أكريلول. إن مخطط التفاعل يبدأ باضافة نيوكليوفيلية لمشتقي البريدين 2-أمينو و 4-أمينو بردين الى بولي أكريلول كلورايد ، ليكون البولي أميد المعوض 2(b,a) والتي بتفاعل نيوكليوفيلي أخر مع كلوريد الأديبويل أدت الى تكون البولي إيمايد 3(b,a). وعند معاملته مع الهايدرازين المائي أعطى البولي إيمايد حامض الهيدرازايد 4(b,a)، والذي عند تكثيفه مع ثنائي كبريتيد الكربون أعطى البولي إيمايد الحاوي على حلقة غير متجانسة. تم تشخيص المركبات المحضرة بمطيافية FT-IR، ^{1}H-NMR و ^{13}C-NMR.