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Synthesis and characterization of new Organosoluble Poly (ether-amide)s bearing Xylene, sulfoxide and sulfone in the main chain: Theoretical study

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Abstract

New poly (thioether-amide)s containing thiosalicylic acid units were prepared and their solubility and viscosity were evaluated. The viscosities of polyamides are in the range of 0.41-0.56. These polyamides showed good solubility in common organic solvents. Theoretical calculation were performed on the monomers.

Keywords: Poly (thioether-amide), thiosalicylic acid, xylene, synthesis, microwave, theoretical study

1. Introduction

Aromatic polyamides and polyimides are high performance polymers with some advantages such as, good thermal stability, efficient mechanical properties, low flammable, good processable, easy applicable and low density materials [1-4]. Because of their excellent properties, they are used as good alternatives for a series of industrial materials in applications [5]. The new industry and technology requires high performance materials with a series of properties and stable in vigorous conditions such as elevated temperatures, high acidic and basic media and humid and cold regions [6]. Polyamides and polyimides are important candidates for these advanced materials have ability to change their properties with a series of improvements and gain desired application [7]. Wholly aromatic polyamides (*aramides*) have a few disadvantages such as poor solubility, difficult processability and high melting and thus restricted applications [8]. Several procedures were examined for achieve these drawbacks containing the use of softening aliphatic chains, ethers, esters and sulfides in the polymer main chain, insertion of three dimensional and bulky pendant groups (for example; alkyl, sulfone, thio and ether groups) for avoid crystallinity, close packing and gain low melting, good soluble and processable polymers with good thermal stability [9-11].

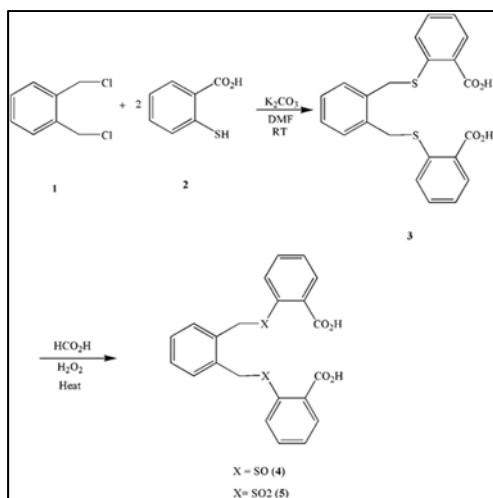
In continuation of our previous research works on the synthesis of polymers [12], in this research work new organo-soluble poly (ester-amide-imide)s containing amino acids and diphenylsulfone in the main chain were synthesized and their properties were studied.

2. Materials and Methods

2.1 Materials and apparatus

The reactions for the synthesis of monomer and purification of polymers were carried out in an efficient hood. All the materials were purchased from Merck, Fluka, Across Organics and Aldrich chemical companies. N-Methyl-2-pyrrolidinone (NMP, Merck) was purified by distillation under reduced pressure over calcium hydride and stored over 4A ° molecular sieves. FT-IR spectra were recorded in potassium bromide pellets on a Bruker apparatus. The ¹H NMR and ¹³C NMR spectra were obtained using BRUKER AVANCE DRX 500 MHz apparatus and mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. Inherent viscosities ($\eta_{inh} = \ln \eta / c$ at a concentration of 0.5 g dL⁻¹) were measured with an Ubbelohde suspended-level viscometer at 30 °C using DMSO as solvent. Theoretical studies were performed with Gaussian 09 program and semi-empirical functions and PM6 and AM1 basis sets were used to calculations. Gauss View 5.0 software was used for the processing of output files.

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Scheme 1: Synthesis of diacids (4, 5).

2.2 Synthesis of diacid disulfide (3) ¹¹³¹

To the mixture of **1** (α,α' -Xylyldibromide, 0.264 g, 1 mmol) and DMF (20 mL) was added thiosalicylic acid (0.308 g, 2mmol) and K_2CO_3 (0.56 g, 4mmol) at room temperature. The mixture was stirred at room temperature for 24h. After completion of the reaction (monitored by TLC), water was added and the mixture was neutralized using HCl solution. The resulting precipitate left for 12h and then filtered. Crystallization in ethanol afforded diacid as a white powder in 97% yield and melting point of 204-205 °C (uncorrected); IR (KBr): 2964, 2639, 1678, 1253, 1052, 740 cm^{-1} ; 1H NMR (300 MHz, DMSO- d_6) δ : 4.32 (s, 4H), 7.21 (t, 2H, $J=6$ Hz), 7.28 (t, 2H, $J=3$ Hz), 7.47 (s, 6H), 7.89 (d, 2H, $J=6$ Hz), 12.36 (s, 2H) ppm; MS (EI) m/z (relative intensity %): 395 $[M-15]^+$ (6%), 362 (2%), 339 (3%), 317 (8%), 257 (42%), 228 (48%), 179 (27%), 151 (26%), 121 (100%), 105 (29%), 91 (49%), 72 (56%), 28 (42%); Analytical calculated for $C_{22}H_{18}O_4S_2$ (410.51): C, 64.37; H, 4.42; Found, C, 64.39; H, 4.41.

2.3 Synthesis of diacid disulfoxide (4)

To Formic acid (30 mL) were added **3** (1mmol, 0.806g) and hydrogen peroxide solution (2 mmol) at room temperature. The reaction mixture was stirred at room temperature for 30 Min. and then heated at 70 °C for 6 hours. After completion of the reaction (monitored by TLC), water was added and the resulting white precipitate was filtered and recrystallized in ethanol to afford a white solid in 96% yield; IR (KBr) ν : 2500-3110, 2433, 1677, 1256, 1048, 980 cm^{-1} ; 1H NMR (500 MHz, DMSO- d_6) δ : 4.16 (d, $J=15$ Hz, 1H), 4.59 (d, $J=13$ Hz, 2H), 7.21-7.23 (m, 2H), 7.28-7.30 (m, 2H), 7.46-7.49 (m, 4H), 7.65-7.67 (m, 2H), 7.80-7.81 (m, 1H), 7.89-7.91 (m, 2H), 8.06-8.08 (m, 1H), 13.51-13.61 (b, 2H) ppm; MS (EI, m/z , Intensity, %): 442 $[M]^+$ (2), 270 (100), 254 (82), 181 (100), 165 (48), 136 (100), 91 (100).

2.4 Synthesis of diacid disulfone (5)

To Formic acid (30 mL) were added **3** (1mmol, 0.806g) and hydrogen peroxide solution (4 mmol) at room temperature. The reaction mixture was stirred at room temperature for 30 Min. and then heated at 70 °C for 6 hours. After completion of the reaction (monitored by TLC), water was added and the resulting white precipitate was filtered and recrystallized in ethanol to afford a white solid in 99% yield; IR (KBr) ν : 2918-3300, 2421, 1698, 1239, 979 cm^{-1} ; 1H NMR (500 MHz, DMSO- d_6) δ : 4.18 (d, $J=13.5$ Hz, 2H), 4.61 (d, $J=13.5$ Hz, 2H), 7.20-7.23 (m, 2H), 7.28-7.30 (m, 2H), 7.46-7.49 (m,

4H), 7.63-7.67 (m, 1H), 7.58-7.82 (m, 1H), 7.90-7.91 (d, $J=7$ Hz, 1H), 8.06-8.08 (m, 1H), 13.54-13.58 (b, 2H) ppm; ^{13}C NMR (500 MHz, DMSO- d_6) δ : 168.34, 167.77, 167.62, 148.38, 148.34, 142.01, 135.76, 134.21, 133.33, 133.10, 132.89, 132.68, 132.46, 131.80, 131.72, 131.60, 131.45, 128.76, 128.64, 128.56, 126.84, 125.49, 125.01, 59.52, 59.15 ppm; MS (EI, m/z , Intensity, %): 474 $[M]^+$ (3), 409 (5), 408 (49), 289 (2), 165 (12), 136 (100), 119 (73), 108 (52), 91 (74).

2.5 Synthesis of polymers (11-16)

Polyamides were synthesized through the Yamazaki phosphorylation reaction of diacids (4,5) with various diamines (6-10) as shown in Scheme 2 and 3. A typical example for the preparation of polyamide (11) is given. To **5** (1mmol) in quartz tube were added **6** (1mmol), NMP (4mL), TPP (0.6 mL), Py (0.6 ml). The mixture was stirred at room temperature for 30min. and then, irradiated under microwave in 600W for 9 Min. (3 \times 3 Min.) and the rest time of 10 Min. (2 \times 5 Min.). After cooling to room temperature, the resulting viscose reaction mixture was poured into 300 mL of boiling methanol. The resulting crude product was precipitated and then filtered. The resulting polymer (**14**) was washed with hot methanol (50 mL), hot water (twice, 50 mL) and then hot methanol (50mL), respectively; and dried under vacuum at 100 °C overnight. Spectral data, viscosity and solubility of these polyamides were reported in the following tables and figures.

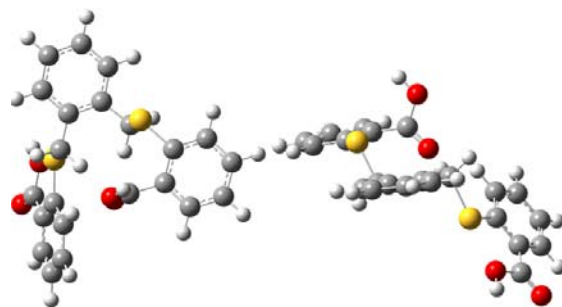


Fig 1: Semi-empirical PM6 optimized structure of diacid sulfide (3).

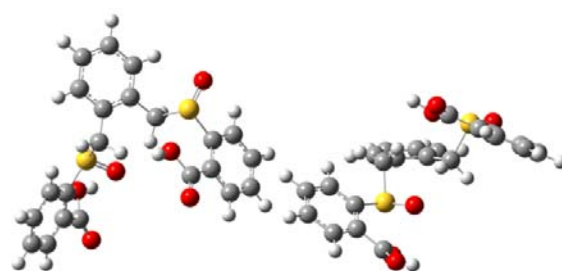


Fig 2: Semi-empirical PM6 optimized structure of diacid sulfoxide (4).

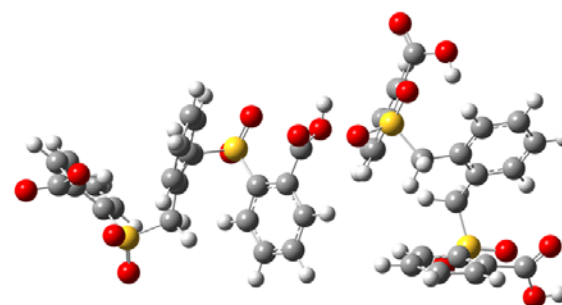
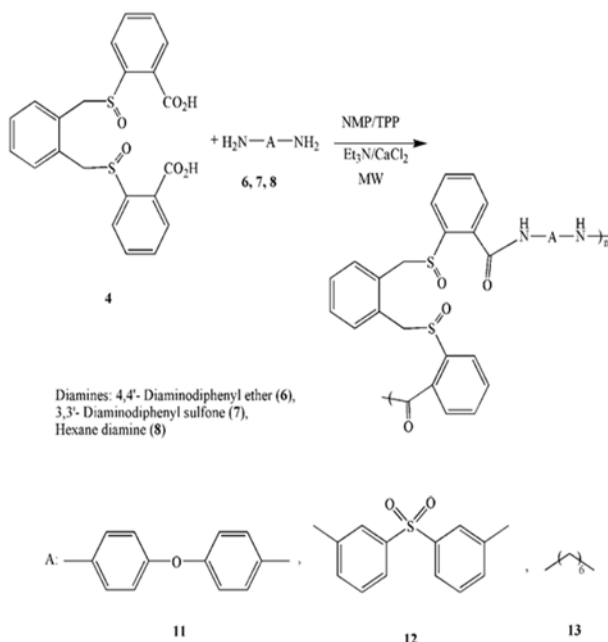
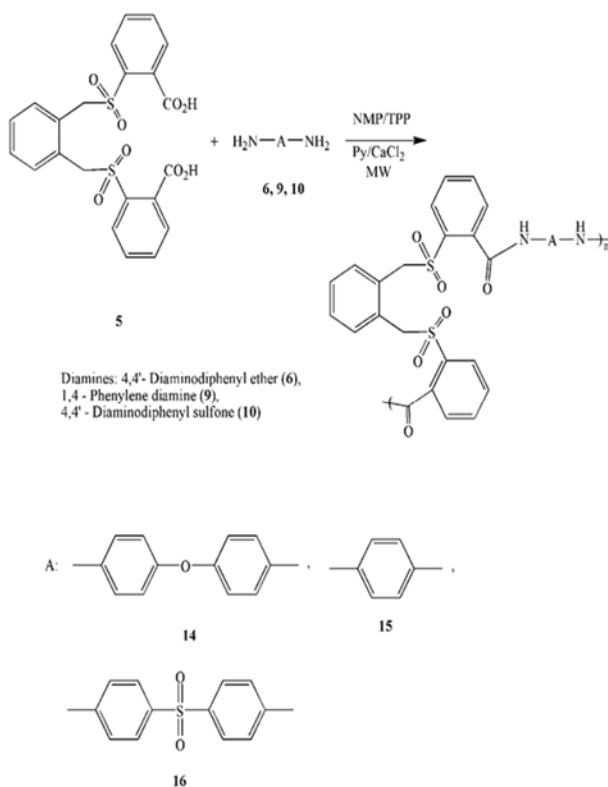
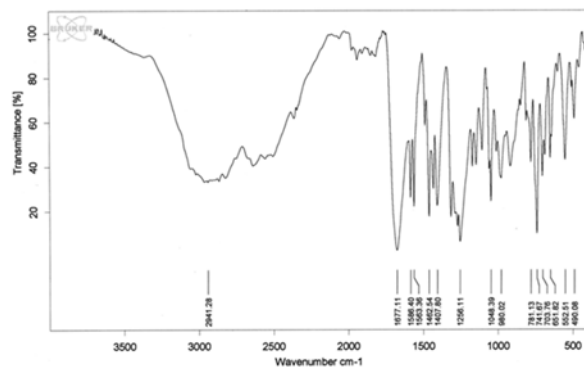
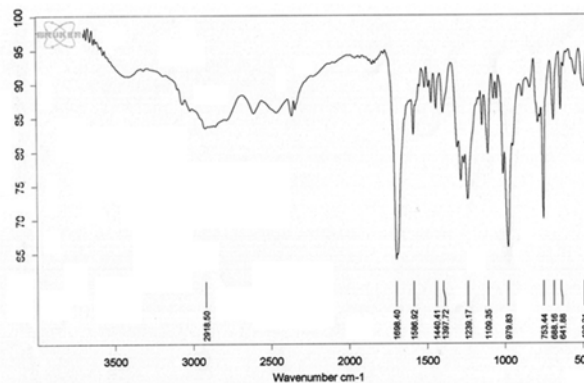
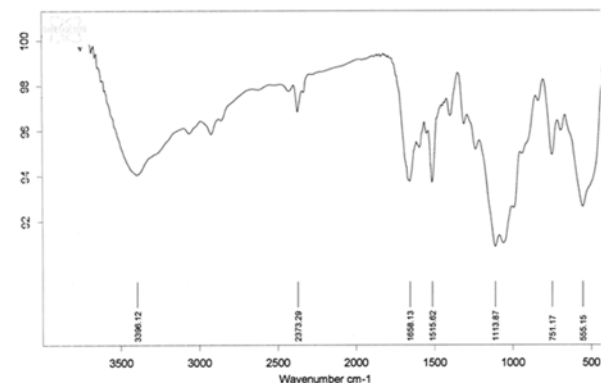


Fig 3: Semi-empirical PM6 optimized structure of diacid sulfone (5).

Table 1: Calculated physical properties of diacids (3, 4, 5) using Semi empirical PM6 basis set.

Entry	3	4	5
Energy/A.U.	-0.165418	-0.238521	-0.317154
E _{HOMO} /ev	-0.30918	-0.30756	-0.36568
E _{LUMO} /ev	-0.03874	-0.03651	-0.05184
Band Gap/ev	0.27044	0.27105	0.31384
Hardness	0.17396	0.172035	0.20876
Polarizability	339.772	275.253	339.059
Dipole Moment/Debye	8.3533	4.9415	4.8967

**Scheme 2:** Synthesis of polymers (11-13)**Scheme 3:** Synthesis of polymers (14-16)**Fig. 4:** FT-IR spectrum of diacid (4).**Fig 5:** FT-IR spectrum of diacid (5).**Fig 6:** FT-IR spectrum of polyamide (15).

3. Results and Discussion

In this research work, we wish to report the synthesis and characterization of poly (thioether-amides) obtained from the reaction of a new diacids (4, 5), containing xylene and thiosalicylic acid with sulfoxide and sulfone functional groups. 4, 5 were prepared from the corresponding diacid (3) through oxidation by appropriate amounts of hydrogen peroxide (Scheme 1). Theoretical study of diacids (3, 4, 5) were performed using Gaussian 09 program and semiempirical method via PM6 basis set and the optimized structures of 3 and 4 and 5 were appeared in Fig. 1 and Fig. 2 and Fig. 3, respectively. Calculated physical properties of diacids (3, 4, 5) were reported in Table-1.

FT-IR spectra of 4 and 5 are appeared in Fig. 4 and Fig. 5. poly (thioether-amide)s (11-16) were prepared from the reaction of diacids (4 and 5) and diamines (5-10) in NMP under microwave irradiation (Scheme 2 and 3). FT-IR spectrum of 15 is appeared in Fig. 6, and showed the

corresponding structure according to the main functional groups. The inherent viscosities and the yields of polyamides were reported in Table-2. FT-IR and ¹H NMR spectra of polymers summarized in table 3 and table 4 and are in agreement with corresponding structures.

The solubility behavior of polymers was investigated qualitatively in a series of organic solvents such as N-methylpyrrolidinone (NMP), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), N, N-dimethylacetamide (DMAc) and *m*-cresol, and the results are summarized in Table-5. All the polymers showed reliable solubility in polar organic solvents. This might be due to the presence of aliphatic units which decreased intramolecular and intramolecular hydrogen bonding.

Sulfoxide and sulfone units reduced the flexibility and increased close packing and crystallinity. Theoretical studies on the monomers showed the differences of structures. The polymers have different structures and pore sizes for many applications.

Table 2: Inherent viscosity and the yields of polymers (11-16).

Polymer	Yield (%)	$\eta_{inh}(g/dL)^a$
11	91	0.46
12	89	0.43
13	90	0.41
14	92	0.48
15	93	0.53
16	96	0.56

Table 3: Spectral data of polymers (11-13).

Entry	IR (cm ⁻¹)	¹ H NMR (500 MHz, DMSO-d ₆): δ (ppm)
11	3367, 2432, 1664, 1127, 1043, 988.	4.26 (d, J=10 Hz, 2H), 4.36 (d, J=10 Hz, 2H), 6.97-6.99 (m, 2H), 7.11-7.15 (m, 2H), 7.17-7.19 (m, 2H), 7.30-7.39 (m, 8H), 7.49-7.55 (m, 2H), 7.70-7.72 (m, 2H), 7.83-7.86 (m, 2H), 10.38 (s, 1H), 10.41 (s, 1H).
12	3399, 2391, 1655, 1511, 1113, 984.	4.28 (d, J=22.5 Hz, 2H), 4.33 (d, J=25 Hz, 2H), 7.10-7.13 (m, 2H), 7.24-7.28 (m, 4H), 7.36-7.38 (m, 4H), 7.44-7.46 (m, 2H), 7.51-7.58 (m, 4H), 7.61-7.63 (m, 2H), 7.90-7.94 (m, 2H), 8.43 (s, 2H), 10.73-10.76 (m, 2H).
13	3397, 2396, 1665, 1513, 1115, 986.	1.39-1.41 (m, 4H), 1.59-1.62 (M, 4H), 2.73-2.76 (M, 4H), 4.18 (d, J=15 Hz, 1H), 4.57 (d, J=13 Hz, 2H), 7.24-7.27 (m, 2H), 7.29-7.31 (m, 2H), 7.49-7.52 (m, 4H), 7.68-7.69 (m, 2H), 7.83-7.86 (m, 1H), 7.87-7.90 (m, 2H), 8.09-8.10 (m, 1H), 10.65-10.68 (m, 2H).

Table 4: Spectral data of polymers (14-16).

Polymer	IR (cm ⁻¹)	¹ H NMR (500 MHz, DMSO-d ₆): δ (ppm)
14	3313, 2381, 1665, 1214, 1125, 941	4.35 (s, 4H), 6.97-6.98 (m, 4H), 7.18-7.51 (m, 12H), 7.70-7.71 (m, 4H), 10.37 (s, 2H).
15	3396, 2373, 1658, 1515, 1113, 1051.	4.34 (s, 4H), 7.16-7.24 (m, 4H), 7.27-7.31 (m, 4H), 7.37-7.39 (m, 2H), 7.45-7.52 (m, 4H), 7.64-7.66 (m, 2H), 10.34 (s, 2H).
16	3397, 2392, 1653, 1512, 1111, 986.	4.35 (s, 4H), 7.11-7.13 (m, 4H), 7.24-7.26 (m, 12H), 7.84-7.86 (m, 4H), 10.39 (s, 2H).

Table 5: The solubility of polymers (11-16).

Polymer ^a	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
11	++	++	++	++	++	+
12	++	++	++	++	+	+
13	++	++	++	++	++	±
14	++	++	++	++	++	+
15	++	++	++	++	+	±
16	+	+	+	±	±	±

(++) Soluble at room temperature; (+) soluble upon heating; (±) partially soluble.

^a Solubility measured at a polymer concentration of 0.05 g/ml.

4. Conclusion

A series of new poly (thioether-amide)s bearing thiosalicylic acid in the main chain were successfully prepared via Yamasaki phosphorylation under microwave irradiation (MW). The polymers showed reliable solubility and viscosity. This is due to the presence of aliphatic methylene groups in the presence of tetrahedral sulfoxide and sulfone functional groups. Thus, we afforded polymers with improved solubility. Theoretical study of monomers showed different three dimensional structures.

5. Acknowledgements

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