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Synthesis of new polyamides bearing diphenyl ether and thioglycolic acid amide in the main chain

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Abstract

New poly (thioether - ether - amide)s containing thioglycolic acid and 4,4'-(diamidodiphenyl) ether units were prepared and their solubility and viscosity were evaluated. The viscosities of polyamides are in the range of 0.41-0.48. These polyamides showed good solubility in common organic solvents.

Keywords: Polyamide, 4,4'-diaminodiphenyl ether, microwave, synthesis, polymer

1. Introduction

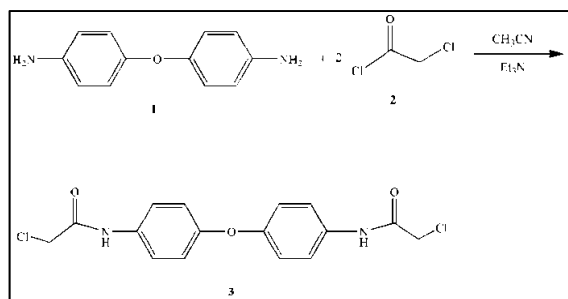
Aromatic polyamides are high performance polymers with some advantages such as, good thermal stability, efficient mechanical properties, low flammable, good processable, easy applicable and low density [1-4]. Because of their exceptional properties, they are used as good alternatives for a series of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

In continuation of previous research works on the synthesis of polymers [12], in this research work new organosoluble poly (thioether-amide)s containing 4,4'-diaminodiphenyl ether and thioglycolic acid in the main chain were synthesized.

2. Materials and Methods

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) and pyridine (Py, Merck) were purified by distillation under reduced pressure over calcium hydride and stored over 4A ° molecular sieves. Triphenyl phosphite (TPP, Merck) was purified by fractional distillation under vacuum. 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 and 400 MHz apparatus and mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. The MicroSYNTH system of Milestone which is a multi-mode platform and equipped with a magnetic stirring plate was used for the synthesis. Inherent viscosities ($\eta_{inh} = \ln \eta_r / c$ at a concentration of 0.5 g dL⁻¹) were measured with an Ubbelohde suspended-level viscometer at 30 °C using DMSO as solvent.

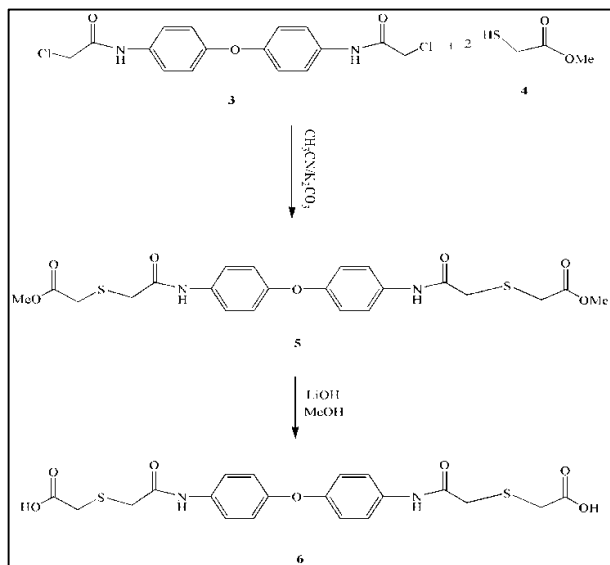
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Scheme 1: Synthesis of 3.

2.1 Synthesis of dichloroamide (3)

To acetonitrile (30 mL) were added 4,4'-diaminodiphenyl ether (1, 1mmol, 0.20g), triethylamine (2 mmol, 0.28 mL) and chloroacetyl chloride (2, 2 mmol, 0.16mL) at room temperature. The reaction mixture was stirred at room temperature for 48 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 3 as a white solid in 91% yield; IR (KBr): 3598, 3508, 3314, 3110, 2987, 1684, 1534, 1302, 1107, 836 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, DMSO-d_6) δ : 4.24 (s, 4H), 7.75 (d, $J=9\text{Hz}$, 4H), 7.85 (d, $J=9\text{Hz}$, 4H), 10.68 (s, 2H) ppm; $^{13}\text{C NMR}$ (125 MHz, DMSO-d_6) δ : 166.27, 143.75, 136.64, 129.44, 120.34, 44.39 ppm.



Scheme 2: Synthesis of diacid (6) monomer.

2.2 Synthesis of diester (5)

To acetonitrile (50 mL), were added 3 (1 mmol, 0.352g) and methylthioglycolate (4, 2 mmol, 0.20 mL) at room temperature. The mixture was stirred at room temperature for 2h and was refluxed for 24h under nitrogen. After completion of the reaction (monitored by TLC), water was added and the resulting mixture was extracted with chloroform (3 \times 100 mL), washed with water (2 \times 100 mL), dried (Na_2SO_4) and evaporated to obtain 5 as crude product. The resulting mixture was purified by dry flash chromatography using n-hexane/ethylacetate as eluent. Then, the resulting mixture was evaporated under reduced pressure to afford 5 in 93% yields as a white precipitate; IR (KBr): 3595, 3507, 3311, 3115, 2985, 1693, 1682, 1538, 1322, 1155, 1043, 928 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, DMSO-d_6) δ : 4.05 (s, 4H, CH_2), 4.66 (s, 6H,

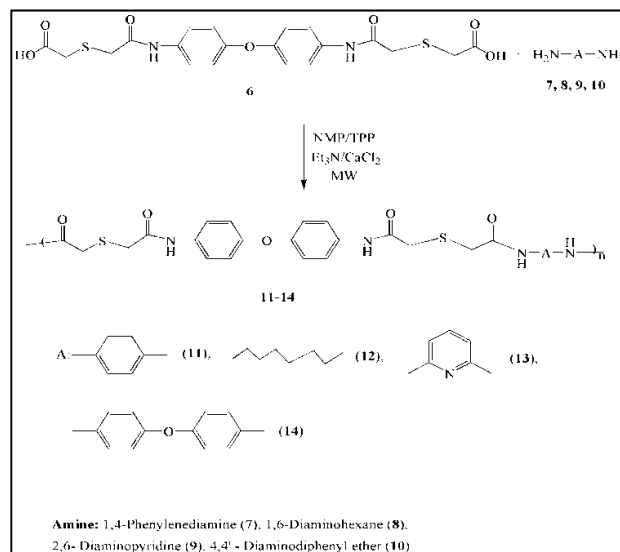
CH_3), 4.25 (s, 4H), 7.76 (d, $J=9\text{Hz}$, 4H), 7.83 (d, $J=9\text{Hz}$, 4H), 10.65 (s, 2H) ppm.

2.3 Synthesis of diacid (6)

To the mixture of 5 (1mmol, 0.492g) and methanol (30 mL) was added LiOH (2mmol, 0.04g) and water (one drop) 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 was filtered, dried and recrystallized in ethanol to afford diacid (6) as a white precipitate in 94% yield, IR (KBr): 3591, 3504, 3323, 3119, 2973, 1692, 1685, 1542, 1384, 1186, 1081, 901 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, DMSO-d_6) δ : 3.92 (s, 4H), 4.21 (s, 4H), 7.73 (d, $J=9\text{Hz}$, 4H), 7.82 (d, $J=9\text{Hz}$, 4H), 10.65 (s, 2H), 12.34-12.36 (b, 2H) ppm.

2.4 Synthesis of polymers (11-14)

Polyamides were synthesized through the phosphorylation reaction of monomer diacid (6) with a series of diamines as shown in Scheme 3. A typical example for the preparation of polyamides is given. A mixture of 6 (1 mmol, 0.464g), p-phenylenediamine (1 mmol, 0.11 g), 0.3 g of CaCl_2 , 0.6 mL of TPP, 0.5 mL of triethylamine, and 4 mL of NMP were added to the tube and 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 was washed with hot methanol (50 mL), hot water (twice, 50 mL) and then hot methanol (50 mL), respectively; and dried under vacuum at 100 $^\circ\text{C}$ overnight. The yields were almost quantitative. Spectral data, viscosity and solubility of these polyamides were reported in the Tables.



Scheme 3: Synthesis of polyamides (11-14).

3. Results and Discussion

In this research work, we wish to report the synthesis and characterization of poly (thioester-ether- amide) s synthesized from the reaction of a new diacid monomer (6), containing amide and thioether units, and aromatic rings. 3 was prepared from the reaction of 4,4'-diaminodiphenyl ether and chloroacetyl chloride in acetonitrile in the presence of triethylamine (Scheme 1).

Diester (5) was prepared from the reaction of dichloroamide (3) and methylthioglycolate (4) in acetonitrile and in the presence of potassium carbonate at reflux conditions (Scheme 2). Diacid (6) was prepared from the reaction of 5 and lithium hydroxide and one drop of water in methanol at room temperature (Scheme 2). Polyamides were synthesized from the reaction of diacid (6) and diamines in NMP and in the presence of TPP, triethylamine and CaCl₂ under microwave irradiation (Scheme 3). FT-IR and ¹H NMR spectra of polymers summarized in Table 1 and are in agreement with corresponding structures. The inherent viscosities and the yields of polyamides were reported in Table 2.

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 3. All the polymers showed reliable solubility in polar organic solvents. This might be due to the presence of thioether and ether units which increased flexibility and decreased rigidity, crystallinity and close packing. The viscosities of polymers were measured in DMSO at 30 °C and are in the range of 0.41-0.48 (Table 2).

Table 1: Spectral data of polymers (11-14).

Polymer	IR (cm ⁻¹)	¹ H NMR (400 MHz, DMSO-d ₆): δ (ppm)
11	3501, 3321, 3173, 2954, 1694, 1687, 1572, 1365, 1172, 1085, 951	3.22 (s, 4H), 4.03 (s, 4H), 7.51-7.53 (m, 4H), 6.94-6.95 (m, 4H), 7.64-7.67 (m, 4H), 10.32 (s, 2H), 10.45 (s, 2H)
12	3508, 3027, 2975, 2936, 1691, 1655, 1543, 1464, 1338, 1182, 1066, 996	1.22-1.24 (m, 4H), 2.15-2.18 (m, 4H), 2.68-2.69 (m, 2H), 3.18 (s, 4H), 3.98 (s, 4H), 6.92-6.94 (m, 4H), 7.60-7.63 (m, 4H), 11.56-11.57 (m, 4H)
13	3504, 3323, 3221, 2973, 2156, 1697, 1684, 1545, 1389, 1175, 1072, 958	3.31 (s, 4H), 4.09 (s, 4H), 6.91-6.93 (m, 4H), 7.65-7.68 (m, 4H), 8.10-8.30 (m, 3H, pyr-H), 9.20 (s, 2H, 2NH), 10.63 (s, 2H)
14	3503, 3325, 3117, 2976, 1691, 1687, 1540, 1385, 1187, 1084, 905	3.20 (s, 4H), 3.95 (s, 4H), 6.92-6.94 (m, 4H), 7.60-7.63 (m, 4H), 11.43-11.44 (m, 4H)

Table 2: Inherent viscosity and the yields of polyamides (11-14)

Polymer	Yield (%)	η_{inh} (g/dL) ^a
11	97	0.46
12	91	0.41
13	95	0.48
14	93	0.44

^aMeasured at a polymer concentration of 0.5 g/dL in DMSO solvent at 30 °C.

Table 3: The solubility of polyamides (11-14).

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

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

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

4. Conclusion

A series of new poly (thioether-ether-amide) s bearing 4, 4'-diaminodiphenyl ether and thioglycolic acid in the main chain were successfully prepared in Yamazaki phosphorylation conditions under microwave irradiation (MW). The polymers showed reliable solubility and viscosity. This is due to the presence of ether, thioether and amide groups in the main chain. Thus, we afforded polymers with improved solubility.

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