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Research Article

## Synthesis and Characterization of New Organosoluble Poly (Thioether-Amide) S Bearing 2-Aminothiophenol Structure in the Main Chain

Esmael Rostami\* and Amin khaksabz

Department of chemistry, Payame Noor University, PO BOX 19395-3697 Tehran, Iran.

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**Abstract:** New polyamides containing 1,3-bis (2-thio-2- (4-carboxyphenyl) -1-oxo) benzene structure were prepared under microwave irradiation using Yamasaki phosphorylation method and their solubility, thermal behavior and viscosity were evaluated. The structures of polymers were characterized using IR and  $^1\text{H}$  NMR spectroscopy. These polyamides showed good solubility, viscosity, high thermal stability and glass transition temperatures. Their viscosities and glass transition temperatures are in the range of 0.42-0.48 and 184-201 °C, respectively.

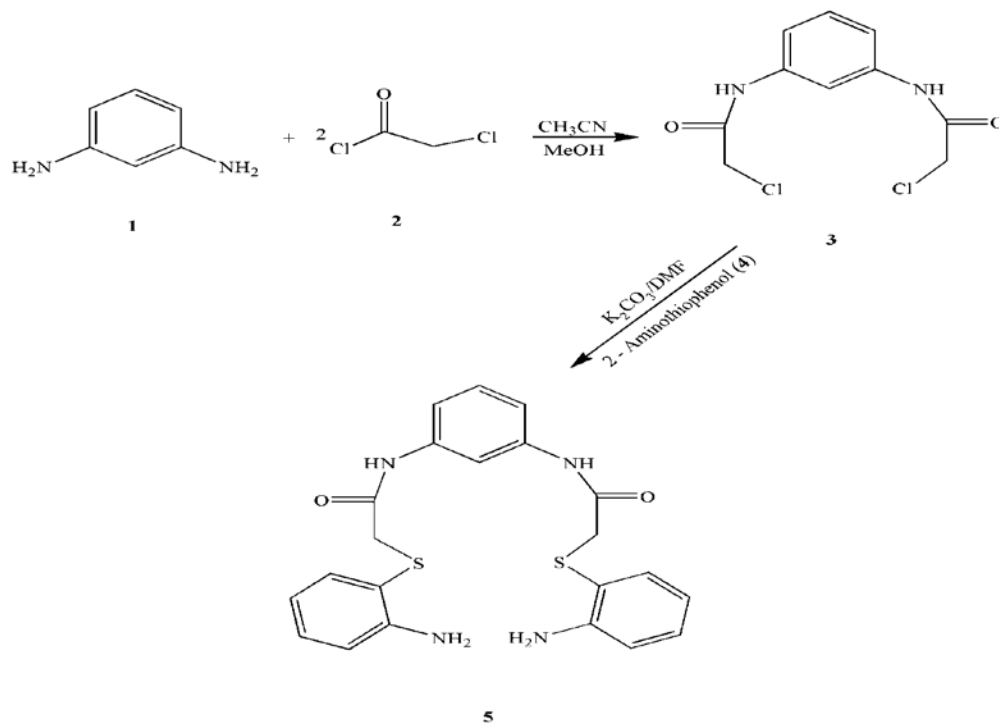
**Keywords:** Poly (thioether amide)s, Synthesis, 2-Aminothiophenol, Microwave, Theoretical Study.

### INTRODUCTION

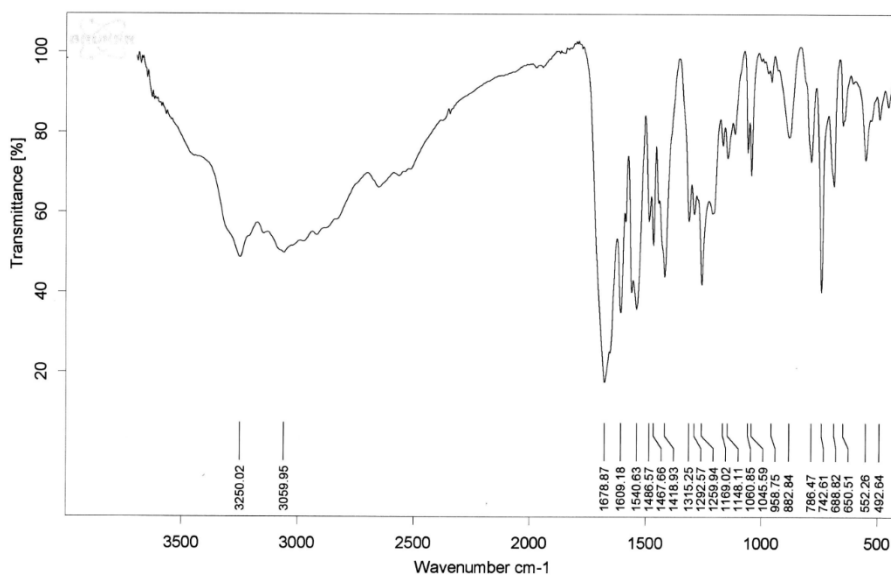
Aromatic polyamides (aramides) explore high thermal stability, good chemical resistance, excellent mechanical properties and a series of good properties that have broad applications in many areas of science and engineering<sup>1-3</sup>. However, all of these polymers have the main problem of being difficult to process and fabrication because of their high melting and poor solubility in common organic solvents. The reasons are strong interchain interactions, inherent macromolecular rigidity, or crystallinity.

There has been an increased attention in the preparation of polyamides with different substituents or chain irregularities to improve their processability without lowering their other desired properties. These studies include entering flexible adducts into the polymer main chain<sup>4-6</sup>, replacing symmetrical aromatic rings by unsymmetrical ones<sup>7, 8</sup>, introducing bulky and reliable pendent groups to minimize crystallization<sup>9, 13</sup> and forming a non-coplanar and nonsymmetrical structure<sup>14, 15</sup>.

Since the first published reports on the use of microwave irradiation to improve chemical transformations by Gedye and Giguere / Majetich<sup>16</sup> in 1986, a large number of researches have been published in this active field, referred to as microwave-assisted organic synthesis (MAOS)<sup>17, 18</sup>. Microwave heating compared to conventional heating procedures, has a number of advantages such as, reduce reaction times, increase product yields, and enhance product purities by reducing byproducts. The advantages of this efficient technology have also been explored in the context of multistep total synthesis<sup>19</sup>, medicinal chemistry and drug discovery<sup>20</sup>. Also, these methods were used in a series of fields such as polymer synthesis<sup>21</sup>, material sciences<sup>22</sup>, nanotechnology<sup>23</sup>, and biochemical processes<sup>24</sup>. The uses of microwave irradiation in polymer chemistry and polymer synthesis has thus become such a popular technique that a series of chemists will probably use microwave energy to heat chemical reactions on a laboratory scale to prepare a large number of polymers<sup>25</sup>. This significant method of organic synthesis has been used in a large number of polymer reactions such as, step-growth polymerization for the synthesis of polyamides<sup>26</sup>, polyimides<sup>27</sup>, poly(amide-imide)s<sup>28</sup>, polyesters<sup>29</sup> polyurea and polythiourea<sup>30</sup>. Also, chain growth polymerization under microwave (MW) irradiation has been used for the synthesis of a series of polymers and macromolecules<sup>31</sup>. In this research work new polyamides containing 1,3-phenylene diamine thioether-amide units in the main chain were synthesized under microwave irradiation and characterized. They are soluble in a series of common organic solvents and showed thermal resistance.



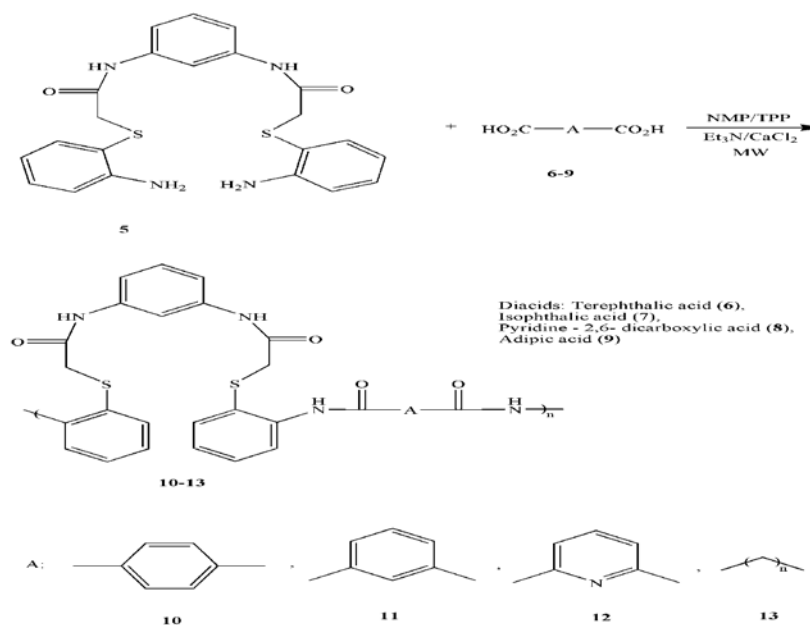
**Scheme 1:** Synthesis of diamine monomer (5).



**Figure 1:** Optimized Structure of diamine monomer (**5**) using PM6 method.

**Table 1:** Calculated physical properties of monomer (**5**).

Energy/A.U.	0.36178 -	DipoleMoment/Debye	4.5604
$E_{\text{HOMO}}/\text{ev}$	-0.31799	Hardness	0.171345
$E_{\text{LUMO}}/\text{ev}$	0.02470-	Polarizability	162.517
Band Gap/ev	0.29329	Ionization Potential	0.31799
Band Gap/Kcal/mol	183.89283	Electron Affinity	0.02470



**Scheme 2:** Synthesis of poly (thioether-amide) s (**10-13**).

## MATERIAL AND METHODS

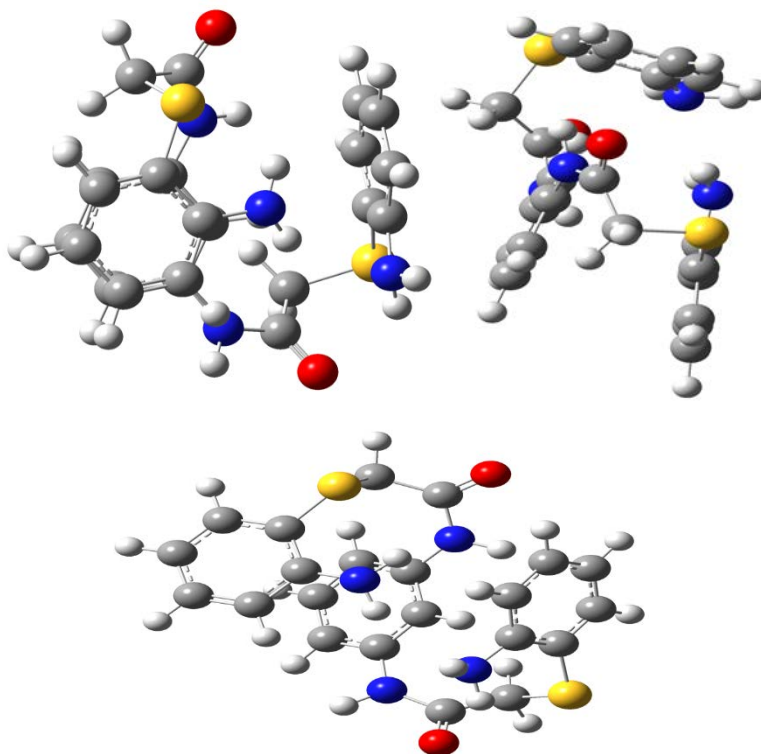
The reactions for the synthesis of monomer were carried out in an efficient hood. All the materials were purchased from Merck, Fluka, Across Organics and Aldrich chemical companies. N-Methyl-2-pyrrolidinone (NMP, Merck) and pyridine (Py, Merck) were purified by distillation under reduced pressure over calcium hydride and stored over 4A° molecular sieves. Triphenylphosphite (TPP, Merck) was purified by fractional distillation under vacuum. Reagent grade aromatic diamine (Aldrich) 1,3-phenylenediamine (**1**) was recrystallized from ethanol. Terephthalic acid (**6**), isophthalic acid (**7**), pyridine – 2,6 – dicarboxylic acid (**8**) and adipic acid (**9**) were purchased from Merck chemical company and were used without further purification. The melting points (uncorrected) were measured with a Barnstead Electrothermal engineering LTD 9100 apparatus. Elemental analysis was performed by a CHN-O- Rapid Heraeus elemental analyzer. FT-IR spectra were recorded in potassium bromide pellets on a Bruker apparatus. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained using BRUKER AVANCE DRX 500 MHz apparatus and mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. Scanning electron micrograph (SEM) images were obtained using a XL30 (Philips) apparatus. The MicroSYNTH system of Milestone which is a multi-mode platform and equipped with a magnetic stirring plate was used for the microwave synthesis. Inherent viscosities ( $\eta_{inh} = \ln \eta_r / c$  at a concentration of 0.5 g dL<sup>-1</sup>) were measured with an Ubbelohde suspended-level viscometer at 30°C using DMSO as solvent. Differential Scanning Calorimetry (DSC) was recorded on a V 4.OB DuPont 2000 system under argon atmosphere at a heating rate of 10 °C Min.<sup>-1</sup>.

**Synthesis of 1, 3-bis (1-aza-2-oxo – 3 – chloro propyl) benzene (**3**):** To acetonitrile (30 ml) were added 1,3-phenylene diamine (1 mmol), triethylamine (2mmol) and chloroacetyl chloride (2 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 24h at room temperature. After completion of the reaction (monitored by TLC) water was added and the resulting precipitate was filtered and recrystallized in ethanol to afford **3** in 94% yields. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 4.25 (s, 4H), 7.26-7.34 (m, 3H), 7.95 (s, 1H), 10.36 (s, 2H) ppm. Analytical calculated for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 46.00; H, 3.86; N, 10.73; Found: C, 46.07; H, 3.85; N, 10.76

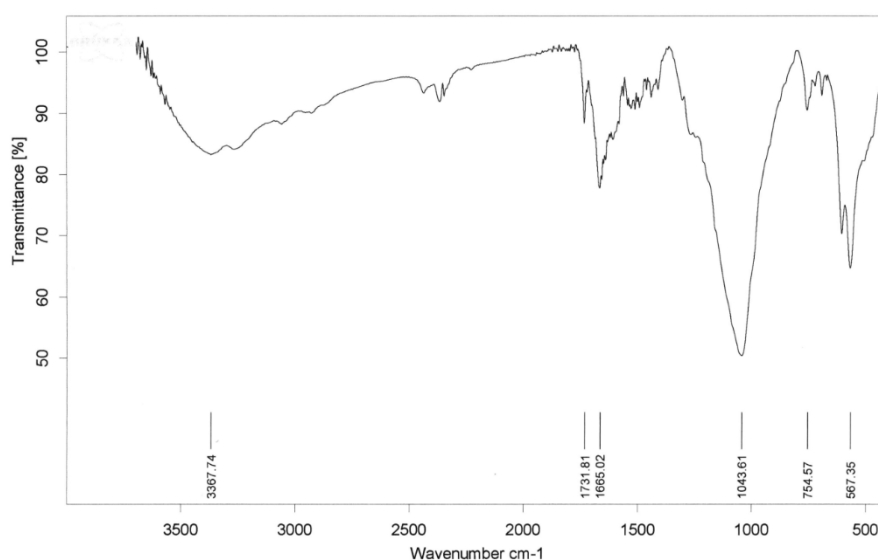
**Synthesis of 1, 3-bis (1-aza-2-oxo - 4-thio-4- (2-aminophenyl) butyryle) benzene (**5**):** To DMF (30 mL) were added 1,3-bis (2-chloro-1-oxo) phenylene diamine (**3**, 1mmol, 0.258 g), K<sub>2</sub>CO<sub>3</sub> (4 mmol, 0.56 g) and 2-aminothiophenol (**4**, 2 mmol) at room temperature. The reaction mixture was stirred at room temperature for 24 hours. After completion of the reaction (monitored by TLC), water was added and the reaction mixture was neutralized with HCl solution. After standing for 2h, the resulting precipitate was filtered and recrystallized in ethanol/water to obtain diamine (**5**) in 92% yield. IR (KBr)  $\nu$  cm<sup>-1</sup>: 2950-3300, 1678, 1667. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 3.87 (s, 4H), 7.21-7.24 (m, 3H), 7.30-7.32 (m, 2H), 7.51-7.56 (m, 4H), 7.90-7.91 (d, J=10 Hz, 2H), 7.95 (s, 1H), 10.36 (s, 2H), 13.11 (b, 2H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 168.31, 167.78, 141.55, 140.12, 133.29, 131.83, 129.93, 128.66, 126.56, 125.08, 115.21, 110.90, 37.45 ppm. MS (EI) m/z (relative intensity %): 412 [M]<sup>+</sup> (1), 302 (24), 284 (66), 177 (100), 108 (100), 77 (28).

**Synthesis of polyamides (**10-13**):** Polyamides were synthesized through the phosphorylation reaction of **5** with various diacids as shown in Scheme 2. A typical example for the preparation of polyamides is given. A mixture of **5** (1 mmol, 0.440 g), terephthalic acid (1 mmol, 0.168 g), 0.3 g of CaCl<sub>2</sub>, 0.6 mL of TPP, 0.5 mL of pyridine, and 4 mL of NMP were added to the quartz tube and irradiated under microwave in 600W for 9 Min. (3×3 Min.) and the rest time of 10 Min. (2×5 Min.). After cooling to room

temperature, the resulting viscous 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 °C overnight. The yields were almost quantitative. Spectral data, thermal properties, viscosity and solubility of these polyamides were reported in the following tables and figures.



**Figure 2:** FT-IR spectrum of diamine monomer (5).



**Figure 3:** FT-IR spectrum of polyamide (10).

## RESULTS AND DISCUSSION

In this research work, we wish to report the synthesis and characterization of polyamides obtained from the reaction of a new monomer (**5**), containing 1, 3-bis (1-aza-2-oxo - 4-thio-4- (2-aminophenyl) butyryle) benzene units, and diacids under microwave irradiation. Dichloroamide (**3**) was prepared from the reaction of **1** and chloroacetyl chloride. Diamine monomer (**5**) was prepared from the reaction of **3** and 2-aminothiophenol (**4**) in DMF at room temperature. Optimized structure of diamine monomer (**5**) were calculated using gaussian 09 programs using semiempirical method with PM6 basis set. The calculated physical property of **5** is reported in **Table 1**. The IR spectrum of diamine (**5**) is appeared in **Figure 2**. Polymerization were performed using Yamasaki phosphorylation reaction of diamine and diacids in the presence of triphenylphosphite (TPP), pyridine (Py), N-methylpyrrolidinone (NMP) and calcium chloride (CaCl<sub>2</sub>) under microwave irradiation almost in quantitative yields (**Table 2**). Polymers were precipitated in boiling methanol and washed with hot water and methanol, respectively. The inherent viscosities and the yields of polyamides were reported in **Table 2**. The viscosities of polyamides were measured in DMSO at 30 °C and are in the range of 0.42-0.48 (**Table 2**). The IR and <sup>1</sup>H NMR spectra of polyamides were showed the correct structures (**Table 3**). The IR spectra of polyamide **10** is appeared in **Figure 3**; and showed the corresponding structure according to the main functional groups (**Table 3**).

The thermal stability of polyamides was evaluated by Differential Scanning Calorimetry (DSC). Glass transition temperatures (T<sub>g</sub>) of polyamides were evaluated by differential scanning calorimetry (DSC) and are in the range of 184-201 °C. The results are summarized in **Table 2**. According to the structure of diacid, insertion of the methylene groups in the diamine structure is increased the overall flexibility of the polymer chains and decreased the T<sub>g</sub> value. The polymers containing diacids without other flexible groups (such as terephthalic and isophthalic acid and 2, 6-pyridinedicarboxylic acid derivatives) have high T<sub>g</sub>, because of the lower flexibility of the overall polymer chains.

The solubility behavior of polyamides 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 4**. All the polymers showed reliable solubility in polar organic solvents. This might be due to the presence of aromatic and methylene units which decreased intermolecular and intramolecular hydrogen bonding but amine, amide and thioether units increases the intermolecular and intramolecular hydrogen bonding and flexibility and then increase the crystallinity and close packing. According to the above discussions the solubility of polyamides were affected by the several variables and the solubility varies according to the structure of diamine monomer (**5**) and aromatic diacids.

**Table 2:** Inherent viscosity, glass transition temperature and the yields of polyamides (**10-13**).

Polymer	Yield (%)	$\eta_{inh}(g/dL)^a$	T <sub>g</sub> /°C
<b>10</b>	98	0.48	195
<b>11</b>	95	0.42	189
<b>12</b>	96	0.45	201
<b>13</b>	93	0.44	184

<sup>a</sup>Measured at a polymer concentration of 0.5 g/dL in DMSO solvent at 30 °C.

**Table 3:** Spectral data of polymers (**10-13**).

Polymer	IR (cm <sup>-1</sup> )	<sup>1</sup> H NMR (500 MHz, DMSO-d <sub>6</sub> ): $\delta$ (ppm)
<b>10</b>	2970-3540, 1731, 1665, 1043.	3.95 (s, 4H), 6.74-6.78 (m, 2H), 7.14-7.17 (m, 1H), 7.34-7.36 (m, 4H), 7.50-7.55 (m, 2H), 8.08 (s, 1H), 8.13-8.18 (m, 1H), 8.35 (s, 4H), 9.31 (s, 1H), 10.12 (b, 2H), 10.16 (b, 2H).
<b>11</b>	2981-3536, 1734, 1667, 1049.	3.41 (s, 4H), 6.74-6.78 (m, 2H), 7.14-7.17 (m, 2H), 7.27-7.33 (m, 2H), 7.44-7.56 (m, 4H), 7.68-7.74 (m, 1H), 8.01-8.01 (m, 2H), 8.24-8.34 (m, 1H), 8.51-8.53 (m, 1H), 9.32 (s, 1H), 10.46 (s, 2H), 10.47 (s, 2H).
<b>12</b>	2974-3542, 1739, 1663, 1045.	3.42 (s, 4H), 6.88-6.92 (m, 2H), 7.16-7.18 (m, 2H), 7.34-7.36 (m, 2H), 7.52-7.57 (m, 4H), 8.09-8.12 (m, 2H), 8.29-8.36 (m, 1H), 8.52-8.55 (m, 1H), 9.33 (s, 1H), 10.49 (s, 2H), 10.53 (s, 2H).
<b>13</b>	3150-3650, 2434, 1664, 1661, 1123, 1056, 984.	2.37 (s, 4H), 3.46 (s, 4H), 3.77 (s, 4H), 6.74-6.78 (m, 7.14-7.17 (m, 4H), 7.25-7.27 (m, 2H), 7.29-7.30 (m, 1H), 7.54-7.55 (m, 1H), 7.91-7.92 (m, 1H), 9.31 (s, 1H), 9.86 (s, 2H), 10.12 (s, 2H).

**Table 4:** The solubility of polyamides (**10-13**).

Polymer	NMP	DMAc	DMF	DMSO	m-Cresol	THF
<b>10</b>	++	++	++	++	±	-
<b>11</b>	++	++	++	++	+	-
<b>12</b>	++	++	++	++	-	-
<b>13</b>	++	++	++	++	-	+

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

<sup>a</sup> Solubility measured at a polymer concentration of 0.05 g/ml.

## CONCLUSION

A series of new polyamides based on the 1, 3-phenylene diamine and 2-aminothiophenol were successfully obtained through the direct polycondensation reaction of 1, 3-bis (1-aza-2-oxo - 4-thio-4- (2-aminophenyl) butyryl) benzene with various diamines via Yamazaki method under microwave irradiation (MW). The polymers showed reliable solubility and high thermal stability. This is due to the presence of phenylene and methylene groups in the presence of tetrahedral sulfide functional group. The presence of higher symmetric and rigid structures in the diamine and as a result in the overall polymer chains showed the higher thermal stability. Thus, we afforded polyamides with improved solubility and high heat resistance.

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**Corresponding author: Esmael Rostami**

Department of chemistry, Payame Noor University, PO BOX 19395-3697  
Tehran, Iran.