ISSN : 0974 - 7486 Volume 11 Issue 9

Materials Science

An Indian Journal

Full Paper

MSAIJ, 11(9), 2014 [302-310]

Microwave assisted synthesis and characterization of new organosoluble and thermally stable poly (thioether-amide)s bearing aminothiophenol and xylyl units in the main chain

EsmaelRostami*, Akram Khodadadi, Zahra Heidari, Zahra Keshavarz, Mahmood Feraidooni, Maryam Bagherzadeh, Zahra Abshirini, Masume Zangooei

Department of chemistry, Payame Noor University, PO BOX 19395-3697 Tehran, (IRAN)

E-mail : esmrostami@yahoo.com

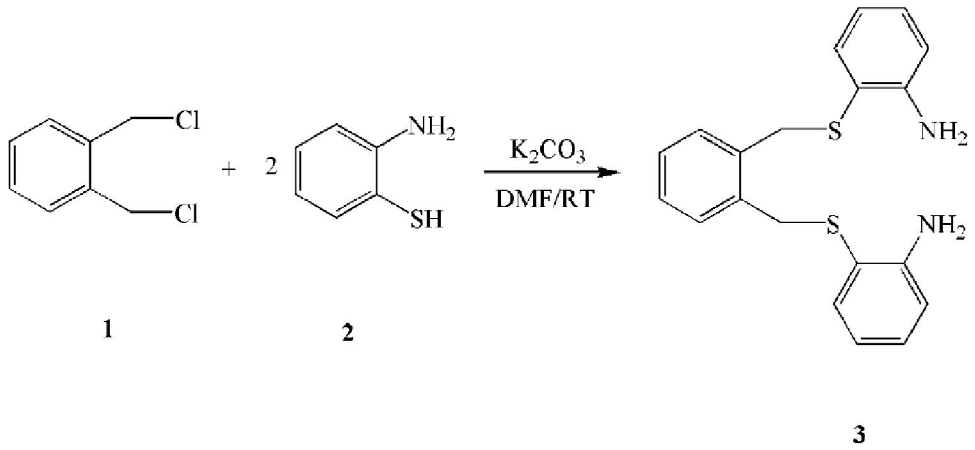
ABSTRACT

New polyamides containing aminothiophenol, xylyl and thioether units were prepared under microwave irradiation and their solubility, thermal behavior, viscosity and surface morphology were evaluated. The viscosities of polyamides are in the range of 0.39-0.49 and glass transition temperatures (T_g) are in the range of 245-276°C. Decomposition temperatures of 10% weight loss T (10) rangingfrom 133 to 274 °C,also, the temperature of 50% weight loss T (50) are in the range of 291-318 °C and char yields ranging from 5 to 17% at 540 °C. These polyamides showed good solubility in common organic solvents. Surface morphology of these polymers showed amorphous and microsphere structure.

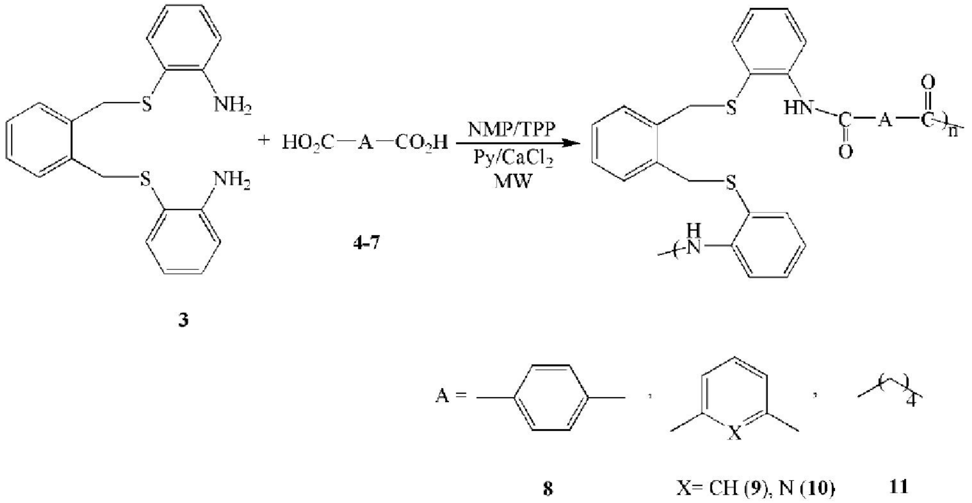
INTRODUCTION

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 materials[1-4]. Because of their excellent properties, they are used as good alternatives for a series of industrial materials such as metals and ceramics in applications[5]. The new industry and technology requires high performance materials with several properties and stable in vigorous conditions such as elevated temperatures, high acidic and basic media and humid and cold regions[6]. Polyamides are important candidates for these advanced materials have ability to change their properties with a series of modifications and gain desired application[7]. Wholly aromatic polyamides (aramides) have a few disadvantages such as poor solubility, difficult processability and high melting and as a result restricted applications[8]. Several procedures were examined for achieve these drawbacks containing the use of softening aliphatic chains, ethers 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].

Microwave irradiation (MW), as a nonconventional heating procedure, was used for the preparation of a large number of compounds[12]. In comparison with conventional heating this method of synthesis have a series of advantages such as high yields, short reaction times, the use of small volume of solvents or the syntheses in dry media without solvent (solventless synthesis), ecofriendly and environmentally benign[13]. In polymer and material science, microwave irradiation was used in broad range from polymer synthesis to processing[14]. A large number



Scheme 1 : Synthesis of diamine (3)



Scheme 2 : Synthesis of polyamides (8-11)

of polymer synthetic routes were reported using microwave irradiation[15]. Various polymeric materials such as polyamides, polyesters, polyimides, polyethylene, polystyrene and polyurea and polythiourea were prepared under microwave irradiation using different kinds of polymer syntheses routes; for example, step-growth and chain growth polymerization[15,16].

In continuation on previous research works on the synthesis of polyamides[17], in this research work new organosuloble and thermally stable poly (thioether-amide)scontaining aminothiophenoland xylylunits in the main chain were synthesized under microwave irradiation. The morphology of these polymers was studied using scanning electron microscopy and showed amorphous and microsphere structures.

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 ^{O} molecular sieves. Triphenylphosphite (TPP, Merck) was purified by fractional distillation under vacuum. FT-IR spectra were recorded in potassium bromide pellets on a Bruker apparatus. The ^{1}H NMR and ^{13}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 multimode platform and equipped with a magnetic stirring plate was used for the synthesis. Inherent viscosities

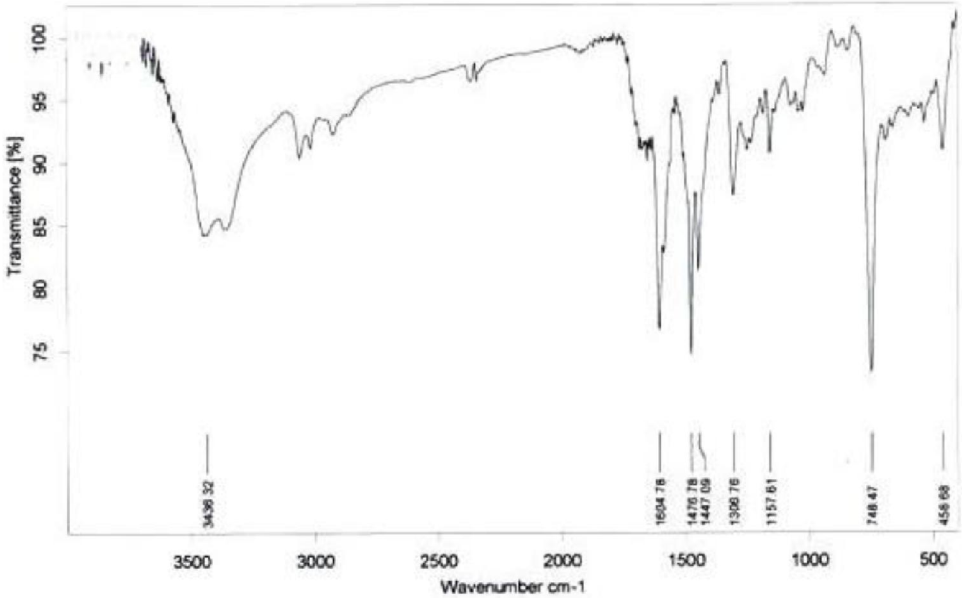


Figure 1 : FT-IR spectrum of diamine (3, DA)

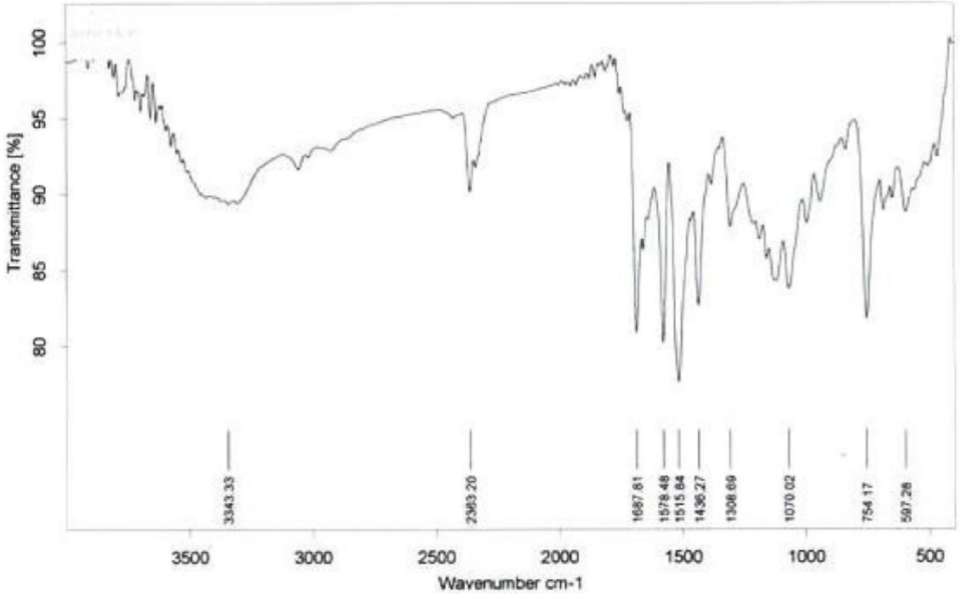


Figure 2 : FT-IR spectrum of polyamide (10, PPY)

(η_{inh} = lnηr/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.

TABLE 1: Inherent viscosities and the yields of polyamides

Polymer	Yield (%)	η_{Inh}(g/dL)^a
PPH (8)	98	0.49
PMP (9)	96	0.41
PPY (10)	94	0.42
PAD (11)	95	0.39

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

Thermogravimetric analysis (TGA) were recorded on a V 5.1A DuPont 2000 system under argon atmosphere at a heating rate of 10 °C Min.$^{-1}$, and differential scanning calorimetry (DSC) recorded on a V 4.OB DuPont 2000 system under argon atmosphere at a heating rate of 10 °C Min.$^{-1}$.

Synthesis of diaminemonomer (3, DA)

To 1 (2 mmol, 0.18g) under N_2, was added potassium carbonate (4 mmol, 0.56 g), dimethylformamide (DMF, 30 mL) and 2-aminothiophenol (4 mmol) at room tempearture. The mixture was stirred at room tem-

TABLE 2 : Spectral data of polymers

Polymer	IR (cm^{-1})	^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm)
PPH (8)	3339, 3105, 2986, 1733, 1676, 1499, 1431, 1068, 754.	4.19 (s, 4H), 7.05-7.08 (m, 3H), 7.14-7.17 (m, 3H), 7.29-7.36 (m, 3H), 7.41-7.45 (m, 1H), 7.48-7.52 (m, 2H), 7.58-7.62 (m, 2H), 7.95-7.97 (m, 2H), 8.34 (s, 1H), 10.06 (s, 2H).
PMP (9)	3342, 3145, 2982, 1677, 1578, 1510, 1042, 755.	4.51 (s, 4H), 6.76-6.78 (m, 1H), 7.06-7.08 (m, 1H), 7.11-7.14 (m, 3H), 7.25-7.27 (m, 3H), 7.29-7.32 (m, 3H), 7.91 (dd, J= 1, 8Hz, 1H), 7.69-7.71 (m, J= 7.5 Hz, 1H), 8.23-8.25 (m, 2H), 8.56 (d, J= 1Hz, 1H), 10.39 (s, 2H).
PPY (10)	3343, 3121, 2991, 1687, 1515, 1070, 754.	4.50 (s, 4H), 6.77-6.80 (m, 1H), 7.07-7.09 (m, 1H), 7.13-7.16 (m, 3H), 7.28-7.31 (m, 3H), 7.32-7.36 (m, 3H), 7.95 (dd, J= 1, 8Hz, 1H), 8.20 (d, J= 7.5 Hz, 1H), 8.31-8.32 (m, 1H), 8.44 (d, J= 8Hz, 1H), 10.41 (s, 2H)
PAD (11)	3331, 3107, 2985, 1731, 1678, 1495, 1436, 1062, 755.	1.53 (s, 4H), 2.24 (s, 4H), 4.19 (s, 4H), 7.05-7.08 (m, 3H), 7.14-7.17 (m, 3H), 7.29-7.36 (m, 3H), 7.41-7.45 (m, 1H), 7.95-7.97 (m, 2H), 8.34 (s, 1H), 10.06 (s, 2H)

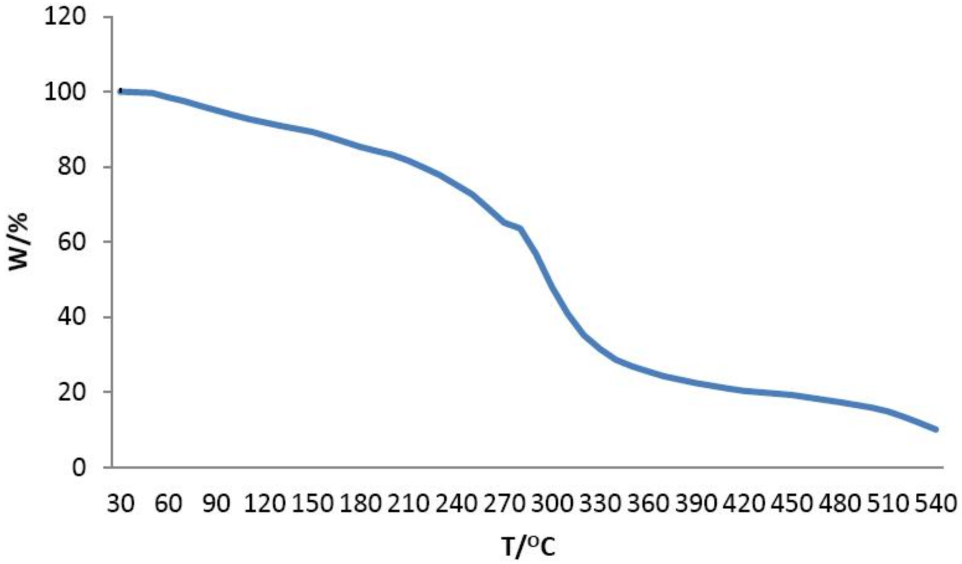


Figure 3 : TGA of polyamide (8, PPH)

TABLE 3 : Thermal properties of polyamides

Char yields[c] (%)540 °C	T_{50}[b] (°C)	T_{10}[a] (°C)	T_g (°C)	Polymer
17	301	147	276	PPH (8)
12	311	136	271	PMP (9)
5	318	274	267	PPY (10)
11	291	133	245	PAD (11)

[a]Temperature of 10% weight loss determined in argon atmosphere; [b]Temperature of 50% weight loss determined in argon atmosphere; [c]Char yield calculated as the percentage of solid residue after heating from room temperature to 550 °C under argon.

TABLE 4 : The solubility of polyamides (8-11)

THF	m-Cresol	DMSO	DMF	DMAc	NMP	Polymer[a]
+	++	++	++	++	++	PPH (8)
+	+	++	++	++	++	PMP (9)
±	++	++	++	++	++	PPY (10)
+	++	++	++	++	++	PAD (11)

(++) Soluble at room temperature; (+) soluble upon heating; (±) partially soluble; [a]Solubility measured at a polymer concentration of 0.05 g/ml

perature for 24h. After completion of the reaction (monitored by TLC), water was added and extracted to chloroform (3×50 mL). The combined chloroform layers were dried (sodium sulfate) and evaporated to afford crude reaction mixture. The resulting mixture was purified with short column chromatography on silica gel using n-hexane/ethyl acetate as eluent to afford diamine (3, DA) as an oil in 91% yield; IR (KBr): 3436, 3351, 2981, 1604, 1476, 1447, 1306, 748 Cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 4.03 (s, 4H), 5.33-5.37 (b, 4H), 6.44-6.45 (m, 2H), 6.73 (d, J= 8Hz, 2H), 7.01-7.07 (m, 6H), 7.18-7.20 (m, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 150.22, 136.95, 135.94, 133.98, 131.18, 130.80, 130.36, 130.02, 129.61, 128.63, 127.98, 127.77, 120.17, 117.33, 116.49, 115.22, 48.41, 36.33, 36.04 ppm; MS EI (electron impact) m/z (relative intensity %): 352 $[M]^+$ (49), 228 (76), 194 (100), 124 (78), 80 (100).

Synthesis of polyamides

Polyamides were synthesized by the Yamasaki phosphorylation reaction of diamine (3, DA) with various diacids (terphthalic acid (4), isophthalic acid (5), 2,6-pyridine diarboxylic acid (6) and adipic acid (7)) as shown in Scheme 2. A typical example for the preparation of polyamides is given. A mixture of 3 (1 mmol), terphthalic acid (4, 1 mmol), 0.3 g of $CaCl_2$, 0.6 mL of TPP, 0.5 mL of pyridine, and 4 mL of NMP were added to the microwave cell and irradiated under microwave in 600W for 9 Min. (3×3 Min.) and the rest time of 10 Min. After cooling at room temperature, the resulting viscose reaction mixture was poured into 300 mL of boiling methanol. The resulting crude polymer was precipitated and then filtered. The 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. Thermal properties, viscosity, solubility and surface studies of these polyamides were reported in the following tables and figures.

RESULTS AND DISCUSSION

In this research work, we wish to report the synthesis and characterization of new organosoluble and thermally stable polyamides. Diamine monomer (3, DA) was prepared from the reaction of 1,2-bis chloromethyl benzene (1) and 2-aminothiophenol (2) in the presence of K_2CO_3 in dimethylformamide (DMF) at room temperature (scheme 1). The IR spectrum of monomer (3, DA) is appeared in figure 1. Polyamideswas prepared from the reaction of monomer (3, DA), containing sulfide and benzene units and appropriate diacids (terphthalic acid (4), isophthalic acid (5), 2,6-pyridine dicarboxylic acid (6), adipic acid (7)) under microwave irradiation. Polymerization were performed using Yamazaki phosphorilation reaction of diamine(3) and diacids (4-7) in the presence of triphenylphosphite (TPP), pyridine (Py), N-methylpyrolidinone (NMP) and calcium chloride ($CaCl_2$) under microwave irradiation and four new polyamides were prepared (8-11, scheme 2). Polymers were precipitated in boiling methanol (300 ml) and washed with hot distilled water and methanol, respectively, and then dried under vacuum. The inherent viscosities and the isolated yields (94-98%) of polyamides were reported in TABLE 1. The IR and ^1H NMR spectra of polyamides showed the correct structures (TABLE 2). The IR spectrum of polyamide (10, PPY) is appeared in Figure 2; and showed the corresponding structure according to the major functional groups.

The solubility's of polyamides was investigated in a series of common 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 excellent solubility in polar organic solvents. This might be due to the presence of polarized and tetrahedral thioether groups with flexible and three dimensional structures, increased solvent diffusion and chain solvent interaction, intramolecular hydrogen bonding and reduced the close packing and crystallinity. Also, very flexible CH_2 groups in the main chain increase the diffusion of solvent and thus the solubility is high. The viscosities of polyamides were measured in DMSO at 30 °C and are in the range of 0.39-0.49 (TABLE 1).

The thermal behavior of polyamides was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The entire polymers showed good thermal stability, the results are summarized in TABLE 4 and for 8 (PPH) is appeared in Figure 3. Glass transition temperatures (T_g) of polyamides were obtained by differential scanning calorimetry (DSC) and are in the range of 245-276°C. The results are reported in TABLE 3. According to the structure of diacid, insertion of the aliphathic groups in the diacidstructure is increased the overall flexibility of the polymer chains and decreased the T_g value. The polymers containing diacids without flexible groups have higherT_g values, because of the lower flexibility of the overall polymer chains, increased crystallinity and close paking.

All the polymers using thermogravimetric analysis (TGA) showed good thermal stability, their decomposition at argon atmosphere for temperature of 10% weight loss T (10) was in the range of 133-274 °C and

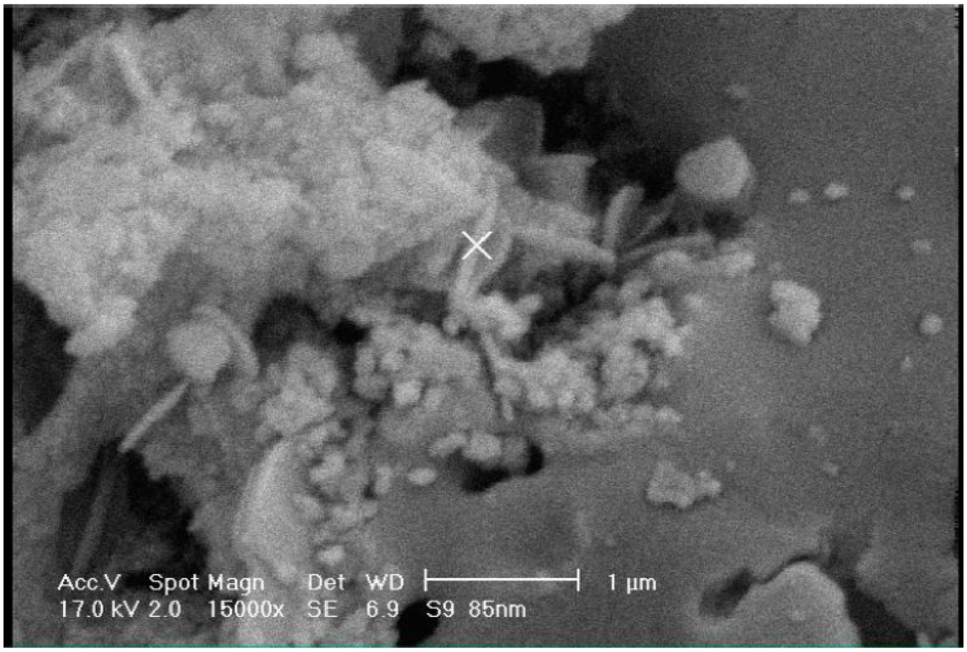


Figure 4 : SEM image of polyamide 8 (PPH)

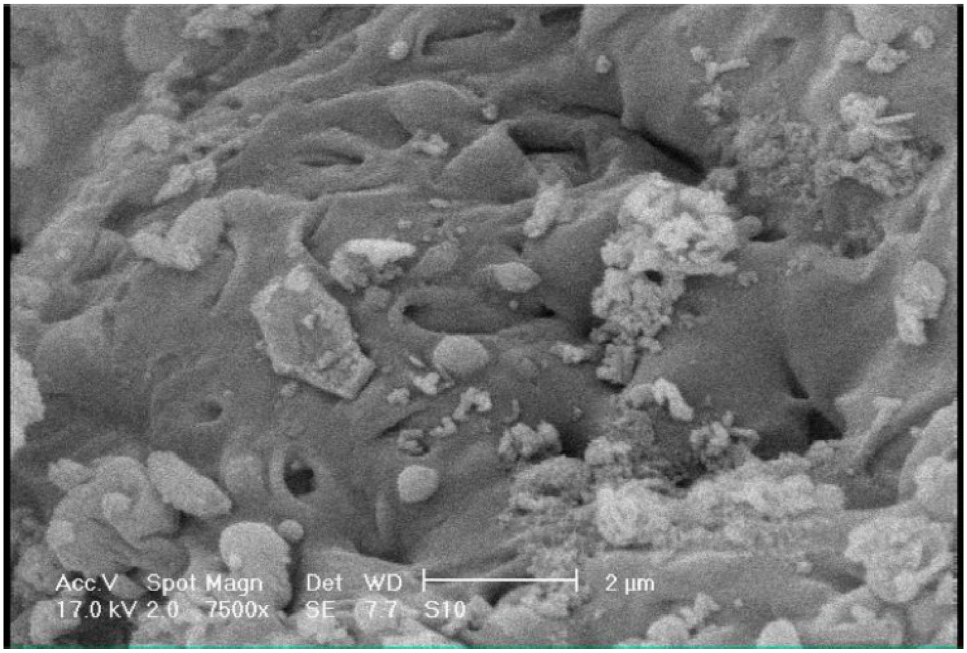


Figure 5 : SEM image of polyamide 9 (PMP)

the temperature of 50% weight loss T (50) was in the range of 291-318 °C which indicates good thermal stability in the prepared polymers. The polymer decomposition temperature for various percent of decomposition and char yield (in the range of 5-17%) at 540 °C for all polymers are summarized in TABLE 3 and according to the obtained data for thermal stability, the polymer with diacid containing the aliphatic subunits show the lower thermal stability in comparison with the polymers containing diacids without these groups and more symmetric structures.

The surface morphology of polymers was studied using scanning electron microscopy (SEM) images, and showed amorphous and nanoparticle structures (Figures 4, 5, 6 and 7). Polymers bearing aromatic diacid are amorphous structure and aliphatic diacids in the polymer main chain lead to microsphere morphology.

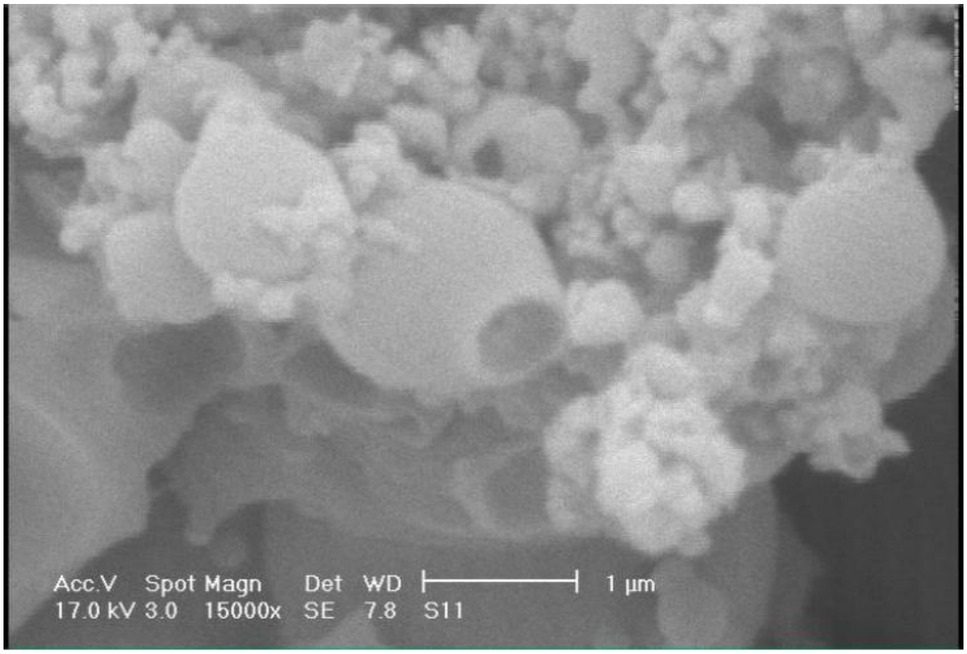


Figure 6 : SEM image of polyamide 10 (PPY)

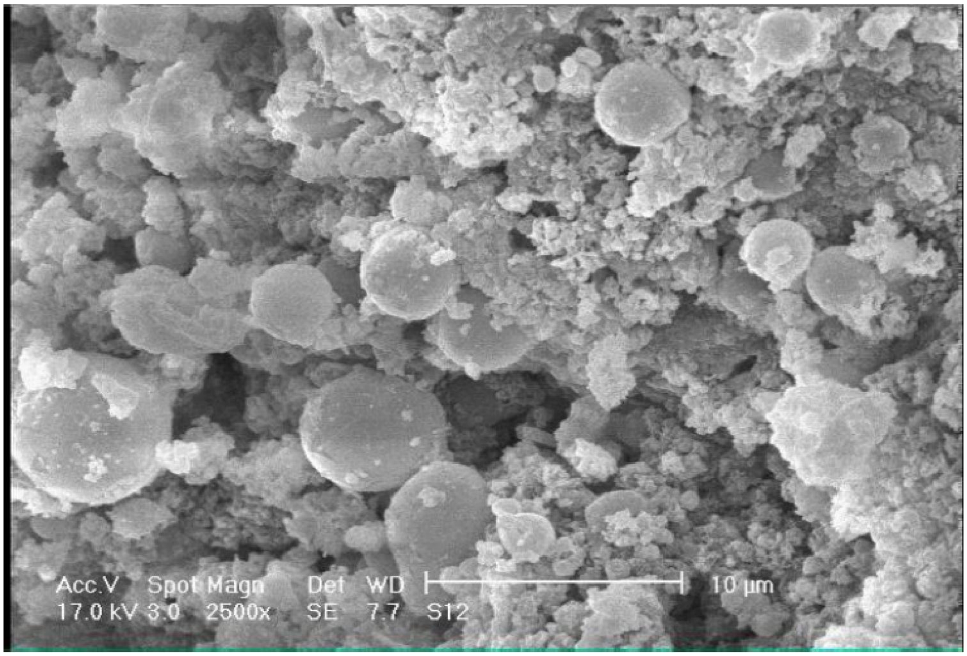


Figure 7 : SEM image of polyamide 11 (PAD)

CONCLUSION

A series of new polyamides based on ortoxylyl, 2-aminothiophenol and appropriate diacids were successfully obtained through the direct polycondensation reaction via Yamazaki method under microwave irradiation (MW). The polymers showed enhanced solubility and high thermal stability. This is due to the presence of tetrahedral sulfide groups in the polymer main chain. The thioether interact with polar solvents and increased diffusion of solvent to the polymer main structure and decreased interchain interactions. The presence of methylene groups in the main chainincreased solubility and decreased thermal stability. Thus, we afforded polyamides which lead to improved solubility and higher heat resistance. Surface study of these polymers showed the amorphous and microsphere structures.

ACKNOWLEDGEMENT

The financial support of this work by Payame Noor University (PNU) Research Council is acknowledged.

REFERENCES

[1] **a)** P.E.Cassidy; Thermally Stable Polymers, Marcel Dekker; New York, **(1980)**; **b)** Z.Wu, Y.Huang, C.Zhang, D.Zhu, Z.Bian, M.Ding, L.Gao, Z.Yang; A simple and efficient way to synthesize optically active polyamides by solution polycondensation of di-*O*-methyl-L-tartaryl chloride with diamines", J.Appl.Polym.Sci.,**117(6)**, 3558-3567 **(2010)**.

[2] **a)** H.H.Yang; Aromatic High-Strength Fibers, Wiley; New York, **(1986)**; **b)** B.Ramezanzadeh, M.M. Attar; Characterization of the fracture behavior and viscoelastic properties of epoxy-polyamide coating reinforced with nanometer and micrometer sized ZnO particles, Prog.Org.Coat.,**71(3)**, 242-249 **(2011)**.

[3] **a)** S.Mallakpour, Z.Rafiee; Microwave-assisted clean synthesis of aromatic photoactive polyamides derived from 5-(3-acetoxynaphthoylamino)-isophthalic acid and aromatic diamines in ionic liquid, Eur.Polym.J., **43(12)**, 5017-5025 **(2007)**; **b)**E.Rostami; Synthesis and characterization of new polyamides containing pyridine thioetherunits in the main chain under microwave irradiation (MW) and their nanostructure, Int.J.Polym.Mat.,**62(3)**, 175-180; **(2013)**.

[4] A.Tundidor-Camba, C.A.Terraza, L.H.Tagle, D.Coll; "Polyamides obtained by direct polycondesation of 4-[4-[9-[4-(4-aminophenoxy)-3-methyl-phenyl] fluoren-9-YL]-2-methyl-phenoxy]aniline with dicarboxylic acids based on a diphenyl-silane moiety", J.Appl.Polym.Sci.,**120(4)**, 2381-2389 **(2011)**.

[5] **a)** A.H.Frazer; High-Temperature Resistant Polymers, Wiley Interscience; New York, **(1968)**; **b)** T.Solomun, A.Schimanski, H.Sturm, R.Mix, E.Illenberger; Surface modification of polyamides by direct fluorination",e-polymers, **008**, **(2004)**.

[6] **a)** T.S.Jo, C.H.Ozawa, B.R.Eagar, L.V.Brownell, D.Han, C.Bae; Synthesis of sulfonated aromatic poly (ether amide)s and their application to proton exchange membrane fuel cells, J.Polym.Sci.Part A: Polym.Chem., **47(2)**, 485-496 **(2009)**; **b)** X.Yu, X.Zhao, C.Liu, Z.Bai, D.Wang, G.Dang, H.Zhou, C.Chen; Synthesis and properties of thermoplastic polyimides with ether and ketone moieties, J.Polym.Sci.Part A: Polym.Chem., **48(13)**, 2878-2884 **(2010)**.

[7] G.Yu, B.Li, J.Liu, S.Wu, H.Tan, C.Pan, X.Jian; Novel thermally stable and organosoluble aromatic polyamides with main chain phenyl-1,3,5-triazine moieties, Polym.Degrad.Stabil., **97(9)**, 1807-1814 **(2012)**.

[8] **a)** Y.C.Kung, G.S.Liou, S.H.Hsiao; Synthesis and characterization of novel electroactive polyamides and polyimides with bulky 4-(1-adamantoxy)triphenylamine moieties, J.Polym.Sci.Part A: Polym.Chem., **47(7)**, 1740-1755 **(2009)**; **b)** J.F.Espeso, A.E.Lozano, J.G.D.L.Campa, I.Garcia-Yoldi, J.D.Abajo; Synthesis and properties of new aromatic polyisophthalamides with adamantylamide pendent groups, J.Polym.Sci. Part A: Polym.Chem., **48(8)**, 1743-1751 **(2010)**.

[9] S.Mehdipour-Ataei, H.Heidari; Synthesis and characterization of novel soluble and thermally stable polyamides based on pyridine monomer, Macromol.Symp., **193(1)**, 159-167 **(2003)**.

[10] M.Ghaemy, M.Hassanzadeh, S.M.A.Nasab, M.Taghavi; Ionic liquids in the synthesis of high-performance fluorinated polyamides with backbones containing derivatives of imidazole and carbazole rings, Polym.J., **45**, 622-630 **(2013)**.

[11] **a)** H.S.Lee, S.Y.Kim; Synthesis of poly (arylene ether amide)s containing CF_3groups by nitro displacement reaction of AB-Type monomers",Macromol. Rapid.Commun., **23**, 665-671 **(2002)**; **b)** M.Hajibeygi, M.Shabanian; Synthesis and characterization of new thermally stable and organosoluble polyamides by direct polycondensation", Des. Monomers Polym., **16(3)**, 222-232 **(2013)**.

[12] A.Loupy; Microwaves in Organic Synthesis, 2nd Edition, Wiley VCH; Weinheim, **(2006)**.

[13] **a)** R.S.Varma; Solvent-free organic syntheses using supported reagents and microwave irradiation, Green Chem., **1(1)**, 43-55 **(1999)**; **b)** A.Loupy; Microwaves in Organic Synthesis", Wiley-VCH; Weinheim, **(2002)**; c) M.Nuchter, B.Ondruschka, W.Bonrath, A.Gumb; Microwave assisted synthesis – a critical technology overview, Green Chem., **6(3)**, 128-141 **(2004)**.

[14] **a)** S.Sinnwell, H.Ritter, Recent advances in microwave-assisted polymer synthesis, Aust.J.Chem., **60(10)**, 729-743 **(2007)**; **b)** R.Hoogenboom,

U.S.Schubert; Microwave-Assisted Polymer Synthesis: Recent Developments in a Rapidly Expanding Field of Research, Macromol. Rapid Commun., **28(4)**, 368-386 **(2007)**; **c)** S.Ren, M.J.Bojdys, R.Dawson, A.Laybourn, Y.Z.Khimyak, D.J.Adams, A.I.Cooper; Porous, Fluorescent, Covalent Triazine-Based Frameworks Via Room-Temperature and Microwave-Assisted Synthesis, Adv.Mater., **24(17)**, 2357–2361 **(2012)**.

[15] **a)** F.Wiesbrock, R.Hoogenboom, U.S.Schubert; Microwave Assisted Polymer Synthesis: State of the Art and Future Perspectives, Macromol.Rapid Commun., **25(22)**, 739-1764 **(2004)**; **b)** G.Sen, S.Mishra, G.U.Rani, P.Rani, R.Prasad; Microwave initiated synthesis of polyacrylamide grafted Psyllium and its application as a flocculant, Int.J.Biol.Macromol., **50(2)**, 369-375 **(2012)**.

[16] **a)** S.Mallakpour, Z.Rafiee; Application of microwave-assisted reactions in step-growth polymerization: a review, Iranian Polym.J., **17(12)**, 907-935 **(2008)**; **b)** R.Rahul, U.Jha, G.Sen, S.Mishra; A novel polymeric flocculant based on polyacrylamide grafted inulin: Aqueous microwave assisted synthesis”, Carbohyd.Polym., **99**, 11-21 **(2014)**.

[17] **a)** E.Rostami, M.Ghaedi, M.K.Z.Zadeh; Synthesis and characterization of newpolyamides bearing dibenzosulfoneunits in themainchain:Microwave conditions and nanostructures, Macromol.Ind.J., **8(1)**, 12-18 **(2012)**; **b)** E.Rostami, H.Fathi, A.N.Ziarati; Synthesis and characterization of new polyamides bearing 1,1.- thiodi (2-methoxy-3-naphthoyl) structure in the main chain: Microwave synthesis, nanostructures, Nanosci.Nanotech.Ind.J., **6(1)**, 21-27 **(2012)**; **c)** E.Rostami, A.Zare, M.Zangooei; Synthesis and characterization of new polyamides bearing xylyldithiophenoxide units in the main chain: Microwaveirradiation, nanostructures, Mat.Sci.Ind.J., **8(6)**, 245-250 **(2012)**.