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Synthesis and characterization of new polyamides bearing 2,2'-thiobis (1- naphthoxy) units in the main chain; microwave irradiation, nanostructures

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ABSTRACT

A new-type of sulfide containing diacid (2,2'-thiobis (1-naphthoxy acetic acid)) (NA) was synthesized from 1-naphthol in three steps. The obtained diacid (NA) was used to prepare novel thermally stable poly (sulfide ether amide)s via polyphosphorylation reaction. The properties of these new polyamides were investigated. These polyamides showed inherent viscosities in the range of 0.47–0.59 dL g^{-1} in N,N-dimethylsulfoxide (DMSO) at 30 °C and at a concentration of 0.5 g dL^{-1}. All the polyamides were readily soluble in a variety of polar solvents and showed thermal resistance. The morphology of polymers shows nanoparticles and nanostructures.

KEYWORDS

Poly (sulfide-ether-amide)s;
1-naphthol;
Microwave synthesis;
Thermal stability;
2,2.-thiobis (1-hydroxy naphthalene);
Nanoparticle;
Nanostructure.

INTRODUCTION

Aromatic polyamides have good thermal stability, high chemical resistance, and excellent mechanical properties that make them important candidates for applications in many areas of science and technology[1–4]. However, some of disadvantages such as poor solubility and high melting point make all of these polymers difficult to process and application. The reasons for these properties are strong interchain interactions, high symmetric units and chains and thus macromolecular rigidity and semicrystallinity. A large number of researches were performed to prepare polyamides with substituents structural irregularities to minimize crystallinity, chain symmetric and macromolecular rigidity and improve solubility without compromising their other desired properties. These efforts include introducing flexible and irregular segments into the polymer chain[5–9], replacing symmetrical aromatic rings and substituents by unsymmetrical ones[10–14], introducing bulky and aliphatic pendant groups to minimize interchain forces and interactions and thus, preparation of a polyamide with low crystallization properties[15–19], and as a results synthesis of a polyamide with non-coplanar structure[20–23].

Generally, one important approach to increase the solubility and processability of polyamides without sacrificing their high thermal stability is the introduction of large and nonpolar pendant groups into polymer backbone.

Insertion of flexible linkages and groups into the polymer main chain (e.g. –S-, -SO-, –O– and –SO2–) lowers the segmental rotational barrier and increase the degree of conformational freedom, thus the glass transition temperature (Tg) and crystallinity were reduced and solubility and processability were increased. The introduction of polyalicyclic aromatic units such as naphthalene into the polymer backbone would facilitate less polymer-polymer chain interaction and increase the solubility of polymer. Naphthalene is a bulky and rigid structure which also has high heat resistance[24,25]. Incorporation of naphthalene group may disrupt and reduced the crystal packing, reducing interchain interactions and improving solubility of the polyamide[26]. Poly (phenylene sulfide)s (PPS) are classified as processable thermoplastic with flame-resistance character[27]. As a result, insertion of sulfide in the polymer backbone enhances the processability, thermal stability and solubility of resulting polymers[28].

In continuation of our researches on the synthesis of new polyamides[29], in this research, new high thermal resistance polyamides bearing sulfide and naphthalene units in the polyamide backbone were prepared[30], we proposed improved solubility together with retained high thermal stability could be achieved by introduction of bulky naphthalene rings with bridged sulfide group. The present study describes the synthesis of new ether diacid monomer and its derived polyamides. The obtained diacid was reacted with aromatic diamines via phosphorylation polycondensation reaction to synthesize novel thermally stable poly (sulfide-ether-amide). The surface morphology of polymers was evaluated using scanning electron microscopy and their SEM images were showed the nanoparticle and nanostructures.

EXPERIMENTAL

The reactions for the synthesis of monomer were carried out in an efficient hood cupboard. 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. Reagent grade aromatic diamines (Aldrich) including 1,5-diaminonaphthalene (DAN) and 3,3'-diaminodiphenylsulfone were recrystallized from ethanol. 4,4'-Oxydianiline (ODA) and p-phenylene diamine (PPD) were purified by sublimation. 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. IR spectra were recorded in potassium bromide pellets on a Perkin Elmer 843, the ^1H NMR and ^{13}C NMR spectra were obtained using BRUKER AVANCE DPX 300 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^{-1}) were measured with an Ubbelohde suspended-level viscometer at 30ºC using DMSO as solvent. Thermogravimetric analysis (TGA) were recorded on a V 5.1A DuPont 2000 system under argon atmosphere at a heating rate of 10 ºC $Min.^{-1}$, and differential scanning calorimetry (DSC) recorded on a V 4.OB DuPont 2000 system under argon atmosphere at a heating rate of 10 ºC $Min.^{-1}$.

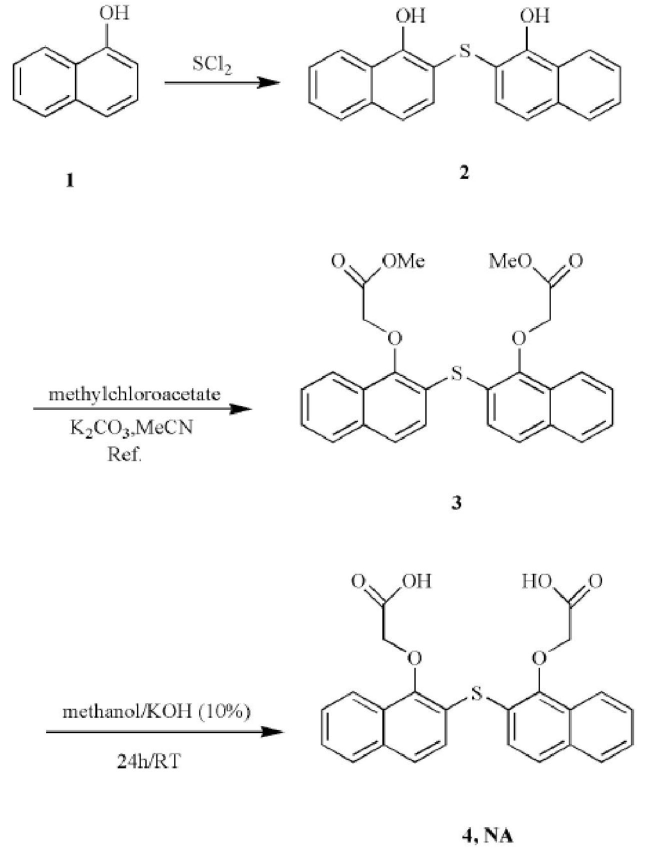
Synthesis of 2,2'-thiobis-(1-naphthoxy acetic acid) (4, NA)

Into a 250 mL single-necked flask containing methanol (20 mL), water (40 ml) and diester (3, 2 mmol, 0.924 g)[31] at 25 °C, sodium hydroxide pellets (8.5 mmol, 0.34 g) were added, and the mixture was stirred at room temperature. After 24 h, the reaction was completed (monitored by TLC), water (30 ml) was added and acidified with HCl (10%). The resulting white precipitate was collected, washed with water and dried. Pure 4 (NA) was obtained after recrystallization from ethanol, with melting point of 254-255°C. IR (KBr): 3450, 3125, 2921, 2470, 1720, 1420, 1223, 800 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 4.84 (s, 4H), 7.27 (d, J = 9.5Hz, 2H), 7.29 (d, J = 4Hz, 2H), 7.37 (t, J =

7.5Hz, 2H), 7.76 (d, J = 8Hz, 2H), 7.84 (d, J = 9.5Hz, 2H), 8.51 (d, J = 8.5Hz, 2H), 13.10-13.14 (b, 2H) ppm, ^{13}C NMR (500 MHz, DMSO-d$_6$) δ: 171.17, 157.08, 135.49, 130.85, 130.17, 129.05, 127.83, 126.17, 124.66, 117.79, 115.15, 66.45 ppm; Elemental analysis calculated for $C_{24}H_{18}O_6S$: C, 66.35; H, 4.18. Found: C, 66.32; H, 4.16.

Synthesis of polyamides

Polyamides were synthesized through the phosphorylation reaction of 2,2'-thiobis-(1-naphthoxy acetic acid) (4, NA) with a series of diamines as shown in Scheme 2. A typical example for the preparation of polyamides is given. A mixture of 4 (1 mmol, 0.434 g), p-phenylenediamine (1 mmol, 0.11 g), 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 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, a viscose reaction mixture was obtained and the polymer afforded in almost quantitative yield after purification. Spectral data, thermal properties, viscosity and solubility of these polyamides were reported in the following tables and figures.



Scheme 1 : Synthesis of diacid (4, NA).

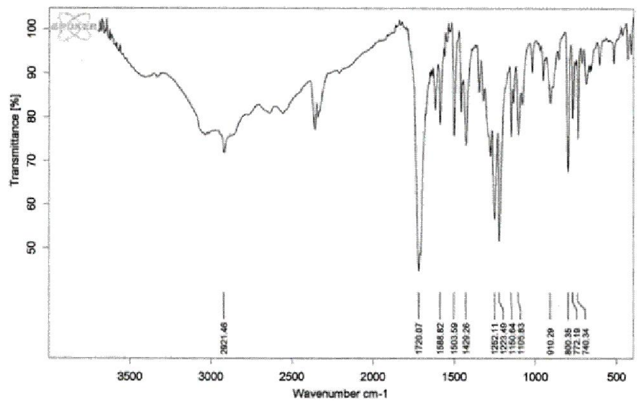
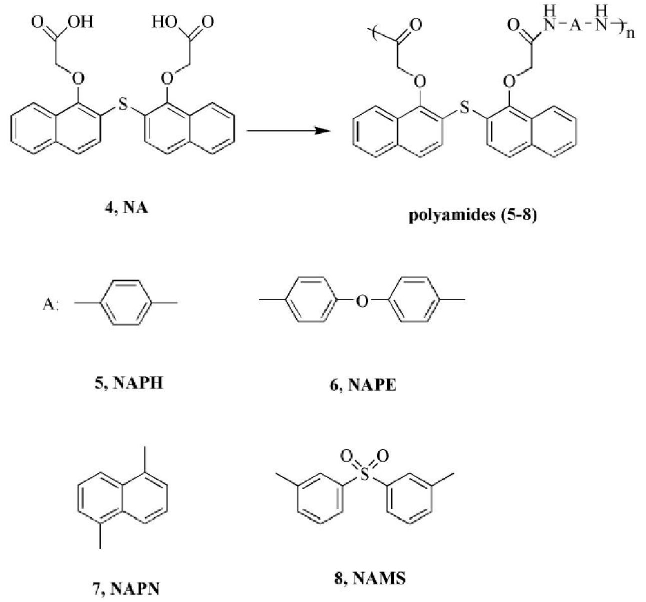


Figure 1 : IR spectrum of diacid (4, NA).

RESULTS AND DISCUSSION

A new diacid was synthesized according to the syn-



Scheme 2 : Synthesis of polyamides.

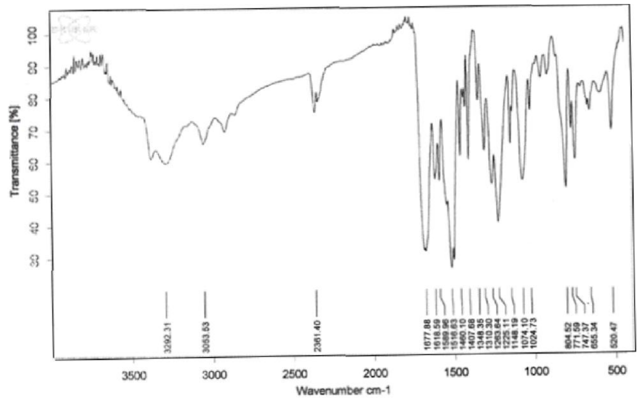


Figure 2 : IR spectrum of 5 (NAPH).

TABLE 1 : Inherent viscosity and the yields of polyamides.

Polymer	Yield (%)	η Inh (g/dL)[a]
NAPH (5)	96	0.51
NAPE (6)	91	0.47
NAPN (7)	97	0.57
NAMS (8)	96	0.59

[a]Measured at a polymer concentration of 0.5 g/dL in DMSO solvent at 30 °C.

TABLE 2 : Elemental analyses of polymers.

Polymer	Formula	Elemental Analysis					
		Calculated (%)			Found (%)		
		C	H	N	C	H	N
5	$C_{30}H_{22}N_2O_4S$	71.13	4.38	5.53	71.19	4.35	5.56
6	$C_{36}H_{26}N_2O_5S$	72.22	4.38	4.68	72.31	4.33	4.75
7	$C_{34}H_{24}N_2O_4S$	73.36	4.35	5.03	73.43	4.39	5.11
8	$C_{36}H_{26}N_2O_8S_2$	63.71	3.86	4.13	63.75	3.82	4.16

TABLE 3 : Spectral data of polymers

Polymer	IR (cm^{-1})	^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm)
NAPH (5)	3292, 3053, 2361, 1677, 1516, 1263, 804.	4.58 (s, 4H), 7.23-7.28 (m, 2H), 7.36-7.40 (d, J= 7 Hz, 2H), 7.65 (d, J=8.5Hz, 2H), 7.67 (d, J=7.6Hz, 2H), 7.84 (t, J=7.6Hz, 2H), 8.11 (t, J=8.5Hz, 2H), 8.34 (d, J=9Hz, 2H), 8.79 (d, J=9.1Hz, 2H), 9.83 (s, 2H)
NAPE (6)	3380, 2972, 2 468, 1685, 1498, 1218, 1072, 748.	4.77 (s, 4H), 6.92-6.95 (m, 4H), 7.28-7.32 (b, 24H), 7.34-7.43 (m, 4H), 7.54-7.58 (m, 4H), 7.78-7.80 (b, 2H), 7.85-7.87 (b, 2H), 8.50-8.53 (b, 2H), 10.01 (s, 2H).
NAPN (7)	3356, 3271, 2429, 1672, 1617, 1049, 788.	4.95 (s, 4H), 7.18-7.21 (m, 2H), 7.28-7.32 (m, 3H), 7.46-7.55 (m, 4H), 7.66-7.69 (m, 2H), 7.78-7.82 (m, 3H), 7.85-7.92 (m, 4H), 8.51-8.53 (m, 2H), 9.91 (s, 2H).
NAMS (8)	3386, 3089, 2477, 1719, 1608, 1153, 725, 809.	4.66 (s, 4H), 7.15-7.19 (m, 2H), 7.25-7.35 (m, 4H), 7.45-7.52 (m, 2H), 7.55-7.59 (m, 2H), 7.61-7.74 (m, 3H), 7.75-7.78 (m, 3H), 8.24 (s, 2H), 8.54 (d, J=8.5Hz, 2H), 10.32 (s, 2H).

thetic procedure shown in Scheme 1. The reaction of 1-naphthol and sulfur dichloride afforded a dinaphthol (2) according to reported procedures[32]. The reactions of alkoxides and alkyl halides are well known as Williamson's reaction as a classical but convenient synthetic method for preparation of ethers. This reaction was applied for the synthesis of diester (3) from the reaction of dinaphthol (2) and methylchloroacetate in nucleophilic conditions[30]. The diacid compound (4) was synthesized by hydrolysis of diester (3) in basic condition using methanol and KOH (10%) at room temperature. The structure of diacid monomer was confirmed by FTIR, ^{1}H and ^{13}C-NMR, Mass spectroscopy and elemental analysis (Figure 1.FTIR).

The objective of this study was the preparation of novel thermally stable polyamides under microwave irradiation and improvement of their solubility. Four new polyamides containing thiodi (1-hydroxy naphthalene) groups were prepared from the reaction between diacid monomer (4) and various commercially available diamines, such as 1,4-phenylene diamine, 4,4'-diaminodiphenylether, 1,5-diaminonaphthalene and 3,3'-diaminodiphenylsulfone by direct polycondensation reaction using triphenyl phosphite and pyridine as condensing reagents (Yamazaki reaction conditions)[33], in the presence of N-methylpyrolidinone (NMP) and calcium chloride ($CaCl_2$) under microwave irradiation as shown in Scheme 2. The inherent viscosities of the polyamides were in the range of 0.47–0.59 dL/g (TABLE 1). As the inherent viscosity is a good criterion for estimation of molecular weight, the prepared polyamides should have medium molecular weights. FTIR spectrum of a representative polymer, 5 (NAPH), is shown in Figure 2 and the FTIR data of polymers appeared in TABLE 3. The elemental analysis values were in good agreement with the calculated ones (TABLE 2). The further results from ^{1}H-NMR spectroscopy demonstrated that the polyamides have the expected chemical structures (TABLE 3).

The solubility behavior of the new polyamides was determined at concentration of 5% (W/V) in a number of solvents, and the results are tabulated in TABLE 5.Almost all prepared polyamides exhibited excellent solubility in polar aprotic solvents such as N-methylpyrolidinone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and even in less polar solvents like Tetrahhydrofuran (THF). The good solubility should be the result of the introduction of the bulky naphthalene groups in polymer backbone and thus, weaker interchain hydrogen bonding and interactions and thus less crystallinity. The bulky and flexible groups increase the chain distance and decrease the chain interactions, inhibit the chain packing; consequently, the solvents molecules are able to penetrate easily and interact with the polar groups of polymer chains and to solubilize the polymer chains. The nanostructure of the polyamides was also reflecting their good organosolubility. We believe, however, that the nanostructure of polymers increases the interaction of solvents and polymer chains and thus improve the solubility of polyamides.

DSC and TGA methods applied to evaluate the thermal properties of the polyamides. Thermal analysis data from the TGA and DSC curves of the polyamides are summarized in TABLE 4. The polyamides showed Tg in the range of 161–232 ºC under argon atmosphere. As we expected, the Tg values of the polyamides showed dependence on the structure of the diamines component and decreased with increasing flexibility of the polyamides backbone. It is evident that ether group in diamine structure, facilitating bond rotation, reduced Tg. Among all the synthesized polyamides, 8 based on the3,3'-diaminodiphenyl sulfone showed the highest Tg value because of the highest rigidity, which inhibited the molecular motion. Thermal stability of polyamides was evaluated by TGA in argon atmosphere at a heating rate of 10 ºC /min. Because the polyamides are hygroscopic materials, a small weight loss (1–2%) is recorded between 90 and 210 ºC due to loss of moisture. The temperatures of 10% weight loss were in the range of 212–287 ºC and the temperatures of 50% weight loss are in the range of 309-332 ºC. In addition, the residual weight retentions at 550 ºC for the resulting polyamides were in the range of 13–34%. The TGA curve for one polyamide (5) is shown in Figure 3. To compare thermal behavior, the polyamides 8 and 6 have the highest and the lowest thermal stability, which is due to the presence of rigid diphenylsulfone and flexible diphenyl ether units, respectively, in the polyamides backbone.

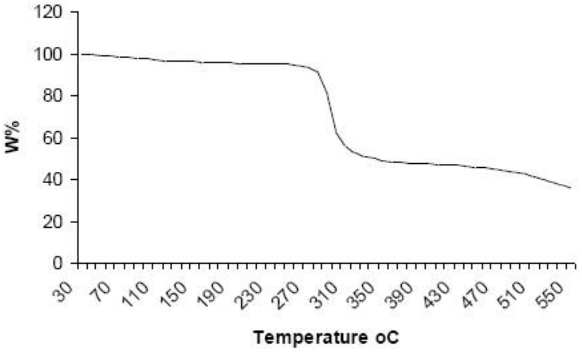


Figure 3 : TGA of polyamide (5).

TABLE 4 : Thermal properties of polyamides.

Polymer	T_g (°C)	T_{10}^{a} (°C)	T_{50}^{b} (°C)	Char yields[c] (%) 550 °C
NAPH (5)	199	287	321	34
NAPE (6)	161	212	309	13
NAPN (7)	208	276	325	26
NAMS (8)	232	262	332	19

[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 580 ºC under argon.

TABLE 5 : The solubility of polyamides (5-8).

Polymer[a]	NMP	DMAc	DMSO	DMF	THF
NAPH (5)	++	++	++	++	+
NAPE (6)	++	++	++	++	+
NAPN (7)	++	++	++	++	±
NAMS (8)	++	++	++	++	±

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

(-) insoluble; [a]Solubility measured at a polymer concentration of 0.05 g/ml

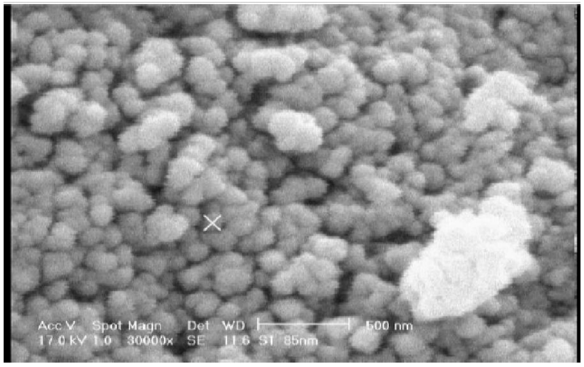


Figure 4 : SEM image of 5.

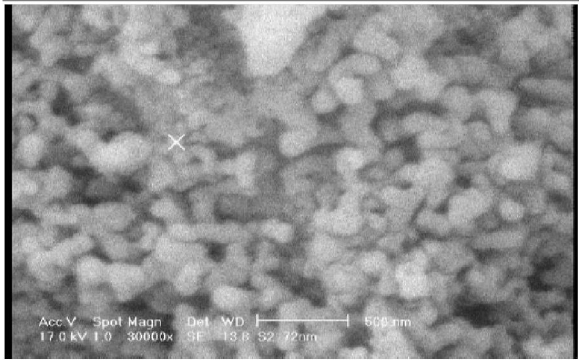


Figure 5 : SEM image of 6.

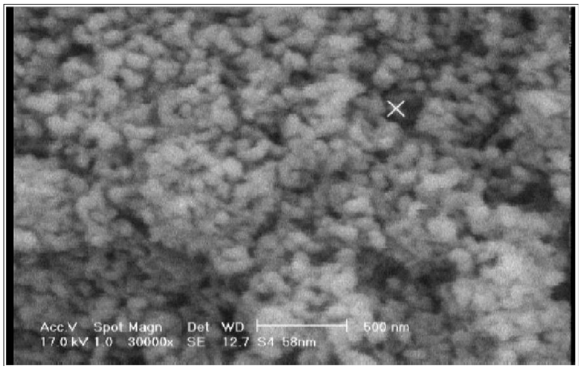


Figure 6 : SEM image of 7

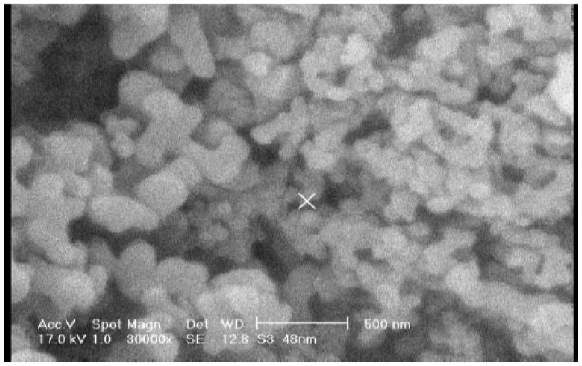


Figure 7 : SEM image of 8.

The surface morphology of polymers (precipitated in methanol) were studied using scanning electron microscopy (SEM) images, and showed the nanoparticles and nanostructures (Figures 4,5,6 and 7).

CONCLUSION

A novel diacid based on the dinaphthosulfide structure has been synthesized in good yields and high purity from readily available reagents and in reliable conditions. A series of polyamides have been prepared from this diacid and various aromatic diamines via the direct phosphorylation polycondensation. The introduction of the dinaphthosulfide group into the polymer backbone leads to significantly improved solubility of the polymer in various organic solvents. Most of these polymers exhibited a desired combination of properties, such as high thermal stability and excellent solubility in organic solvents, required for high-performance materials.

REFERENCES

[1] P.E.Cassidy, Marcel Dekker; 'Thermally Stable Polymer', New York **(1980)**.

[2] J.Preston, H.F.Mark, N.M.Bikales, C.G.Overberger, G.Menges; 'Encyclopedia of Polymer Science and Technology', Wiley, New York **(1988)**.

[3] **(a)** H.H.Yang; 'Aromatic High-Strength Fibers', Wiley, New York **(1989)**; **(b)** J.Yu, X.Huang, L.Wang, P.Peng, C.Wu, X.Wu, P.Jiang; Polym. Chem., **2**, 1380 **(2011)**.

[4] **(a)** M.Doğan, A.Yılmaz, E.Bayramli; Polym.Adv. Tech., **22**, 5600 **(2011)**; **(b)** M.Ghaemy, S.Khajeh; Chinese J.Poly.Sci., **30**, 82 **(2012)**.

[5] **(a)** S.H.Hsiao, P.C.Huang; Macromol.Chem.Phys., **198**, 4001 **(1997)**; **(b)** J.F.Espeso, A.E.Lozano, J.G.D.L.Campa, I.G.Yoldi, J.D.Abajo; Polym.Sci. Part A:Polym. Chem., **48**, 1743 **(2010)**.

[6] S.Sheng, T.Li, J.Jiang, W.He, C.Song; Polym.Int., **59**, 1014 **(2010)**.

[7] C.P.Yang, S.H.Hsiao, K.H.Chen; Polymer, **43**, 5095 **(2002)**.

[8] D.J.Liaw, B.Y.Liaw, C.W.Yu; Polymer, **42**, 5175 **(2001)**.

[9] M.Ghaemy, M.Barghamadi; Appl.Polym.Sci., **110**, 1730 **(2008)**.

[10] J.Jiang, S.Huang, Y.Liu, S.Sheng, Z.Huang, C.Song; Chin.J.Chem., **28**, 102 **(2010)**.

[11] M.Nechifor; J.Appl.Polym.Sci., **116**, 1450 **(2010).**

[12] F.Akutsu, M.Inoki, K.Sunouchi, Y.Sugama; Polymer, **39**, 1637 **(1998)**.

[13] S.H.Hsiao, C.W.Chen, G.S.Liou; Polym.Sci.Part A:Polym.Chem., **42**, 3302 **(2004)**.

[14] R.R.Pal, P.S.Patil, M.M.Salunkhe, N.N.Maldar, P.P.Wadgaonkar; Eur.Polym.J., **45**, 953 **(2009)**.

[15] M.Ghaemy, M.Barghamadi; Appl.Polym.Sci., **114**, 3464 **(2009)**.

[16] P.Blondin, J.Bounchard, S.Beapre, M.Belletete, G.Durocher, M.Leclerc; Macromolecules, **33**, 5874 **(2000)**.

[17] S.H., Chen, C.S.Shiau, L.R.Tsai, Y.Chen; Polymer, **47**, 8436 **(2006)**.

[18] D.J.Liaw, W.H.Chen; Polymer, **44**, 3865 **(2003).**

[19] H.J.Yen, G.S.Liou; Polym.Sci.Part A:Polym.Chem., **46**, 7354 **(2008)**.

[20] Z.Holik, M.Danek, M.Manas, J.Cerny; Int. J.Mechanics, **5**, 218 **(2011)**.

[21] D.J.Liaw, B.Y.Liaw, C.M.Yang; Macromolecules, **32**, 7248 **(1999)**.

[22] Y.L.Liu, S.H.Tsai; Polymer, **43**, 5757 **(2002)**.

[23] G.S.Liou, S.H.Hsiao, M.Ishida, M.Kakimoto, Y.Imai; Polym.Sci.Part A:Polym.Chem., **40**, 2810 **(2002)**.

[24] W.Dixon, M.M.Harris, Z.R.Mazengo; Chem.Soc.B, 775 **(1971)**.

[25] D.R.Puts, Y.D.Sogah; Macromolecules, **28**, 390 **(1995)**.

[26] J.D.Liaw, C.F.Chang, K.M.Leung, Y.M.Chou. K.Muellen; Macromolecules, **38**, 4024 **(2005)**.

[27] M.E.Mirault, K.Scherrer, L.Hansen; Eur.Biochem., **23**, 372 **(1971)**.

[28] H.Kondo, M.Sato, M.Yokoyama; Eur.Polym., **18**, 181 **(1982)**.

[29] **(a)** E.Rostami; Int.J.Polym.Mater., **60**, **(2012)**; **(b)** E.Rostami, M.Ghaedi, M.K.Z.Zadeh; Macromolecules: An Indian J., **8**, 12 **(2012)**; **(c)** E.Rostami, H.Fathi, A.N.Ziarati; Nano Sci.and Nano Technology: An Indian J., **6**, 21 **(2012)**; **(d)** E.Rostami, A.Zare, M.Zangooei; Materials Science: An Indian Journal, **8**, 245 **(2012)**.

[30] A.Shockravi, S.Mehdipour-Ataei, E.Abouzari-Lotf, A.Yousefi; Eur.Polym.J., **42**, 133 **(2006)**.

[31] E.Rostami; Phosphorus, Sulfur, and Silicon, **186**, 1694 **(2011)**.

[32] **(a)** W.S.Gump, J.C.Vitucci; Am.Chem.Soc., **67**, 238 **(1945)**; **(b)** M.Gazdar, S.Smiles; Chem.Soc., **97**, 2248 **(1910)**; **(c)** H.A.Hageman; 'US Patent', 3758440, **(1973)**; **(d)** A.Yamaguchi, K.Yamaguchi, H.Murakami, T.Kobayashi; 'US Patent', 4275240, **(1981)**.

[33] N.Yamazaki, F.Higashi, J.Kawataba; Polym.Sci. Polym.Chem.Ed., **12**, 2149 **(1974)**.