



Trade Science Inc.

ISSN : 0974 - 7478

Volume 8 Issue 1

Macromolecules

An Indian Journal

Full Paper

MMALJ, 8(1), 2012 [12-18]

Synthesis and characterization of new polyamides bearing dibenzosulfone units in the main chain: Microwave conditions and nanostructures

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Received: 5th January, 2012 ; Accepted: 31st January, 2012

ABSTRACT

New polyamides containing dibenzosulfone Units were prepared under microwave irradiation and their solubility, thermal behaviour, viscosity and their nanostructures were evaluated. These polyamides showed good solubility, viscosity and high thermal stability. Surface morphology of these polymers showed nanoparticle structure.

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KEYWORDS

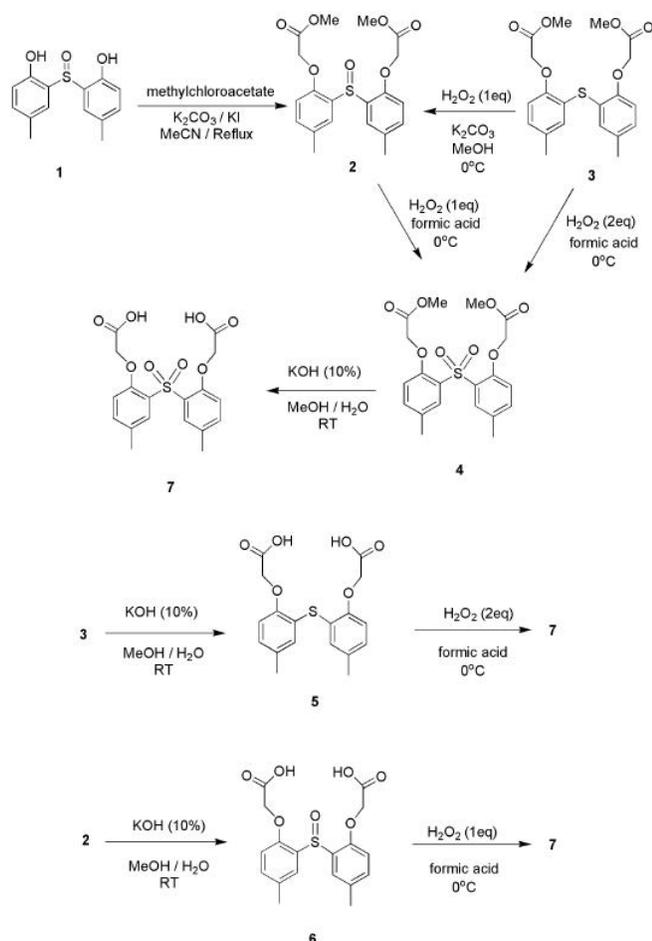
Polyamide;
Synthesis;
Dibenzosulfone;
P-cresol;
Nanostructure;
SEM;
Nanoparticle.

INTRODUCTION

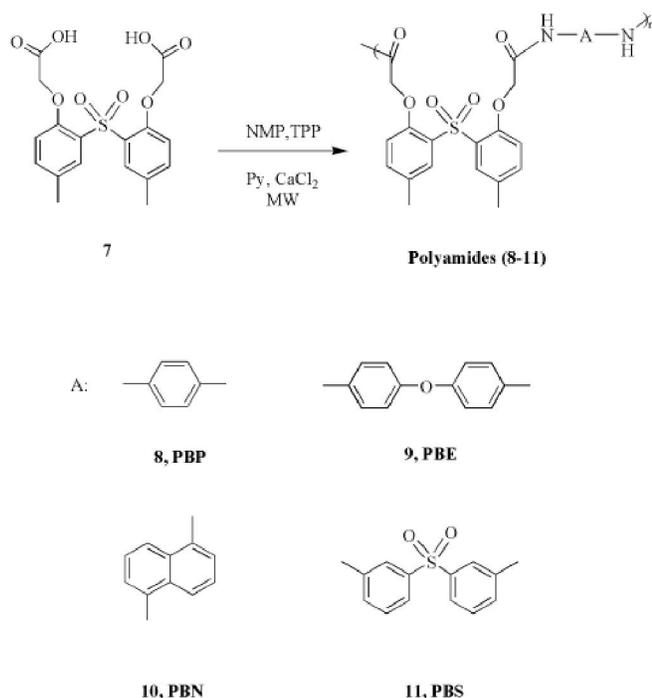
Aromatic polyamides are high performance polymers with good thermally stable, efficient mechanical properties, low flammable, good processable, easy applicable and low density materials^[1-4]. Because of their excellent properties, they are used as good alternatives for a series of conventional materials such as metals and ceramics in engineering applications^[5]. The new industry and technology requires advanced materials with several properties and stable in unusual environments such as elevated temperatures, vigorous acidic and basic media and humid regions^[6]. Polyamides are important candidates for these advanced materials have ability to change their properties and gain desired application via change in structures and preparation condition^[7]. Wholly aromatic polyamides (aramides) have a few disadvantages such as poor solubility, difficult processability and high melting^[8]. Several procedures

were examined for achieve these drawbacks containing the use of softening aliphatic chains 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 points, good soluble and processable polymers^[9-11].

Microwave irradiation (MW) as a nonconventional heating was used for the preparation of the large number of compounds^[12]. In comparison with conventional heating this method of synthesis have a number of advantages such as high yields, short reaction times, the use of small volume of solvents or the syntheses in dry media without solvent, ecofriendly, environmentally benign and the use of nontoxic materials especially solvents^[13]. First syntheses were performed using domestic ovens, but industrial apparatus are more efficient; especially; controlled temperature, pressure and as a result higher safety, reliable and reproducible results^[14].



Scheme 1 : Synthesis of diacid (7).



Scheme 2 : Synthesis of polyamides (8-11).

In polymer science, microwave irradiation was used in broad range from polymer synthesis to processing^[15]. A large number of polymer synthetic routes were reported using microwave irradiation^[16]. 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^[16,17]. The use of this method of synthesis (MW) for the preparation of polymers is an active route in chemistry and materials science^[18].

In this research work new polyamides containing dibenzosulfone units in the main chain were synthesized under microwave irradiation. They are soluble in a series of organic solvents and showed thermal resistance. SEM images of these polymers showed nanoparticle structures.

EXPERIMENTAL

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. Triphenyl phosphite (TPP, Merck) was purified by fractional distillation under vacuum. Reagent grade aromatic diamines (Aldrich) including 1,5-diaminonaphthalene (DAN) and 3,3'-diaminodiphenyl sulfone 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. FT-IR spectra were recorded in potassium bromide pellets on a Bruker apparatus. The 1H 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

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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. 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 2,2'-sulfoxobis(1-(1,4-dioxo-3-oxopentoxo)-4-methylbenzene) (4,BDE) from 2 and 3

To formic acid (50 ml), were added diester (2, 1mmol, 0.408 g; or 3, 1mmol, 0.392 g) and hydrogen peroxide (30%, for the reaction with 2, 1mmol, 0.09 ml and for 3, 2mmol, 0.18 ml) at 0°C and the reaction were stirred for 6h. After completion of the reaction (monitored by TLC), water was added and the resulting precipitate filtered and washed with water and dried. The crude product was recrystallized in ethanol/THF to afford 4 in 93% yield and melting point of 122-123 °C; IR(KBr): 2934, 2541, 2219, 1736, 1610, 1483, 1243, 1093, 718 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆) δ: 2.33 (s, 6H), 3.61 (s, 6H), 4.56 (s, 4H), 6.93 (d, J=10Hz, 2H), 7.37 (dd, J=1.5, 8Hz, 2H), 7.86 (d, J=1.5Hz, 2H) ppm; ¹³C NMR (125 MHz, DMSO-d₆) δ: 168.93, 153.78, 136.28, 131.64, 131.02, 129.45, 114.99, 66.39, 52.64, 20.78 ppm; MS (EI) m/z (relative intensity %): 422 [M]⁺ (3%), 389 (100%), 347 (36%), 329 (79%), 286 (18%), 195 (28%), 151 (54%), 135 (27%), 91 (29%), 45 (100%); Anal. C₂₀H₂₂O₈S (422.45): C, 56.86; H, 5.25 %; Found, C, 56.88; H, 5.26 %.

Synthesis of 2,2'-sulfoxobis(1-(1,4-dioxo-3-oxobutoxy)-4-methylbenzene) (7, BDA) from 4

To the mixture of 4 (BDE, 1mmol, 0.424 g) and methanol (10 mL) was added KOH solution (10%, 50 ml) 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 etha-

nol to afford diacid (7, BDA) as a white precipitate in 96% yield and melting point of 233-234 °C; IR (KBr): 3567, 3441, 3329, 2928, 2557, 2216, 1777, 1745, 1495, 1249, 1157, 1091, 824, 819 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆) δ: 2.18 (s, 6H), 4.56 (s, 4H), 7.11 (d, J=10 Hz, 2H), 7.41 (dd, J=1.5, 8 Hz, 2H), 7.93 (d, J=1.5 Hz, 2H), 10.35-10.37 (b, 2H) ppm; ¹³C NMR (125 MHz, DMSO-d₆) δ: 171.15, 158.61, 136.34, 132.76, 132.42, 131.89, 115.78, 67.59, 53.23 ppm; MS (EI) m/z (relative intensity %): 396 [M+2]⁺ (7%), 362 (3%), 348 (2%), 317 (11%), 257 (53%), 228 (51%), 179 (36%), 151 (27%), 121 (100%), 105 (29%), 77 (67%); Anal. C₁₈H₁₈O₈S (394.40): C, 54.82; H, 4.60 %; Found, C, 54.85; H, 4.61 %.

Synthesis of 2,2'-sulfoxobis(1-(1,4-dioxo-3-oxobutoxy)-4-methylbenzene) (7, BDA) from 5 and 6

To formic acid (50 ml), were added diacid (5, 1 mmol, 0.364 g; or 6, 1mmol, 0.380 g) and hydrogen peroxide (30%, for the reaction with 5, 1mmol, 0.09 ml and for 6, 2mmol, 0.18 ml) at 0 °C and the reaction were stirred for 10h. After completion of the reaction (monitored by TLC), water was added and the resulting precipitate filtered and washed with water and dried. The crude product was recrystallized in ethanol to afford 4 in 92% and 95% yields, respectively.

Synthesis of polyamides

Polyamides were synthesized by the Yamasaki phosphorylation reaction of diacid (7, BDA) with various diamines as shown in Scheme 2. A typical example for the preparation of polyamides is given. A mixture of 7 (1 mmol, 0.396 g), p-phenylenediamine (1 mmol, 0.11 g), 0.3 g of CaCl₂, 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 and solubility of these poly-

mides were reported in the following TABLES and Figures.

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 (7, BDA), containing sulfone and benzo units and aromatic diamines under microwave irradiation. Diacid (7, BDA) were prepared according to the Scheme 1, through three synthetic routes from dibenzosulfone diester (4), dibenzosulfide diacid (5) and dibenzosulfoxide diacid (6) (Scheme 1).

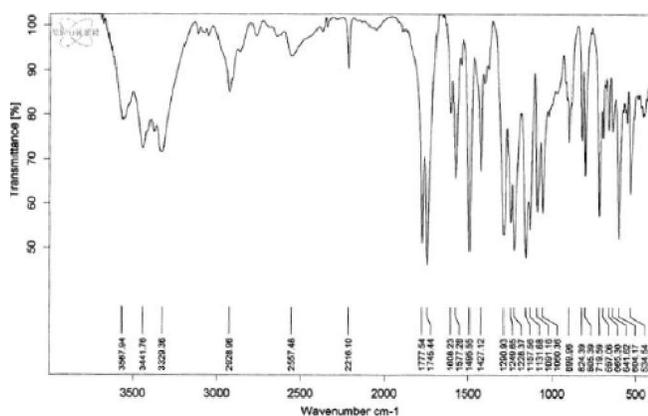


Figure 1 : FT-IR spectrum of benzosulfone diacid (7, BDA).

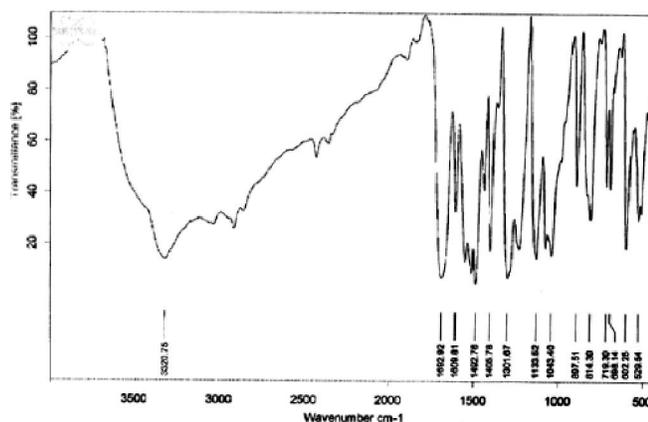


Figure 2 : FT-IR spectrum of polyamide (8, PBP).

TABLE 1 : Inherent viscosity and the yields of polyamides.

Polymer	Yield (%)	η_{inh} (g/dL) ^a
PBP (8)	97	0.48
PBE (9)	95	0.44
PBN (10)	98	0.56
PBS (11)	94	0.52

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

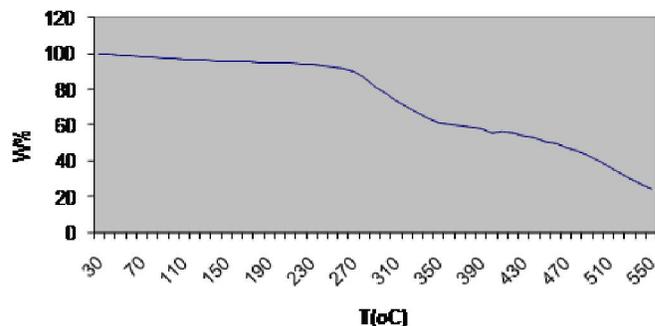


Figure 3 : TGA of polyamide (8, PBP)

TABLE 2 : Elemental analyses of polymers.

Polymer	Formula	Elemental Analysis					
		Calculated (%)			Found (%)		
		C	H	N	C	H	N
PBP	C ₂₄ H ₂₂ N ₂ O ₆ S	61.79	4.75	6.00	61.84	4.71	6.07
PBE	C ₃₀ H ₂₆ N ₂ O ₇ S	64.50	4.69	5.01	64.57	4.64	5.07
PBN	C ₂₈ H ₂₄ N ₂ O ₆ S	65.01	4.68	5.42	65.08	4.65	5.47
PBS	C ₃₀ H ₂₆ N ₂ O ₈ S ₂	59.39	4.32	5.62	59.43	4.39	10.68

TABLE 3 : Spectral data of polymers

Polymer	IR (cm ⁻¹)	¹ H NMR (500 MHz, DMSO-d ₆): δ (ppm)
PBP (8)	3320, 2994, 2491, 1692, 1492, 1301, 1043, 814.	2.15 (s, 6H), 4.62 (s, 4H), 7.09 (d, J= 7.5 Hz, 2H), 7.42 (d, J= 7 Hz, 2H), 7.58-7.59 (m, 2H), 7.65-7.68 (m, 4H), 7.81 (d, J= 10Hz, 2H).
PBE (9)	3324, 2985, 2456, 1694, 1489, 1305, 1136, 1037, 819.	2.16 (s, 6H), 4.62 (s, 4H), 7.02 (d, J=8.5Hz, 4H), 7.09 (d, J=8Hz, 2H), 7.43 (d, J=8Hz, 2H), 7.64 (d, J=8.5Hz, 4H), 7.80 (s, 2H), 9.74 (s, 2H).
PBN (10)	3455, 3362, 2452, 1687, 1138, 1047, 822.	2.15 (s, 6H), 4.64 (s, 4H), 7.11 (d, J= 8.1 Hz, 2H), 7.43-7.48 (m, 4H), 7.80 (s, 2H), 7.95-7.98 (m, 4H), 7.75 (s, 2H).
PBS (11)	3305, 2978, 2453, 1684, 1583, 1322, 1145, 1103, 742.	2.00 (s, 6H), 4.59 (s, 4H), 6.90-6.93 (b, 2H), 7.27-7.30 (b, 2H), 7.60-7.67 (m, 4H), 7.73-7.92 (m, 4H), 8.30-8.34 (b, 2H), 10.17-10.20 (b, 2H).

Dibenzosulfide diester (3) was prepared previously^[19]. Dibenzosulfoxide diester (2) was prepared from 1^[19] and in this research work a new route was performed for the synthesis of 2 from the reaction of dibenzosulfide diester (3) and hydrogen peroxide. 5 and 6 were prepared from basic hydrolysis of 2 and 3, respectively (Scheme 1). Dibenzosulfone diester (4) was prepared from the oxidation of 2 and 3 using hydrogen peroxide

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TABLE 4 : Thermal properties of polyamides.

Polymer	T _g (°C)	T ₁₀ ^a (°C)	T ₅₀ ^b (°C)	Char yields ^c (%) _{550 °C}
PBP (8)	216	276	438	22
PBE (9)	194	131	423	17
PBN (10)	221	167	526	37
PBS (11)	230	144	-	54

^aTemperature of 10% weight loss determined in argon atmosphere; ^bTemperature of 50% weight loss determined in argon atmosphere; ^cChar yield calculated as the percentage of solid residue after heating from room temperature to 550 °C under argon.

TABLE 5 : The solubility of polyamides (8-11).

Polymer ^a	NMP	DMAc	DMF	DMSO	m-Cresol	THF
PBP (8)	++	++	++	++	±	+
PBE (9)	++	++	++	++	+	+
PBN (10)	++	++	++	++	±	±
PBS (11)	++	++	++	++	±	±

(++) Soluble at room temperature; (+) soluble upon heating; (±) partially soluble; ^aSolubility measured at a polymer concentration of 0.05 g/ml.

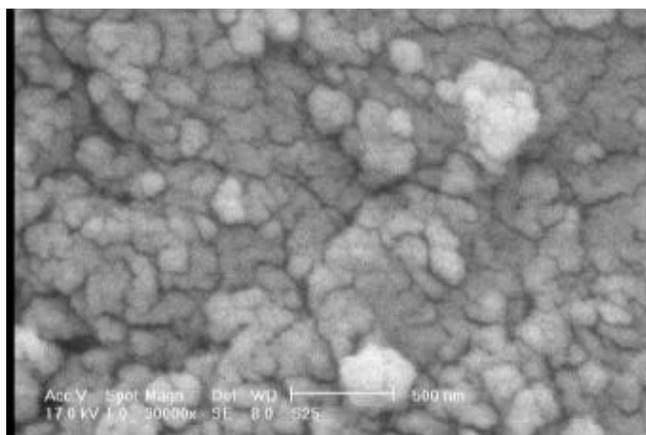


Figure 4 : SEM image of polyamide 8 (PBP).

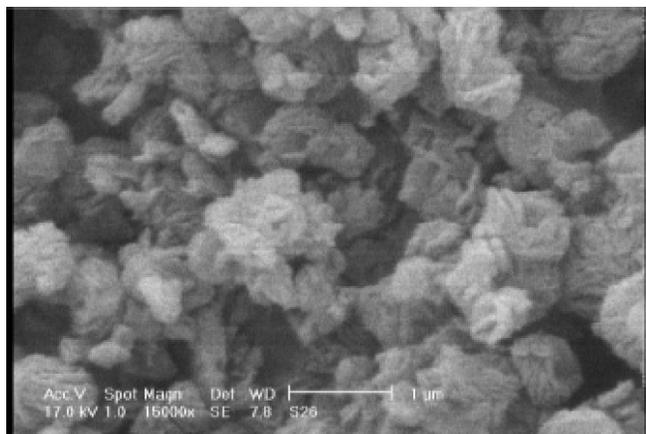


Figure 5 : SEM image of polyamide 9 (PBE).

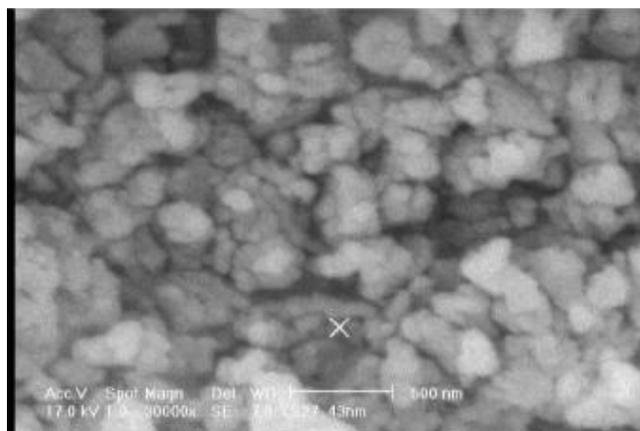


Figure 6 : SEM image of polyamide 10 (PBN).

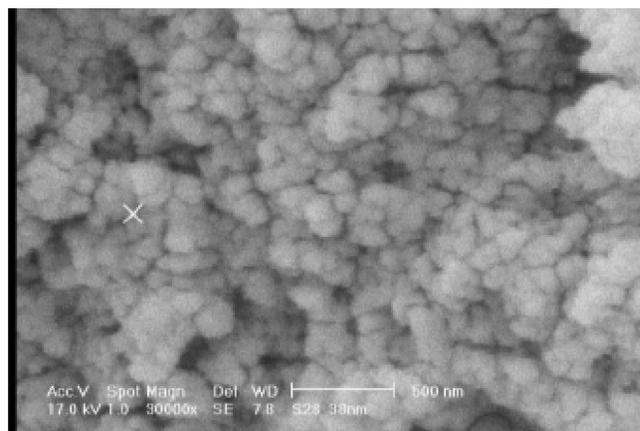


Figure 7 : SEM image of polyamide 11 (PBS).

(1 equivalent and 2 equivalents, respectively) in formic acid, and then was hydrolyzed to dibenzosulfone diacid (7). The IR spectrum of diacid (7, BDA) is appeared in Figure 1. Polymerization were performed using Yamasaki phosphorilation reaction of diacid (7) and diamines in the presence of triphenylphosphite (TPP), pyridine (Py), N-methylpyrrolidinone (NMP) and calcium chloride (CaCl₂) 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 water and methanol respectively, and then dried under vacuum. The inherent viscosities and the isolated yields of polyamides were reported in TABLE 1. The elemental analyses of polymers are reported in TABLE 2. The IR and ¹H NMR spectra of polyamides showed the correct structures (TABLE 3). The IR spectra of polyamide 8 (PBP) is appeared in Figure 2; and showed the corresponding structure according to the major functional groups.

The solubility behavior of polyamides was investi-

gated 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 excellent solubility in polar organic solvents. This might be due to the presence of polarized and tetrahedral SO₂ (sulfone) groups with three dimensional structure and rigid which, increased intramolecular hydrogen bonding and reduced the close packing and crystallinity. On the other hand, because of the presence of very flexible CH₂ groups in the main chain and CH₃ as side chain groups of polyamides solubility is high. The viscosities of polyamides were measured in DMSO at 30 °C and are in the range of 0.44-0.56 (TABLE 1).

The thermal stability of polyamides was evaluated 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 (PBP) is showed in Figure 3. Glass transition temperatures (T_g) of polyamides were evaluated by differential scanning calorimetry (DSC) and are in the range of 194-230°C. The results are summarized in TABLE 4. According to the structure of diamine, insertion of the ether group in the diamine structure is increased the overall flexibility of the polymer chains and decreased the T_g value. The polymers containing diamines without other flexible groups (such as naphthalene and meta and para benzene derivatives) have high T_g , because of the lower flexibility of the overall polymer chains, increased crystallinity and close paking.

The thermal stability of these polymers was studied by thermogravimetric analysis (TGA). All the polymers showed good thermal stability, their decomposition at argon atmosphere for temperature of 10% weight loss T (10) was in the range of 131-276 °C and the temperature of 50% weight loss T (50) was in the range of 423-526 °C which indicates excellent thermal stability in the prepared polymers. For one polymer (11, PBS) T (50) is higher than 550°C. The polymer decomposition temperature for various percent of decomposition and char yield (in the range of 22-54%) at 550 °C for all polymers are summarized in TABLE 4 and according to the obtained data for thermal stability, the polymer with diamine containing the ether linkage show the

lower thermal stability in comparison with the polymers containing diamines without these groups and more symmetric structures. The incorporation of naphthalene and benzene units into the polymers backbone enhanced the thermal stability.

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

CONCLUSIONS

A series of new polyamides based on the dibenzosulfone structure were successfully obtained through the direct polycondensation reaction of a dibenzosulfone diacid with various diamines via Yamazaki method under microwave irradiation (MW). The polymers showed enhanced solubility and high thermal stability. This is due to the presence of tetrahedral sulfone group. The presence of ether group in the diamine decreased thermal stability and polymers with higher symmetric and rigid structures (such as naphthalene and sulfone) in the diamine and as a result in the overall polymer chains showed the higher thermal stability. Thus, we afforded polyamides which lead to improved solubility and higher heat resistance. Surface study of these polymers has been showed the nanoparticle and nanostructures.

ACKNOWLEDGEMENTS

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

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