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Synthesis of new organosolublepoly (ester-amide-imide)s bearing amino acids and 4,4'-(diamidodibenzo) sulfone subunits in the main chain

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ABSTRACT

New poly (ester-amide-imide)s containing aminoacids and4,4'-(diamidodibenzo) sulfone units were prepared and their solubility and viscosity were evaluated. The viscosities of polyamides are in the range of 0.43-0.47. These polyamides showed good solubility in common organic solvents. Theoretical calculation shows the high free volume of polymer chains. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Poly (ester-amide-imide);
Amino acid;
Diphenylsulfone;
Synthesis;
Theoretical study.

INTRODUCTION

Aromatic polyamides and polyimides 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 in applications[5]. The new industry and technology requires high performance materials with a series of properties and stable in vigorous conditions such as elevated temperatures, high acidic and basic media and humid and cold regions[6]. Polyamides and polyimides are important candidates for these advanced materials have ability to change their properties with a series of improvments and gain desired application[7]. Wholly aromatic polyamides (aramides) have a few disadvantages such as poor solubility, difficult processability and high melting and thus restricted applications[8]. Several procedures were examined for achieve these drawbacks containing the use of softening aliphatic chains, ethers, esters 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].

In continuation of our previous research works on the synthesis of polymers[12], in this research work new organosuloble poly (ester-amide-imide)s containing aminoacids and diphenylsulfone in the main chain were synthesized and their properties were studied.

EXPERIMENTAL

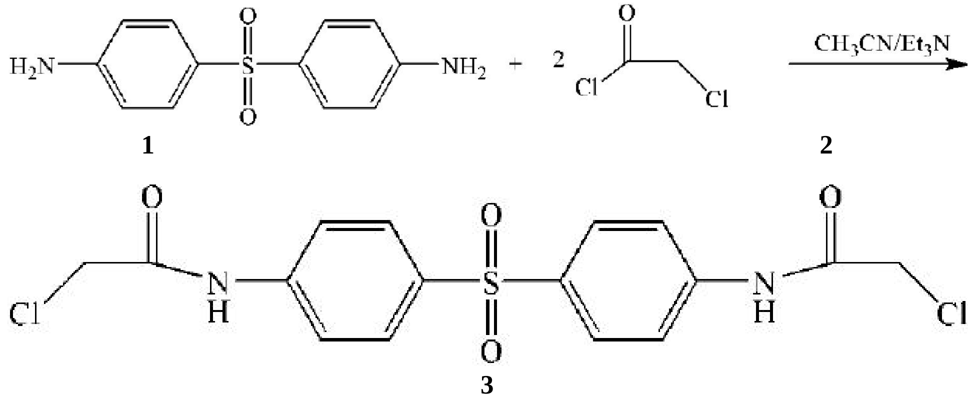
The reactions for the synthesis of monomer and purification of polymers were carried out in an efficient hood. All the materials were purchased from Merck, Fluka, Across Organics and Aldrich chemical companies. N-Methyl-2-pyrrolidinone (NMP, Merck) was purified by distillation under reduced pressure over calcium hydride and stored over 4A Ú molecular sieves. 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. 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 ºC using DMSO as solvent. Theoretical studies were performed using hyperchem 7.0 using semi-empirical functions and AM1 method andthen the molecular structures in Figures 3 and 4 were produced using GaussView 5.0.

Synthesis of dichloroamide (3)

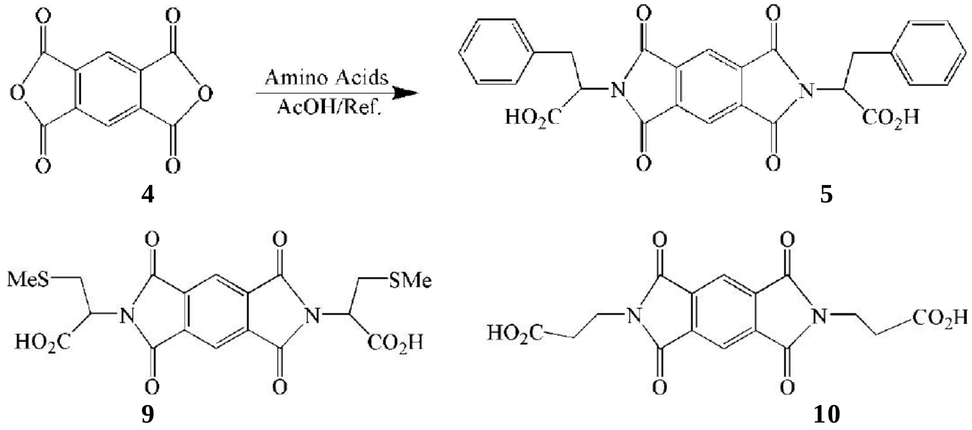
To acetonitrile (30 mL) were added 4,4'-diaminodiphenyl sulfone (1, 1mmol, 0.25g), triethylamine (2mmol, 0.28mL) and chloroacetyl chloride (2 mmol, 0.16mL) at room temperature. The reaction mixture was stirred at room temperature for 48 hours. After completion of the reaction (monitored by TLC), water was added and the resulting white precipitate was filtered and recrystallized in ethanol to afford a white solid in 94% yield; IR (KBr): 3598, 3508, 3314, 3110, 2987, 1684, 1534, 1302, 1107, 836 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ: 4.24 (s, 4H), 7.75 (d, J= 9Hz, 4H), 7.85 (d, J= 9Hz, 4H), 10.68 (S, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d$_6$) δ: 166.27, 143.75, 136.64, 129.44, 120.34, 44.39 ppm; MS (EI) m/z (relative intensity %): 405 [M+1]$^+$ (3), 404 [M]$^+$ (6), 403 [M-1]$^+$ (7), 402 [M-2]$^+$ (33), 401 [M-3]$^+$ (23), 400 [M-4]$^+$ (54), 324 (31), 216 (29), 184 (32), 140 (71), 108 (100), 77 (24), 36 (57); Analytical calculated for $C_{16}H_{14}Cl_2N_2O_4S$ (M=401.26): C, 47.89; H, 3.52; N, 6.98; Found, C, 47.86; H, 3.51; N, 7.03.

Synthesis of diimide-acids (8-10)

To Pyromelliticdianhydride (4, 1mmol) was added aminoacids (5-7, 2mmol) and glacial acetic acid (30mL)

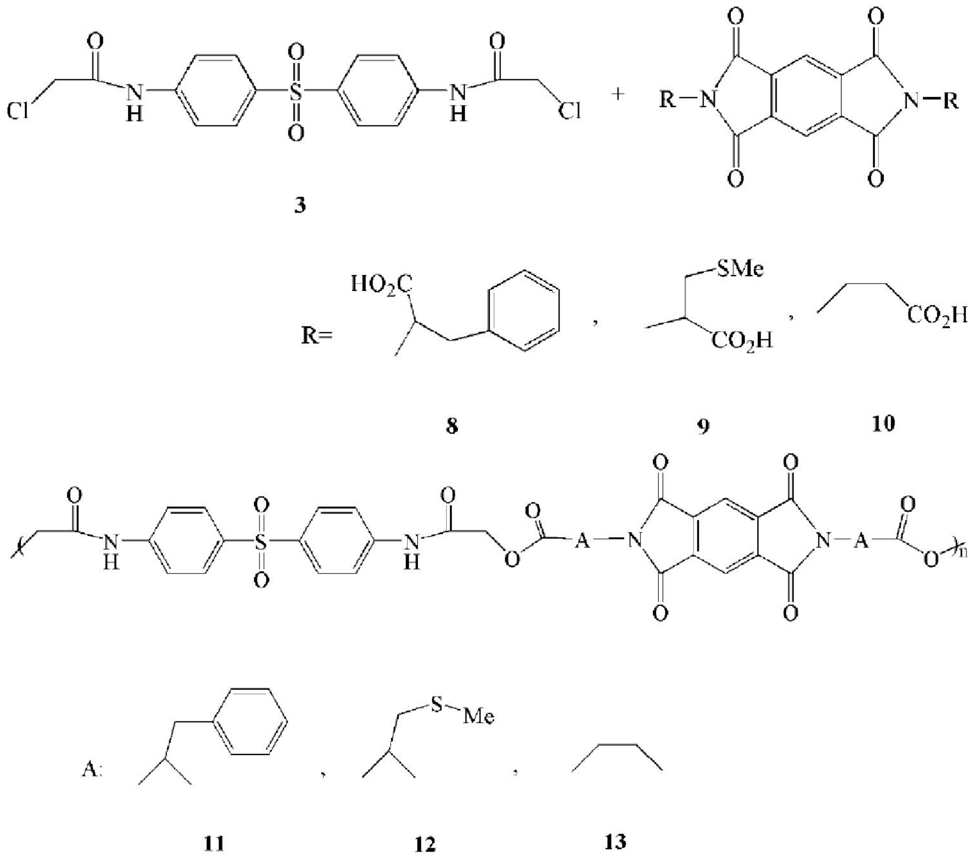


Scheme 1 : Synthesis of dichloroamide (3)



Amino Acids: l-Phenyl alanine (5), l-methionine (6), b-Alanine (7)

Scheme 2 : Synthesis of diimide-acids (8-10)



Scheme 3 : Synthesis of polymers (11-13)

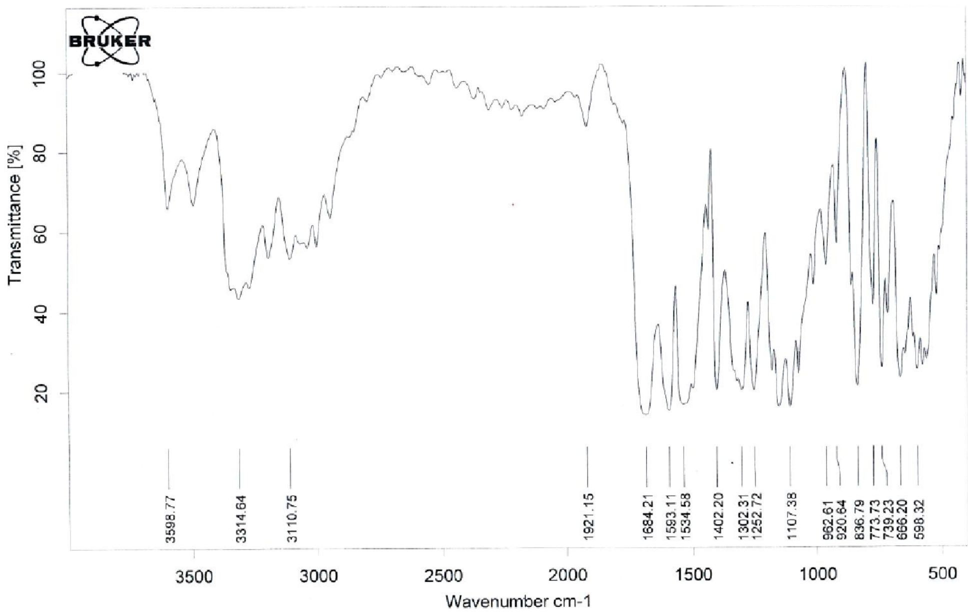


Figure 1 : FT-IR spectrum of diimide-acid (8)

at room tempearture. The mixture was stirred at room temperature for 1h and then was refluxed for 24h. After completion of the reaction (monitored by TLC), water was added and the mixture was left for 24h. Then, the resulting white precipitate was filtered and recrystallized in ethanol to afford diimide-acids (8^{13}, 9^{14}, 10^{15}) in good yields.

Synthesis of polymers (11-13)

Polyamides were synthesized through the nucleo-

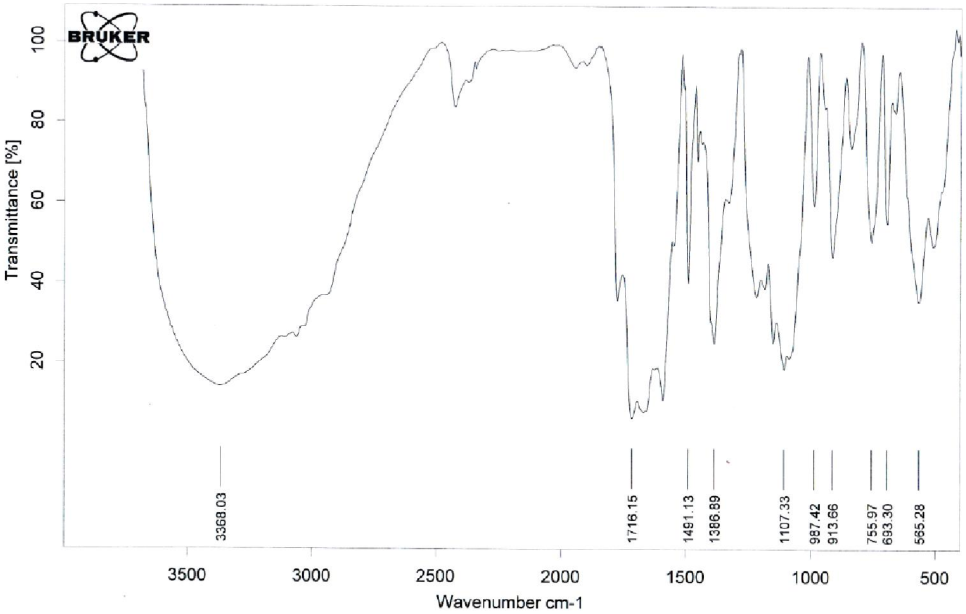


Figure 2 : FT-IR spectrum of polyamide (11)

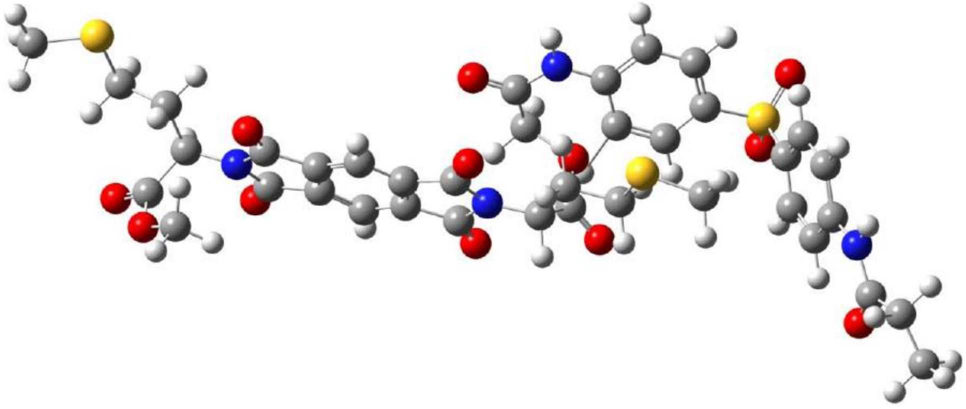


Figure 3 : HyperchemSemi-empirical AM1 optimized structure of polymer (12, side view)

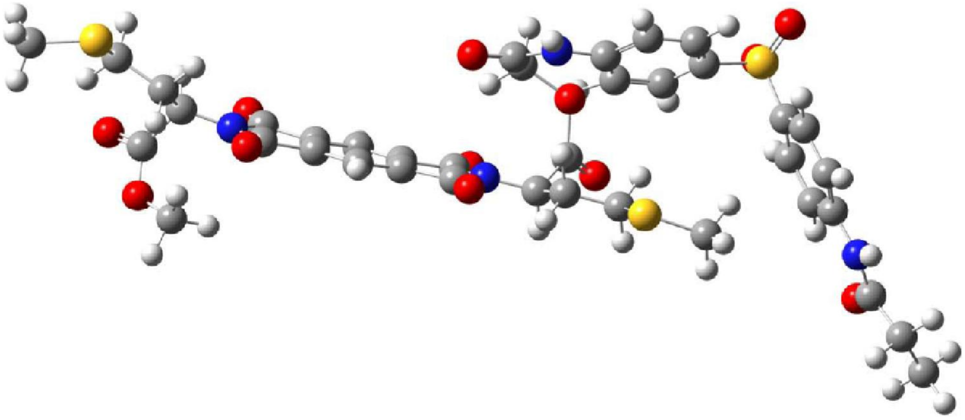


Figure 4 : HyperchemSemi-empirical AM1 optimized structure of polymer (12, top view)

philic reaction of dichloroamide (3) with various diacids (8-10) as shown in Scheme 3. A typical example for the preparation of polyamide (11) is given. To 3 (1mmol, 0.40g) in quartz tube were added 8 (1mmol, 0.51g), NMP (4mL) and triethylamine (2mmol, 0.28mL). The mixture was stirred at room temperature for 30min. and then, irradiated under microwave in 600W for 9 Min. (3×3 Min.) and the rest time of 10

TABLE 1 : Spectral data of polymers (11-13)

Polymer	IR (cm^{-1})	^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm)
11	3368, 3146, 2993, 1716, 1693, 1386, 1107.	3.12-3.15 (b, 4H), 5.31 (S, 4H) 6.71 (t, J= 8.5 Hz, 2H), 6.73-7.24 (m, 10H), 7.71-7.73 (b, 4H), 7.81-7.83 (b, 4H), 8.14-8.16 (b, 2H), 9.29.
12	3366, 3281, 2983, 2431, 1719, 1685, 1401, 1041, 986, 834.	3.15 (s, 6H), 4.56 (S, 4H), 4.73 (S, 4H), 6.99-7.01 (b, 2H), 7.21-7.82 (m, 8H), 8.13-8.16 (m, 2H), 10.56 (S, 2H).
13	3366, 3158, 2986, 2434, 1701, 1688, 1577, 1126, 1040, 990.	3.77-3.89 (m, 8H), 4.62 (S, 4H), 7.56-7.83 (m, 8H), 8.15 (s, 2H), 10.55 (S, 2H).

TABLE 2 : Inherent viscosity and the yields of polymers (11-13)

Polymer	Yield (%)	η_{Inh} (g/dL)[a]
11	91	0.47
12	88	0.45
13	86	0.43

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

Min. (2×5 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 (11) was washed with hot methanol (50 mL), hot water (twice, 50 mL) and then hot methanol (50mL), respectively; and dried under vacuum at 100°C overnight. Spectral data, viscosity and solubility 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 poly (ester-amide-imide) s obtained from the reaction of a new dichloroamidemonomer (3), containing amide and sulfone units, and aromatic rings. 3 was prepared from the reaction of 4,4'-diaminodiphenyl sulfone and chloroacetyl chloride in acetonitrile in the presence of triethtylamine (Scheme 1).

Diimide-acids (8-10) were prepared from the reaction of Pyromelliticdianhydride (4) and aminoacids (l-phenyl alanine (5), l-methionine (6) and β-alanine (7)) in refluxing glacial acetic acid in good yields (Scheme 2). FT-IR spectrum of 8 is appeared in Figure 1. poly (ester-amide-imide)s (11-13) were prepared from the reaction of dichloroamide (3) and diimide-acids (5-7) in NMP under microwave irradiation (Scheme 3). FT-IR spectrum of 11 is appeared in Figure 2, and showed the corresponding structure according to the main functional groups. 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 phenyl sulfone units which decreased intremolecular and intramolecular hydrogen bonding but thiomethoxyand aliphatic groups increases the intramolecular hydrogen bonding and flexibility and then decrease the crystalinity and close paking. On the other hand, sulfone units reduced the flexibility and increased close packing and crystallinity. Also, the aminoacid structure varies the solubility. Theoretical studies on the monomer of 12showed the high free volume in the

TABLE 3 : The solubility of polymers

Polymer[a]	NMP	DMAc	DMF	DMSO	m-Cresol	THF
11	++	++	++	++	++	+
12	++	++	++	++	+	+
13	++	++	++	++	++	±

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

molecule. This phenomenon decreases the crystallinity and close packing, and increase the solubility of polymers (Figure 3 and 4). According to the above discussions the solubility of polymers were affected by the several variables and the solubility varies according to the structure of amino acid in the diacid monomer (8-10). The viscosities of polymers were measured in DMSO at 30 ºC and are in the range of0.43-0.47(TABLE 2).

CONCLUSION

A series of new poly (ester-amide-imide)s bearing aminoacids and diphenylsulfone in the main chain were successfully prepared in nucleophilic conditions under microwave irradiation (MW). The polymers showed reliable solubility and viscosity. This is due to the presence of diphenylsulfone and aliphatic groups of amino acids in the presence of tetrahedral sulfone functional group. Thus, we afforded polymers with improved solubility. Theoretical study showed the high free volume and describes the solubility.

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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 thioether units 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-polymer, **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_3 groups 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)** E.Rostami, M.Ghaedi, M.K.Z.Zadeh; "Synthesis and characterization of newpolyamides bearing dibenzosulfone units in themain chain: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: Microwave irradiation, nanostructures", Mat. Sci. Ind. J., **8(6)**, 245-250 **(2012)**.

[13] Q.Tang, Q.Ai, J.He, X.Li, R.Yang; "Synthesis and characterization of thermally stable poly (urethane–imide)s based on novel diols-containing imideand alkynyl groups" High Perform. Polym., doi: 10.1177/0954008313486280 **(2013)**.

[14] S.Mallakpour, M.Dinari; "Novel nanostructure amino acid-based poly (amide-imide)s enclosingbenzimidazole pendant group in green medium: fabrication andcharacterization" Amino Acids, **43**, 1605-13 **(2012)**.

[15] J.I.Gonzhlez, J.Abajo, S.Gonzglez-Babe, J.Fontan; "Polyanhydride-Imides" Angew.Makromol. Chem., **55**, 85-96 **(1976)**.