

Synthesis and Characterization of Poly (amide-ether)s from Difluoro Compounds

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ABSTRACT: A series of poly(amide-ether)s (PAEs) were synthesized from difluoro compounds viz. (difluorodiphenyltetraphenylthiophene, 4,4'-diaminodiphenylether, 4,4'-difluorodiphenylsulphonediamine, N, N'-1,4-phenylene-bis-(4-fluorobenzenamide)) and bisphenol-A, in quantitative yield by nucleophilic aromatic substitution polycondensation. The polycondensation proceeded in DMAC at 150 °C in the presence of anhydrous potassium carbonate and toluene by azeotropic distillation. These polymers were characterized by IR, NMR, TGA, DSC. The result from IR, NMR indicate that essentially no side reaction, such as cross linking, associated with enolate chemistry took place during the polymerization. Comparison of the viscosity 0.29-0.52 g/dL and TGA of the polymers with difluorodiphenyltetraphenylthiophene to those of the analogs suggested that the DFDPTPTP impart slightly higher viscosity. These new PAE's are all soluble in polar aprotic solvents such as N-methyl-2-pyrrolidone and N, N-dimethylacetamide and could not dissolved in chloroform and tetrahydrofuran. All polymers of difluoro compounds were soluble in conc. H₂SO₄.

Keywords: poly(amide-ether), bisphenolA, crystallinity, thermal properties.

I. INTRODUCTION

Poly(amide-ether)s are widely known as Engineering thermoplastic with excellent hydrolytic and thermal stability [1,2] Although there are several synthetic methods for these polymers, They are mainly synthesized in solution by the nucleophilic aromatic substitution (SNAr) between bisphenol and aromatic dihalides, which require high reaction temperature (typically >150°C) in presence of weak bases such as K₂CO₃ and Na₂CO₃ [3,4]. A large no of polyether amide ether are available today [3-5]. There remain however, some structural modifications of polymer classes that have not been explored. These polymers are difficult to process because of low solubility in organic solvent and M.P. or softening temperature. Many efforts have been made to improve these characteristics to make such polymers more processable by introduction of bulky group of aromatic ring in the backbone. It is known that ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. Aramids containing ether linkages or asymmetric group are significantly more flexible and soluble than conventional aramids. In general these structural modifications leads to lowering of glass transition temperature as well as significant improvement in solubility and processability. Prepared monomer was incorporated into polyether amide by common SNAr route. We report the synthesis and characterization of bisphenolA based polyamide ether.

II. EXPERIMENTAL

Materials

New monomers were synthesized from 4-fluorobenzoic acid with 2,5-bis(4-aminophenyl) 3,4-diphenyl thiophene (TPTPDA) [6] and product were recrystallised by toluene. 2,5-bis(4-amino phenyl)-3,4-diphenyl thiophene, 4,4' diaminodiphenyl ether, sulphonyldiamine, difluorobenzophenone into various steps as same [7]. All the aromatic difluoro compounds and all chemicals were purified before use as per standard procedure. All other diamines were recrystallised from alcohol.

Instrument

Different scanning calorimeter (DSC) scans were obtained using in a nitrogen atmosphere at a heating rate 10°C/min. Thermogravimetric analysis (TGA) was performed with PerkinElmer TGA-7 system at a heating rate of 10°C/min in a nitrogen atmosphere from 60 to 1000°C. NMR. ¹H NMR spectra were recorded with either a Bruker 200 or 400 MHz and 50 MHz for ¹³C measurements using CDCl₃ or DMSO solvent.

The ¹H NMR spectra, used to identify the structures of the monomers, were recorded on a Bruker Avance III (400MHz) instrument. All resonances were referenced with respect to the proton signal tetramethylsilane (TMS). FTIR spectra were recorded at a resolution of 4 cm⁻¹ with co-addition of 32 scans using a Thermo-scientific Nicolet iS10 smart IR. DSC was conducted on a Mettler Toledo DSC at a heating rate of 10 °C/min over a temperature range of 50-350 °C under a nitrogen flowing atmosphere. XRD WAXD

patterns. XRD patterns of polymer were obtained with a Rigaku Micromax-007 X-ray diffractometer operating at 40 kV and 30 Ma.

Synthesis of monomer

Preparation of 2,3,4,5-tetra phenyl thiophene

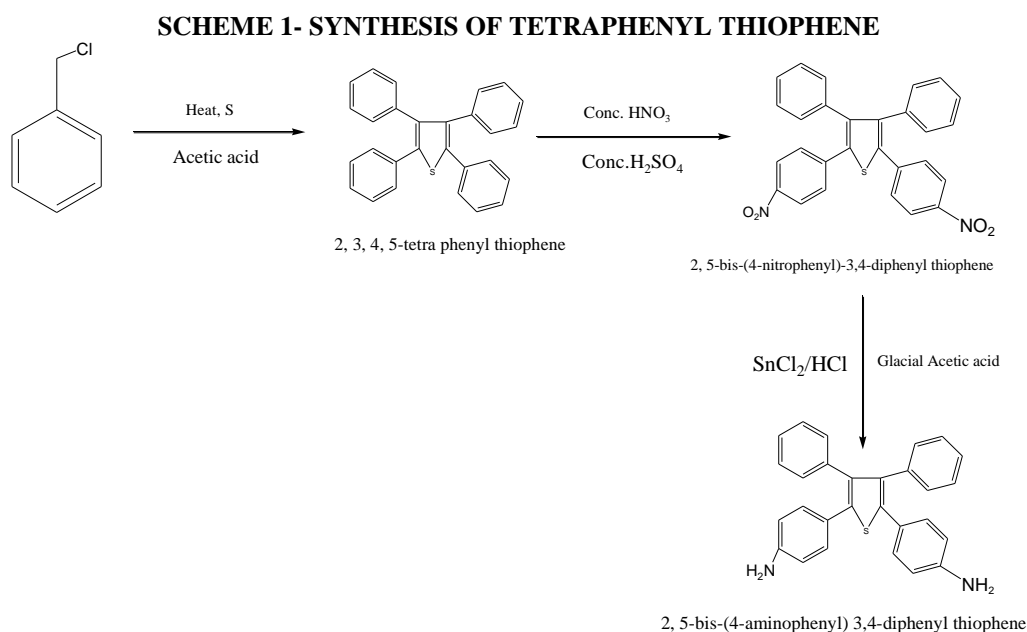
In 500 ml three necked round bottom flask equipped with a reflux condenser and stirrer, a mixture of 126.69 gm (115.1 ml, 1 mol) benzyl chloride and 19.2 gm (0.6 mol) powdered sulphur was stirred under reflux temperature until the reaction temperature reached to 240⁰ C (required about 15 hr). Then the reaction mixture was refluxed for 3 hr. at 240⁰ C and the mixture was allowed to cool to 60⁰ C. Then 100 ml of ethanol were added. The resulting solid was filtered, washed with methanol. The crude tetra phenylthiophene was recrystallised from dichloromethane-methanol system to give white needles. The yield was 39.6 gm (51%) M.P. 184-185⁰ C The IR spectrum (KBr) showed absorption at 3070 (Ar-CH) 1601 (Ar-C=C) and 1437 cm⁻¹ (thiophene)

Preparation of 2,5-bis-(4-nitrophenyl)-3,4-diphenyl thiophene.

10 gm of tetraphenylthiophene stirred with 20 mL glacial acetic acid at 10⁰ C. Adding mixture of 30 ml glacial acetic acid with 21 mL conc. Nitric acid, addition is about 1 hr. Then reaction mixture was refluxed for 30. min after filtration yellow crystals are obtained.

Preparation of 2, 5-bis-(4-aminophenyl) 3,4-diphenyl thiophene

4 gm of nitro T.P.T.P. was dissolved in 40 mL of glacial acetic acid and mixture of 20 g SnCl₂ in 9 mL Conc. HCl was added. The reaction mixture was stirred at 100⁰ C for 4 hr. Then reaction mixture was cooled and content were added to 110 mL 40% NaOH, free diamine was obtained, after refluxing for 30 min. reaction mixture was poured in ice cooled water. The product obtained was filtered, washed with water to make free from alkali, Diamine was extracted with toluene and the filtrate was concentrated. The product was recrystallised twice from toluene to give, white needles. The yield was 53%. M.P. of product 276-277⁰ C.



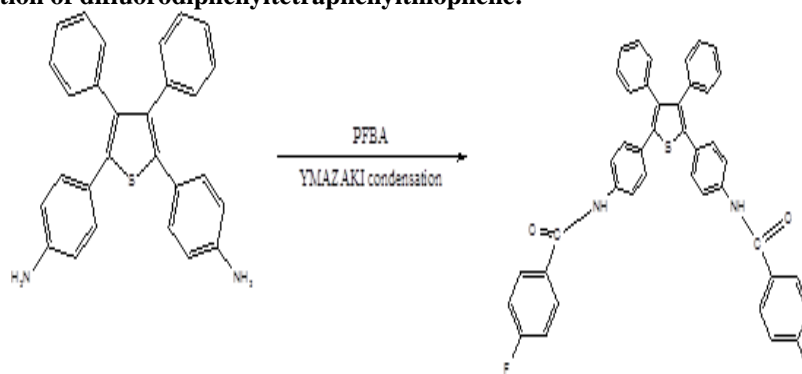
Synthesis of monomer

Preparation of bis(4-fluoro-N-[4-(3-phenyl-thiophen-2-yl)-phenyl]-benzamide

In three necked round bottom flask charge diamino TPTP 0.418 g (0.001 mole) and 0.280 gm PFBA (0.002 mole), NMP(6mL), LiCl(0.5 g), pyridine (1.8mL), TPP(1.2 mL) all are added in flask and mixture was refluxed for 3 hr at 140⁰ C After cooling the solution was poured into stirred methanol with constant stirring and precipitate was filtered off.

IR -(C=O) amide 1643, N-H str.3290, N-H bend 1591, C-F 1000-1400, C=N 1600, C=S thiocarbonyl 1050-1200. NMR -¹H NMR :-Aromatic proton 8.0 d, 7.5 d, 7.0 d.

• **Preparation of difluorodiphenyltetraphenylthiophene:**



Synthesis of 4,4'-bis difluorodiphenoxydiphenyl ether

In three necked R.B. charge ODA gm (0.001 mole) and 0.280 gm PFBA (0.002 mole), NMP(6mL),LiCl(0.5 g), pyridine (1.8mL), TPP(1.2 mL) all are added in flask and mixture was refluxed for 3 hr at 140⁰C. After cooling the solution was poured into stirred methanol with constant stirring and precipitate was filtered off.
IR:- C=Oamide 1643, N-H str.3290, N-H bend 1591, C-F 1000-1400, C=N 1600, C=S thiocarbonyl 1050-1200.

Synthesis of 4,4'-difluorodiphenylsulphonediimine

In three necked R.B. charge ODA gm (0.001 mole) and 0.280 gm PFBA (0.002 mole), NMP(6mL),LiCl(0.5 g), pyridine (1.8mL), TPP(1.2 mL) all are added in flask and mixture was refluxed for 3 hr at 140⁰c. After cooling the solution was poured into stirred methanol with constant stirring and precipitate was filtered off.
IR:- C=O amide 1643, N-H str.3290, N-H bend 1591, C-F 1000-1400, C=N 1600, C=S thiocarbonyl 1050-1200.

Synthesis of N, N'-1,4-phenylene-bis-(4-fluorobenzamide)

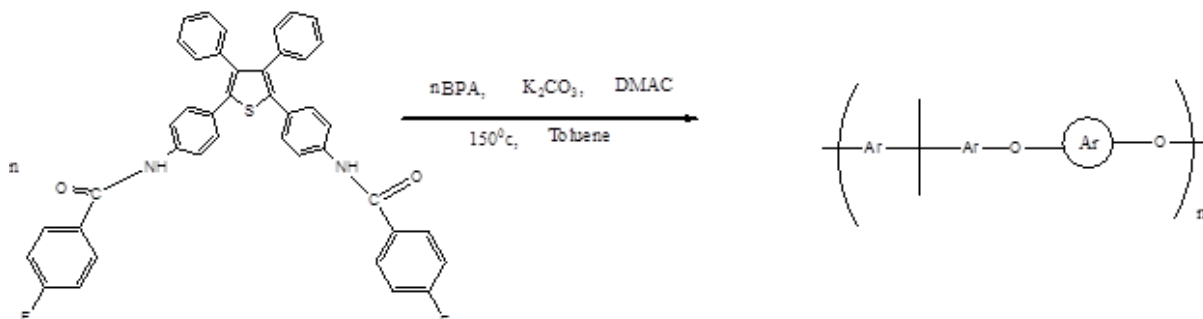
In three necked R.B. charge phenylenediamine 0.108gm (0.001 mole) and 0.280 gm PFBA (0.002 mole), NMP(6mL),LiCl(0.5 g), pyridine (1.8mL), TPP(1.2 mL) all are added in flask and mixture was refluxed for 3 hr at 140⁰C. After cooling the solution was poured into stirred methanol with constant stirring and precipitate was filtered off.By using Yamazaki's amide synthesis method [7] all difluorocompounds were prepared using 4-fluoro benzoic acid.

III. POLYMERISATION

Polymerization of various aromatic difluoro compounds was performed by using BPA,K₂CO₃, in DMAC. The obtained product was dried under vaccum at 130⁰ C for overnight. Same procedure was followed for all the polyamide ethers.

Synthesis of polymer of bis4-fluoro-N-[4-(3-phenyl-thiophen-2-yl)-phenyl]-benzamide with BPA

In three neck R.B. flask with nitrogen inlet, Charge DFDPTPTP 0.614 g (0.001mole) along with BPA 0.228 g (0.001mole), K₂CO₃ 0.276 g (0.002 mole). Reaction mixture was refluxed in DMAC for 3 hr. at 150⁰C. Toluene was added for azeotropic distillation. Yield was 94%
IR:- amide-C=O 1650 cm⁻¹, N-H 3320 cm⁻¹, Ar-O-Ar 1229 cm⁻¹

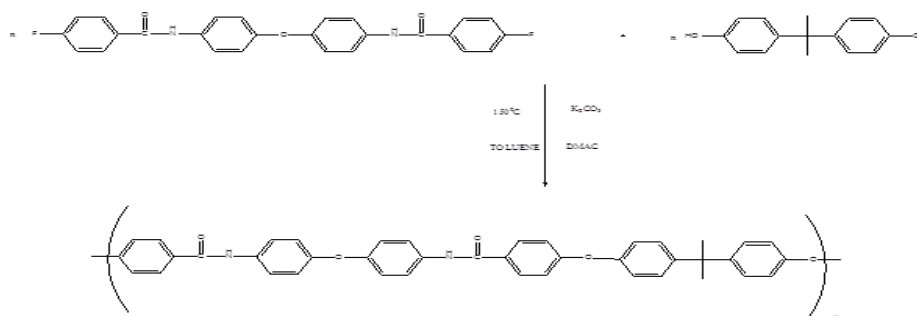


Synthesis of Polymer of N,N'-1,4-phenylene-bis(4-fluorobenzamide)with BPA

In three neck R.B. flask with nitrogen inlet, Charge N,N'-1,4-phenylene bis(4-fluorobenzamide) 4.44 g (0.01mole) along with BPA 2.28 g (0.01mole), K₂CO₃ 0.276 g (0.02 mole). Reaction mixture was refluxed in DMAC for 3 hr. at 150⁰c. Toluene was added for azeotropic distillation. Yield was 94%
IR:- amide-C=O 1620 cm⁻¹, N-H 3200cm⁻¹, Ar-O-Ar1230 cm⁻¹

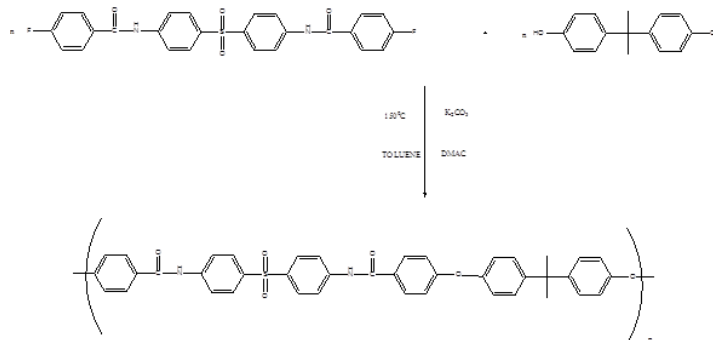
Synthesis of polymer of 4,4'-bis difluorodiphenoxydiphenyl ether with BPA

In three neck R.B. flask with nitrogen inlet, Charge DFDPODA 4.44 gm (0.01mole) along with BPA 2.28 g (0.01mole), K₂CO₃ 0.276 g (0.02 mole). Reaction mixture was refluxed in DMAC for 3 hr. at 150^oC. Toluene was added for azeotropic distillation. Yield was 90%. IR:- amide-C=O 1650 cm⁻¹, N-H 3320 cm⁻¹, Ar-O-Ar 1229 cm⁻¹



Synthesis of polymer of difluorodiphenylsulphonediaminewith BPA

In three neck R.B. flask with nitrogen inlet, Charge DFDPSDA 4.92 g (0.01mole) along with BPA 2.28 g (0.01mole), K₂CO₃ 0.276 g (0.02 mole). Reaction mixture was refluxed in DMAC for 3 hr. at 150^oC. Toluene was added for azeotropic distillation. Yield was 90%



Synthesis of co-polymer of bis4-fluoro-N-[4-(3-phenyl-thiophen-2-yl)-phenyl]-benzamide, 4,4'-bis difluorodiphenoxydiphenyl ether and BPA

In three neck R.B. flask with nitrogen inlet, Charge DFDPTTP 0.460 g (75%), DFDPODA 1.11g (25%) along with BPA 2.28 g (0.01mole), K₂CO₃ 0.276 g (0.02 mole). Reaction mixture was refluxed in DMAC for 3 hr. at 150^oC. Toluene was added for azeotropic distillation. Yield is 90%
IR:- amide-C=O 1650 cm⁻¹, N-H 3305 cm⁻¹, Ar-O-Ar 1303 cm⁻¹, N-H bend 1591

Figures

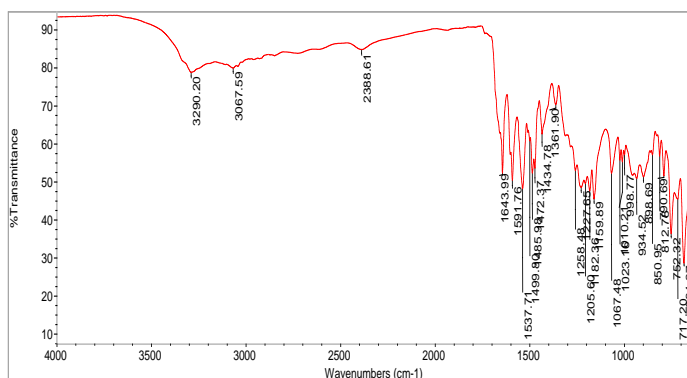


Fig.1 IR of monomer

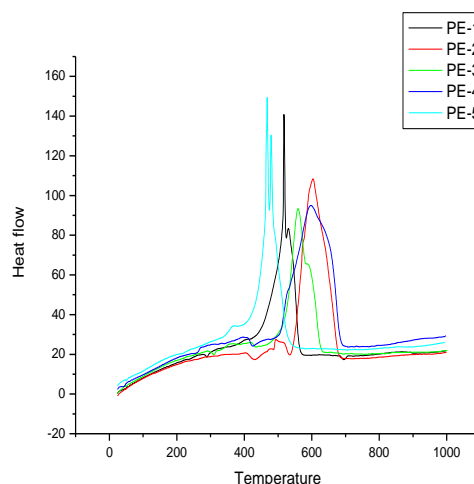
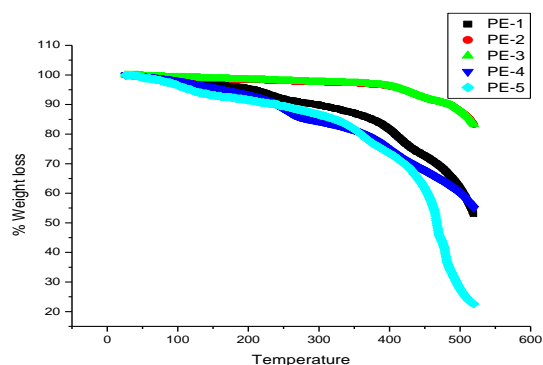
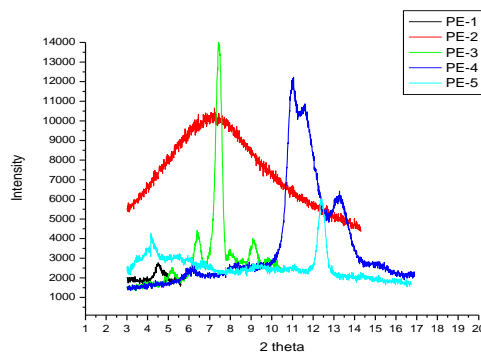


Fig.2 DSC curves of polymers


Fig. 3 TG Curves for PE-1 to PE-5.

Fig. 4 XRD Curves for PE-1 to PE-5.

The crystallinity of poly (amide-ether)s and copoly (amide-ether)s was examined by means of wide-angle X-ray diffraction. The polymer PE-1, containing bulky tetraphenyl pendant groups, showed an amorphous nature, whereas the wide angle X-ray diffractograms of the polymer PE-2 indicated that the polymer PE-2 was semicrystalline (Fig.2). PE-3 to PE-5 showed semicrystallinity nature. Crystallinity of all polymer was reflected in their relatively good solubility behavior in high polar solvents, which is in agreement with the general rule that the solubility increases with decreasing crystallinity.

Tables

Table-(i): Thermal Analysis data^a of poly (amide-ether)s from various difluoro compounds and BPA

Polymer	At initial ^b		At 10 % loss ^c		At 50% loss ^d		At Maximum ^e		T _g (°C) ^f
	Weight (mg)	Temperature °C	Weight (mg)	Temperature °C	Weight (mg)	Temperature °C	Weight (mg)	Temperature °C	
PE-1	4.4	190	3.9	360	2.24	510	1.35	720	288
PE-2	5.4	370	4.8	500	2.7	580	0.3	670	200
PE-3	4.7	250	4.2	360	2.35	520	0.6	650	206
PE-4	7.8	70	7.02	220	3.9	530	1.75	470	320
PE-5	3.4	150	3.05	330	1.75	470	0.7	720	300

- Thermogravimetric analysis at heating rate 10⁰ C/min under nitrogen.
- Temperature at which initial weight loss is observed.
- Temperature at which 10% weight loss is observed.
- Temperature at which 50% weight loss is observed.
- Temperature at which maximum weight loss is observed.
- Determined by DSC.

Table-(ii) Solubility

Polymer	DMAC	DMF	DMSO	NMP	Pyridine	m-cresol	THF	Toluene	Conc.H ₂ SO ₄
PE-1	++	++	+	++	++	+-	--	--	++
PE-2	++	+-	+-	++	++	--	--	--	++
PE-3	++	+-	++	++	++	--	--	--	++
PE-4	++	--	+-	+-	++	--	--	--	++
PE-5	++	++	+-	++	++	+-	--	--	++
PE-6	++	++	+-	++	++	+-	--	--	++
PE-7	++	++	+-	++	++	+-	--	--	++

Table-(iii) Viscosities of polymers

Polymer	Difluoro compound	BPA	Viscosity(□) g/dL
PE-1	DFDPTTP	BPA	0.52
PE-2	DFBP	BPA	0.36
PE-3	DFDPODA	BPA	0.38
PE-4	DFDPSDA	BPA	0.29
Co-Polymer	DFDPTTP + DFDPODA	BPA (mol)	Viscosity(□)g/dL
CPE 5	25% + 75%	1	0.38
CPE 6	50% + 50%	1	0.41
CPE 7	75% + 25%	1	0.51

Table incorporate the thermal data such as glass transition temperature (T_g). Initial decomposition (T_i). temperature at 10% weight loss (T₁₀) and temperature at 50% weight loss (T₅₀) as well as char yield that is remaining after heating T max. For PE-1 to PE-5 have high T_g values. PE-5 i.e. Co-poly ether showed similar pattern of thermal decomposition with no weight loss below 150 °C under nitrogen and T₅₀ in the range of below

470 °C. However along the series of polyamide ether the thermal stability of PE-1 increased in each, as evidenced by T_{10} and T_{50} values.

Solubility and Viscosity

The solubility behavior of the polymer with respect to various solvent is listed in table. All the Polyether were found to be soluble in conc. H_2SO_4 . It is well known that the conventional PEEK and PEKK[11-12] could not dissolved in most organic solvents. In sharp contrast these new polyethers were soluble at room temperature in polar aprotic solvent DMAC, DMSO, except polymer 1.

Viscosities of polymers are in good length from polymer I to VII. All these polymers were obtained in almost quantitative yield (90 to 95%) as a white to pale yellow fibrous material. As mol % in copolymer increased it become more fibrous in nature. The inherent viscosity of the corresponding polymer was increased.

All the polymer were prepared as per procedure. Viscosities of all polymers were measured in conc. H_2SO_4 at $25^\circ C \pm 1^\circ C$.

IV. CONCLUSION

Synthesized polymers and copolymers were characterized by IR, viscosity, solubility, thermal analysis and XRD. Copolymers had better solubility because of random, symmetry-disturbing arrangement of bulky moieties and amorphous nature of copolymers. amide-ether linkages and copolymerization was synergistically more effective for improving the solubility without sacrificing the thermal stability of poly (amide-ether)s polymers[13-16]. Comparison of the viscosities 0.29-0.52 g/dL and suggested that the DFDPTPTP impart slightly higher viscosity. The DSC curves indicate that there is a crystalline melt defined by peak temperature. After the melt transition, the base line return to a slightly lower position than the pre-melt baseline. These new PAEs are soluble in polar aprotic solvents such as N-methyl-2-pyrrolidone and N, N-dimethylacetamide and could not dissolve in chloroform and tetrahydrofuran. All polymers of DFDPTPTP were soluble in conc. H_2SO_4 . Synthesis of poly bis-4-fluoro-N-[4-(3-phenyl-thiophene-2-yl)-phenyl]-benzamide was successfully synthesized in good yield with a one-pot, two step procedure using bisphenol A. The resulting PAEs are amorphous and have high molecular weight, high glass transition temperatures, good thermal stability and mechanical properties. These polymers have remarkably improved solubilities in common organic solvents over the conventional PEEK and PEKK. The excellent solubility makes the polymers potential candidates for practical applications in casting processes.

REFERENCES

- [1] Bower GM, Frost LW. *J PolymSci Part A: PolymChem*(1963), 1, 3135.
- [2] Lee C, Iyer NP, Min K, Pak H, Han H. *J PolymSci Part A: PolymChem*(2004), 42, 37.
- [3] K. Osano et al. Elsevier, *Polymer* (2009), 50, 1144–1149.
- [4] Shou-Ri Sheng et al. *Journal of Applied Polymer Science* (2009), DOI10.1002/app.30628.
- [5] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, *Alternativ polymer systems for proton exchange membranes*, *Chem. Rev.*(2004), 104, 4587–4612 .
- [6] Basutkar PH, et.al, *J ApplPolymSci* (1998), 68, 1523.
- [7] Yamazaki N, et.al, *J PolymChem*(1974), 12, 2149.
- [8] Y.Woo, S.Y.Oh, Y.S.Kang, B.Jung, *Synthesis and characterization of sulfonated polyimide membranes for direct methanol fuel cell*, *J.Membr.Sci.*, (2003), 220, 31–45.
- [9] N. Gourdoupi, A.K. Andreopoulou, V. Deimede, J.K. Kallitsis, *Novel proton-conducting polyelectrolyte composed of an aromatic polyether containing main-chain pyridine units for fuel cell applications*, *Chem.Mater.* (2003), 5, 5044–5050.
- [10] S.C. Yeo, A.J. Eisenberg, *Physical properties and supermolecular structure perfluorinated ion-containing (nafion) polymers*, *J. Appl. Polym.Sci.*(1977), 21, 875–898.
- [11] I.M.Hodge, A. Eisenberg, *Dielectric and mechanical relaxations in anafion precursor*, *Macromolecules*, (1978), 11, 289–293.
- [12] Baijunliu et.al. *Polym.Adv.Technol.*(2003), 14, 221-225.
- [13] *Polym.Bull.* (2013), 7, 1125-1142 .
- [14] *Soluble tetraphenyl thiophene containing poly (amide-imide)s – Synthesis and characterization* A.A Ghanvat, V.P. Ubale *international J. of pharm. Sci. inv.* (2015), 4,2, pp 49-56.
- [15] Imai Y, Maldar NN, Kakimoto M, *J PolymChem*(1984), 22, 2189.
- [16] Imai Y, Maldar NN, Kakimoto M, *J PolymChem*(1984), 22, 3711.
- [17] N.N. Maldar, M.A. Kakimoto, Y. Imai, *J. Polym. Sci. Part A: Polym. Chem. Ed.* 23, (1985), 1797.
- [18] Yamazaki N, et.al, *J PolymChem*(1974), 12, 2149.
- [19] N. Yamazaki, M. Masumoto, F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.* 13, (1975), 1373.
- [20] W. Li et al. / *Polymer* 49 (2008) 4080–4086.
- [21] *Macromol.chem.phys.* (2014) 215, 2260-2267.
- [22] *J Mater Sci.* (2014) 49:7213-7220.
- [23] *Polym Int.* (2012), 62, 791-796.
- [24] *Polymer science, Ser.B.*(2014) vol.56, No.5, 639-644.
- [25] *Polym.Bull.* (2011), 67, 1139-1152.
- [26] Ubale VP, Patil AS, Maldar NN. *Euro Polym J* (2007); 42: 1038.