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Synthesis and Characterization of New Poly(ether sulfones) from 4,4'-(arylpyridine-2,6-diyl)diphenol and Bis(fluorophenyl)sulfone

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Abstract

In this research, a series of new poly(ether sulfone) derivatives were prepared by the direct condensation of 4,4'-(arylpyridine-2,6-diyl)diphenols with bis(fluorophenyl)sulfone in the presence of K_2CO_3 in DMSO/toluene at 180°C. The synthetic polymers show good solubility in polar aprotic solvents, such as DMSO, NMP, DMF, as well as in THF. The resulting gel permeation chromatography (GPC) analysis of poly (ether sulfones) indicates moderate molecular weights (M_w) in the range of 1625-4185 g/mol. Using differential scanning calorimetry, the glass transition temperatures of the poly (ether sulfones) were determined to be within the range of 157–181°C. Thermogravimetric analysis data for these polymers showed the 10% weight loss temperatures to be within the range of 177–377°C. The char yields of the polymers at 600°C ranged from about 43–62%. This method provides a simple polymerization process for the convenient preparation of poly (ether sulfones).

Keywords: Poly(ether sulfone), 4,4'-(Arylpyridine-2,6-diyl)diphenols, Bis(fluorophenyl)sulfone, Polycondensation.

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Introduction

Poly (arylene ether sulfones) are an important engineering thermoplastics that are widely used for the preparation of membrane processes such as microfiltration (MF), ultrafiltration (UF), and gas separation (GS) membranes. This is due to their suitable characteristics like broad operating pH tolerances, wide operating temperature limits, chemical resistance to chlorinated disinfectants, alcohols, acids, aliphatic hydrocarbons, hydrolysis, and oxidation, as well as their good mechanical properties, toughness, and thermal stability [1,2]. Recently, poly(ether sulfone) membranes (or their composites) have been used for oily wastewater treatment [3], pharmaceutical wastewater treatment [4], direct methanol fuel cells [5], removal of bisphenol A from water [6], as catalysts for esterification [7], and for CO_2/N_2 separation [8]. Synthesis of poly (arylene ether sulfones) has been achieved via direct condensation of bisphenol A and dichlorodiphenyl sulfone [9], reaction of chloromethylated poly (ether sulfone) (CMPS) and 9,10-dihydrooxa-10-phosphaphenanthrene-10-oxide (DOPO) [10], reaction between chlorosulfonated poly (ether sulfone) and oligomeric poly (ethylene glycol) (PEG) [11], sulfonation of bisphenol A polysulfone and bisphenol A polysulfone-*b*-PVDF copolymer [12], reaction of disodium-3,3-disulfonate-4,4-dichlorodiphenyl sulfone (SIDCDPS) and 4,4-dichlorodiphenyl sulfone (DCDPS) and bisphenol A (BPA) in DMF/toluene at 130 ^{o}C [13], and reaction from different amounts of 4,4′dihydroxydiphenylsulfone (DHDPS), 4,4-Bis(4-hydroxyphenyl) pentanoic acid (DPA) and stoichiometric amount of 4,4′-dichlorodiphenylsulfone (DCDPS) by nucleophilic aromatic displacement in the presence of potassium carbonate in N-Methyl-2-pyrrolidone (NMP)/ toluene [14]. Also, partially bio-based (co)poly(ether sulfone)s bearing pendant furyl groups were synthesized by aromatic nucleophilic substitution polycondensation of 4,4′-(furan-2-ylmethylene)bis(2-methoxyphenol) (BPF) and various mixtures of BPF and bisphenol-A with bis(4-fluorophenyl) sulfone in *N*,*N*-dimethylacetamide as a solvent [15] and a class of poly(ether sulfone ketone)s containing multiple sulfonic acids on the side chains of the sulfonated structural units were designed and prepared by a convenient and mild post-sulfonation reaction process [16]. Furthermore, a class of poly(ether sulfone) (FPES) block copolymers containing pendent quaternary ammonium (QA) and imidazolium (IM) groups were prepared as anion exchange membranes by reaction involving nucleophilic substitution, benzylic bromination, quaternization and anion exchange with hydroxide ions. Highly reactive hexafluorobenzene (HFB) was utilized as a linkage group between hydrophobic and precursor hydrophilic oligomer blocks [17].

Following our research that provided a suitable method for the preparation of synthetic polymers [18, 19], here, a method for the synthesis of poly (ether sulfone) derivatives from direct condensation of 4,4'-(arylpyridine-2,6-diyl)diphenol and bis(fluorophenyl)sulfone was developed.

The advantage of this method is that it provides a simple and economical process for the preparation of synthetic poly (ether sulfones).

Experimental

General

All chemicals, including bis(fluorophenyl)sulfone, *p*-hydroxy acetophenone, glacial acetic acid, arylaldehyde, K_2CO_3 and solvents, were purchased either from Merck or Aldrich chemical companies. Fourier transform infrared (FTIR) spectra were recorded with a Shimadzu FTIR spectrometer (8900, Japan) using KBr pellets. ^{1}H NMR spectra were recorded in a deuterated dimethylsulfoxide (DMSO-d_6) solution using a Bruker Advance DRX 300 MHz spectrometer (Germany). Elemental analyses were performed using a CHNSO Rapid Heraeus elemental analyzer (Wellesley, MA). DSC and TGA were carried out with a Stanton Redcraft STA-780 (London, UK). Molecular weights were measured by gel permeation chromatography (GPC Agilent 1100, detector: RI (refractometer Index), Tem. 30 °C, Flow: 1 ml/min, Column: PLgel).

Synthesis of 4,4'-(arylpyridine-2,6-diyl)diphenols

In a 250-ml flask equipped with a magnetic stirrer, a mixture of aromatic aldehydes (1 mmol), *para*-hydroxy acetophenone (2 mmol) and ammonium acetate (1.2 mmol) was poured in acetic acid (5 ml) under reflux conditions. The progress of the reaction was monitored by thin-layer chromatography (*n*-hexane/ethyl acetate 4:6). After the reaction ended, the product was recrystallized from ethanol (10 ml) to give pure derivatives of (4-aryl)pyridine-2,6-diyl) diphenol. The structures of the products were confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

4,4'-(4-(4-chlorophenyl)pyridine-2,6-diyl)diphenol **(4a)**

Yield = 98%; FT-IR (KBr, cm^{-1}): 813, 1173, 1226, 1342, 1402, 1465, 1544, 1595, 1641, 3056.^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): δ = 6.92 (d, J=8.1 Hz, 2H, Ar-H), 7.49 (t, J= 8.1 Hz, 2H, Ar-H), 7.65 (d, J= 8.1 Hz, 2H, Ar-H), 7.88-7.97 (m, 2H, Ar-H), 8.09 (d, J= 8.1 Hz, 2H, Ar-H), 10.47 (s, 2H, 2OH). ^{13}C NMR (75 MHz, DMSO-d_6, δ ppm): δ=187.4, 162.7, 141.6, 135.2, 134.3, 131.7, 130.8, 129.5, 129.3, 123.3, 115.8. Anal. calcd for $C_{23}H_{16}NO_2Cl$: C 73.90, H 4.31, N 3.75; found: C 73.92, H 4.33, N 3.76.

4,4'-(4-(2-nitrophenyl)pyridine-2,6-diyl)diphenol **(4b)**

Yield = 97%; FT-IR (KBr, cm^{-1}): 750, 833, 972, 1163, 1228, 1290, 1344, 1436, 1512, 1566, 1612, 1650, 3236. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): δ = 6.92 (d, J=8.7 Hz, 4H, Ar-H), 7.64 (td, J= 8.1, 0.9 Hz, 1H, Ar-H), 7.77-7.84 (m, 1H, Ar-H), 7.89 (d, J=8.7 Hz, 4H, Ar-H), 8.05-8.11 (m, 3H, Ar-H), 8.15 (d, *J*=7.5 Hz, 2H, Ar-H), 10.53 (s, 2H, 2OH). ^{13}C NMR (75 MHz, DMSO-*d₆,* δ ppm): *δ*=187.3, 163.0, 149.1, 137.6, 134.1, 131.9, 130.1, 130.4, 129.8, 129.1, 127.0, 125.0, 115.9. Anal. calcd for $C_{23}H_{16}N_2O_4$: C 71.87, H 4.20, N 7.29; found: C 71.85, H 4.22, N 7.30.

4,4'-(4-(3-nitrophenyl)pyridine-2,6-diyl)diphenol **(4c)**

Yield = 96%; FT-IR (KBr, cm^{-1}): 725, 844, 982, 1166, 1226, 1284, 1301, 1346, 1523, 1556, 1591, 1606, 1649, 3209, 3510. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): *δ* = 6.91 (d, *J*=8.7 Hz, 4H, Ar-H), 7.73 (d, *J*= 8.7 Hz, 4H, Ar-H), 8.10 (d, *J*=5.1 Hz,1H, Ar-H), 8.15 (s, 2H, Ar-H), 8.26 (dd, 2H, *J*= 18, 7.8 Hz, Ar-H), 8.75 (s, 1H, Ar-H), 10.48 (s, 2H, 2OH). ^{13}C NMR (75 MHz, DMSO-d_6, δ ppm): *δ*=187.3, 162.9, 148.8, 140.6, 137.2, 135.3, 131.8, 130.6, 129.3, 125.3, 124.7, 123.2, 115.8. Anal. calcd for $C_{23}H_{16}NO_4$: C 71.87, H 4.20, N 7.29; found: C 71.84, H 4.23, N 7.32.

4,4'-(4-(4-methoxyphenyl)pyridine-2,6-diyl)diphenol **(4d)**

Yield = 95%; FT-IR (KBr, cm^{-1}): 823, 1027, 1107, 1164, 1218, 1255, 1286, 1344, 1423, 1440, 1461, 1510, 1546, 1600, 1658. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): *δ* = 3.76 (s, 3H, OMe), 6.79-7.16 (m, 6H, Ar-H), 7.77 (s, 2H, Ar-H), 7.88-7.95 (m, 2H, Ar-H), 8.13 (d, *J*=8.1 Hz, 2H, Ar-H), 8.23 (d, *J*= 8.1 Hz, 2H, Ar-H), 10.23 (s, 2H, 2OH). ^{13}C NMR (75 MHz, DMSO-d_6, δ ppm): *δ*=187.6, 162.5, 143.2, 133.7, 131.1, 130.8, 129.9, 129.7, 128.8, 115.9, 56.7. Anal. calcd for $C_{24}H_{19}NO_3$: C 78.03, H 5.18, N 3.92; found: C 78.05, H 5.20, N 3.90.

4,4'-(4-(4-(dimethylamino)phenyl)pyridine-2,6-diyl)diphenol **(4e)**

Yield = 94%; FT-IR (KBr, cm^{-1}): 702, 831, 979, 1006, 1105, 1149, 1242, 1292, 1323, 1407, 1487, 1506, 1585, 1656, 2952, 3060, 3550. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): *δ* = 3.01 (s, 6H, $N(CH_3)_2$), 6.94 (m, 6H, Ar-H), 7.65 (m, 4H, Ar-H), 7.91 (s, 1H, Ar-H), 8.16 (d, *J*=8.7 Hz, 2H, Ar-H), 9.88 (s, 2H, 2OH). ^{13}C NMR (75 MHz, DMSO-d_6, δ ppm): *δ*=187.1, 162.5, 146.8, 139.6, 135.2, 133.3, 131.6, 129.4, 128.3, 116.3, 115.8, 41.2. Anal. calcd for $C_{25}H_{22}N_2O_2$: C 78.51, H 5.80, N 7.32; found: C 78.53, H 5.85, N 7.34.

Poly(ether sulfones) synthesis

Potassium carbonate (5 mmol) was added to a solution of 4,4'-(arylpyridine-2,6-diyl)diphenols (5 mmol) and bis(4-fluorophenyl)sulfone (5 mmol) in a dimethylsulfoxide/toluene (25 ml) solvent. The mixture was stirred at 180°C for 24 h. The resulting solution was poured onto water. The precipitate was collected by filtration and washed well with cold water. The polymer was then dried in a vacuum oven at 60°C. All synthesized polymers were identified by IR, ^{1}H-NMR spectroscopy and elemental analysis.

PES-a

Yield = 97%; FT-IR (KBr, cm^{-1}): 833, 1012, 1105, 1152, 1245, 1292, 1323, 1410, 1489, 1584, 1665, 3068. ^{1}H NMR (300 MHz, DMSO-*d₆,* δ ppm): δ = 6.91-8.29 (m, Ar-H). Anal. calcd for $(C_{35}H_{22}NO_4SCl)_n$: C 71.48, H 3.77, N 2.38, S 5.45; found: C 71.53, H 4.80, N 2.40, S 5.48.

PES-b

Yield = 96%; FT-IR (KBr, cm^{-1}): 702, 831, 1151, 1242, 1369, 1525, 1585, 1652, 3083. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): δ = 6.97-8.30 (m, Ar-H). Anal. calcd for $(C_{35}H_{22}N_2O_6S)_n$: C 70.22, H 3.70, N 4.68, S 5.36; found: C 70.25, H 3.75, N 4.71, S 5.40.

PES-c

Yield = 95%; FT-IR (KBr, cm^{-1}): 698, 844, 1006, 1153, 1346, 1438, 1522, 1658, 3073. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): δ = 7.01-8.30 (m, Ar-H). Anal. calcd for $(C_{35}H_{22}N_2O_6S)_n$: C 70.22, H 3.70, N 4.68, S 5.36; found: C 70.26, H 3.74, N 4.72, S 5.42.

PES-d

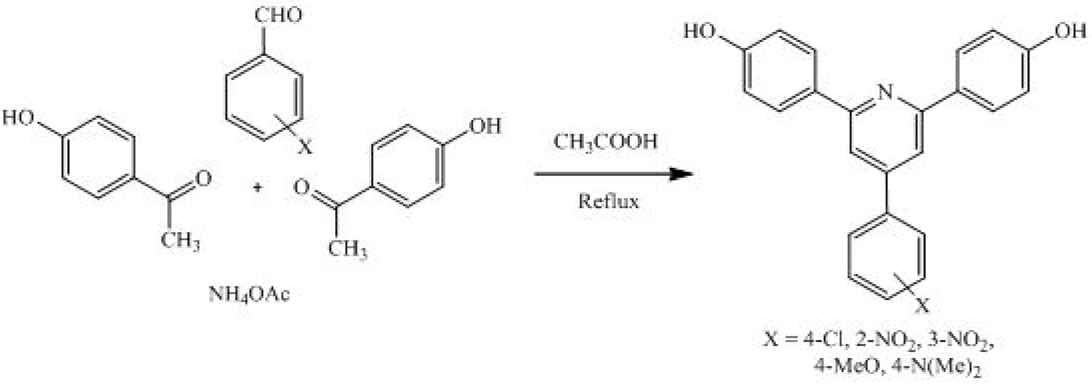
Yield = 94%; FT-IR (KBr, cm^{-1}): 833, 1105, 1151, 1240, 1487, 1502, 1525, 1585, 1654, 3446. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): δ = 3.83 (s, OMe), 7.01-8.06 (m, Ar-H), 8.19 (s, Ar-H), 8.24 (d, J = 8.1 Hz, Ar-H), 8.41 (d, J = 7.8 Hz, Ar-H). Anal. calcd for $(C_{36}H_{25}NO_5S)_n$: C 74.08, H 4.32, N 2.40, 5.49; found: C 74.10, H 4.35, N 2.44, S 5.55.

PES-e

Yield = 95%; FT-IR (KBr, cm^{-1}): 702, 831, 1105, 1149, 1242, 1323, 1407, 1487, 1506, 1585, 1656, 2952, 3060. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): δ = 3.18 (s, $2N(CH_3)_2$), 6.73-8.42 (m, Ar-H). Anal. calcd for $(C_{41}H_{28}N_2O_4S)_n$: C 76.38, H 4.38, N 4.34, 4.97; found: C 76.47, H 4.43, N 4.36, S 5.02.

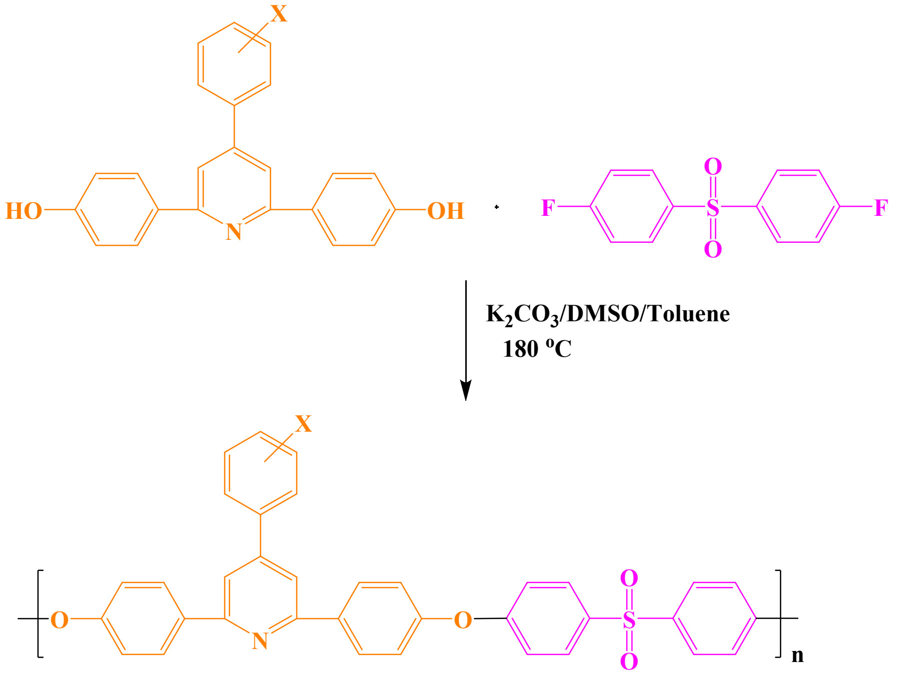
Results and discussion

The present article describes a simple and efficient preparation of poly(ether sulfones) through the condensation of 4,4'-(arylpyridine-2,6-diyl)diphenols with bis(fluorophenyl)sulfone in the presence of K_2CO_3 in DMSO/toluene at 180°C. 4,4'-(Arylpyridine-2,6-diyl)diphenol derivatives were synthesized from the reaction of 4-hydroxyacetophenone, arylaldehyde, and ammonium acetate in acetic acid under reflux conditions (Scheme 1).



Scheme 1. Synthesis of 4,4'-(arylpyridine-2,6-diyl)diphenols.

Scheme 2 shows the synthetic route used for the synthesis of the poly (ether sulfones).



X	p-Cl	o-NO_2	m-NO_2	p-MeO	p-N$(Me)_2$
PES	PES-a	PES-b	PES-c	PES-d	PES-e

Scheme 2. The synthetic route for the synthesis of the poly(ether sulfones).

All poly(ether sulfones) were identified using FT-IR, NMR, and elemental analyses. The FT-IR spectra of the resulting polymers established corresponding ether and sulfone absorptions. For example, the FT-IR spectrum of the PESa polymer (Figure 1) shows bands at about 3068 (Ar–CH stretching), 1665 (C=N stretching), 1584, 1489 (C=C stretching), 1245, 1105 (asymmetric and symmetric SO_2 stretching), and 1152 cm^{-1} (C–O stretching). The ^1H NMR spectrum of prepared poly (ether sulfone) (PES-a) is shown in Figure 2. The hydrogens of the aromatic rings appear at 6.72–8.29 ppm, which can be related to aromatic hydrogens a, b, e, f, in the range of 6.91–7.73 ppm and aromatic hydrogens c, d, g, in the range of 7.78–8.29 ppm. Furthermore, an elemental analysis was carried out on the polymers, and the results are in good agreement with the calculated values.

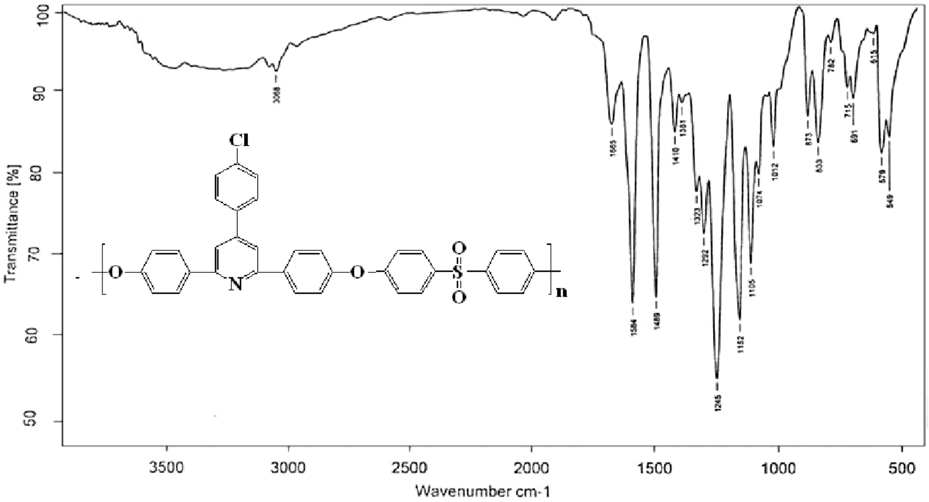


Figure 1. FT-IR spectrum of PES-a.

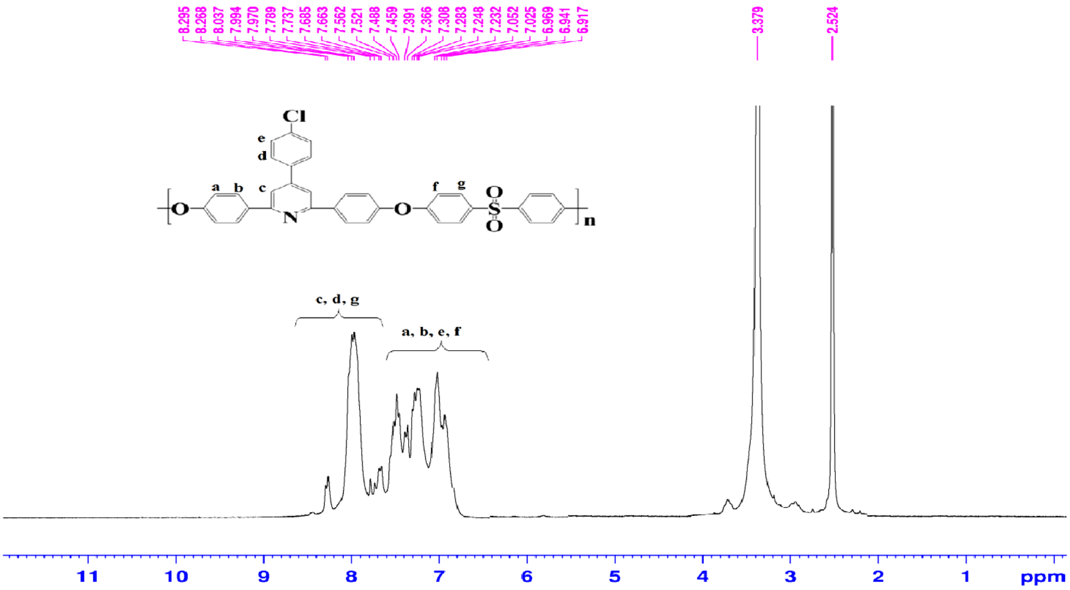


Figure 2. ^1H NMR (300 MHz) spectrum of PES-a.

Gel permeation chromatography (GPC) was used to determine the molecular weight of synthesized poly(ether sulfones). The molecular weights (M_w) of the poly (ether sulfones) were within the range of 1625–4185 g/mol. The resulting poly(ether sulfones) have moderate molecular weights. The DSC thermogram of synthetic poly (ether sulfones) shows that the glass transition temperatures (T_g) of these polymers ranged from 157-181°C. The endothermic peak of the polymer melting temperature is not seen in these thermograms until degradation; thus, it can be concluded that the resulting polymers are non-crystalline (amorphous) (Figure 3). Due to the presence of bulky groups in the main polymer chains, the polymer chains cannot interact sufficiently with each other. As a result of the weak intermolecular forces in them, their structure becomes amorphous. Of all these polymers, PES-d has the lowest T_g, as it has a more flexible dimethylamine substitution.

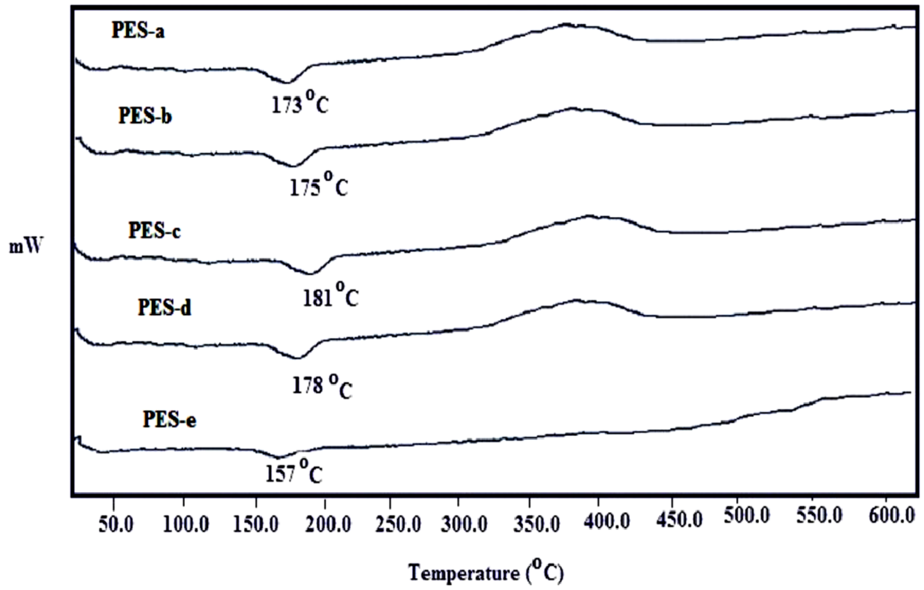


Figure 3. DSC curves of poly(ether sulfones).

The thermal stabilities of the polymers were also evaluated using TGA in nitrogen at a heating rate of 10 °C min^{-1}. The TGA of the polymers indicates that the 10% weight loss temperatures are in the range of 177–377 °C and that the char yields of the polymers at 600°C range from about 43–62%. The results obtained are summarized in Table 2. Representative TGA curves for the polymers are shown in Figure 4.

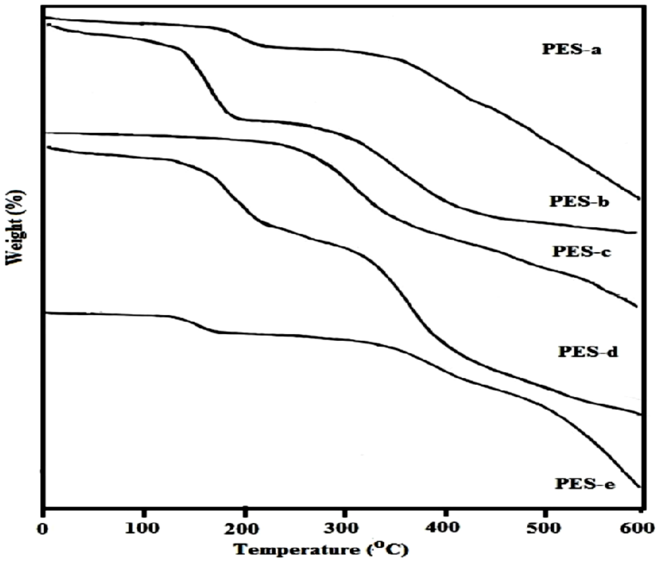


Figure 4. TGA curves of poly(ether sulfones).

The solubility behaviour of the polymers in various solvents was examined (Table 1). All of the poly(ether sulfones) possess good solubility in polar aprotic solvents, such as NMP, DMSO, and DMF, as well as in THF. There are no significant differences between the solubility behaviours of the various poly(ether sulfones). Molecular weights, T_g, T_{10}, T_{20}, and the char yields for the poly(ether sulfones) are given in Table 2.

Table 1 Solubility of poly(ether sulfone)s[a]

Poly(ether sulfone)	NMP	DMSO	DMF	THF
PES-a	++	++	+	++
PES-b	++	++	+	++
PES-c	++	++	+	++
PES-d	++	++	+	++
PES-e	++	++	+	++

[a] Solubility:++, soluble at room temperature;+, soluble in hot solvent.
Solvents: NMP, *N*-methylpyrrolidone; DMF, *N*,*N*-dimethylformamide;
DMAc, *N*,*N*-dimethylacetamide; DMSO, dimethylsulfoxide

Table 2 Molecular weights and thermal characteristic data of poly(ether sulfone)s.

Poly(ether sulfone)	**M_n**	**M_w**	**M_w/M_n**	**T_g** (°C)	**T_5** (°C)	**T_{10}** (°C)	**T_{20}** (°C)	Char yield at 600 °C (%)
PES-a	4157	4185	1.01	173	227	377	468	62.5
PES-b	1226	1626	1.32	175	155	177	219	56.4
PES-c	2439	3071	1.25	189	278	310	340	43.4
PES-d	1353	1953	1.43	178	160	224	360	60.1
PES-e	1526	2345	1.56	157	167	353	430	50.1

Conclusion

A convenient method was applied for the synthesis of a variety of new poly(ether-sulfones) with moderate molecular weights. Furthermore, a thermogravimetric data analysis for these polymers indicates suitable heat resistance under a nitrogen atmosphere. This procedure provides a simple polymerization process for the preparation of poly(ether sulfones) containing pyridine substitutions.

Acknowledgements

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