

ORGANOSOLUBLE, THERMALLY STABLE POLYAMIDES CONTAINING SULFONE AND SULFIDE UNITS

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Abstract A new diamine containing sulfone, sulfide and amide groups was synthesized *via* a three-step reaction process. The nucleophilic substitution reaction of 4-aminothiophenol with 4-nitrobenzoyl chloride in the presence of propylene oxide (PO) afforded *N*-(4-mercaptophenyl)-4-nitrobenzamide (MPNB). The catalytic reduction of the nitro group in MPNB to amino group was accomplished by using Pd/C and hydrazine monohydrate to produce 4-amino-*N*-(4-mercapto phenyl)benzamide (AMPB). Reaction of two moles of AMPB with bis(4-chlorophenyl)sulfone in the presence of K₂CO₃ resulted in preparation of a sulfone sulfide amide diamine (SSAD). The precursors and final monomer were characterized by FTIR, ¹H-NMR and elemental analysis. Polycondensation reactions of the prepared diamine with different commercially available diacid chlorides resulted in the preparation of novel polyamides that were characterized by FTIR, HNMR and elemental analysis. The physical and thermal properties of them such as inherent viscosity, solubility, thermal behavior and thermal stability were studied.

Keywords: Polymerizations; Polycondensation; Nucleophilic substitution; Polyamides; Thermal properties.

INTRODUCTION

Aromatic polyamides have received notable attention in research owing to their useful properties, like excellent mechanical properties, good chemical resistance and thermal stability that cause variety of applications in industry. However, they are difficult to process because of limited solubility in most organic solvents and high glass transition (*T*_g) or melt temperatures due to chain stiffness and intermolecular hydrogen bonding between amide groups. Therefore, research effort has been devoted to this drawback of aromatic polyamides in last decades^[1–5]. In order to improve solubility and maintain thermal stability some modification of the polymer backbone such as introducing soft segments to the main chain of the polymers, disturbing the symmetry and regularity and thereby overthrowing the crystallinity, introducing bulky side groups for diminishing of the crystallization and breaking the hydrogen bonding by *N*-substitution of amide with certain groups were applied. Also, for better processing of polyamides many copolyamides, such as poly(sulfone-amide)s, poly(ether-amide)s and other copolymers have been prepared^[6–10]. On the other hand, poly(phenylene sulfide)s (PPS) are classified as processable thermoplastics with flame-resistance character^[11]. It seems that insertion of sulfide in the polymer structure enhances the processability, thermal resistance and solubility of resulting polymers^[12].

Little attention has been paid to the polyamides having sulfone, sulfide and preformed amide groups within the backbone. Continuing our previous works^[13–17] here we describe synthesis and characterization of new polyamides derived from sulfone sulfide amide diamine (SSAD) and using various diacid chlorides including terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), sebacoyl chloride (SC) and adipoyl chloride (AC). The solubility, crystallinity, thermal and physical properties of the polymers were investigated.

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EXPERIMENTAL

Materials

All chemicals were purchased either from Merck or Aldrich Chemical Co. 4-Aminothiophenol and bis(4-chlorophenyl)sulfone were recrystallized from ethanol. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF) and toluene were distilled over calcium hydride under reduced pressure.

Instruments

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). The H-NMR spectra were recorded in DMSO- d_6 solutions using a Bruker Avance DPX 250 MHz (GmbH, Germany). Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). Inherent viscosities were measured by using an Ubbelohde viscometer. Wide angle X-ray diffraction patterns were performed at room temperature on an X-ray diffractometer (Siemens model D 5000) using Ni-filtered Cu K α radiation (40 kV, 25 mA) with scanning rate of 3 (°)/min. The number-average molecular weight (M_n) was determined by gel permeation chromatography (GPC). GPC was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL/min, and DMF was used as solvent.

Monomer Synthesis

Synthesis of N-(4-mercaptophenyl)-4-nitrobenzamide (MPNB)

A 100 mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube and calcium chloride drying tube was charged with 5.1 mmol of the 4-aminothiophenol and 15 mL of dry NMP. The mixture was stirred at 0°C for 0.5 h. Then about 3 mL of propylene oxide was added, and after a few minutes 5 mmol of 4-nitrobenzoyl chloride was added and the mixture was stirred at 0°C for 0.5 h. The temperature was raised to room temperature, and the solution was stirred for 6 h. MPNB was precipitated by pouring the flask content into water. Then it was filtered, washed with hot water and dried overnight under vacuum at 70°C (yield 82%).

Synthesis of 4-amino-N-(4-mercaptophenyl) benzamide (AMPB)

4.5 g of the MPNB, 0.2 g of 10% Pd-C and 250 mL of ethanol were introduced into a three-necked flask to which 10 mL of hydrazine monohydrate was added dropwise over a period of 1 h at 85°C. After the complete addition, the reaction was continued at reflux temperature for another 4 h. To the suspension, 40 mL of tetrahydrofuran was added to redissolve the precipitated product, and refluxing was continued for 1 h. The mixture was filtered to remove the Pd-C, and the filtrate was poured into water. The product was filtered off, washed with hot water and dried (yield 80%).

Synthesis of sulfone sulfide amide diamine (SSAD)

Into a 100 mL, three-necked, round-bottomed flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath and a magnetic stirrer were placed 0.01 mol of bis(4-chlorophenyl)sulfone, 25 mL of dry NMP, and 15 mL of dry toluene and 0.021 mol of AMPB. Then 0.0315 mol of K₂CO₃ was added to the mixture, and the reaction mixture was heated to 140°C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165°C by removing more toluene and kept at the same temperature for 20 h. During this time, progress of the reaction was monitored by thin-layer chromatography (TLC). The resulting reaction mixture was cooled and poured into water. Then 100 mL of 3% NaOH was added to the mixture, and the mixture was washed repeatedly with a 3% NaOH solution and water. The obtained diamine was dried in a vacuum oven at 60°C (yield 71%).

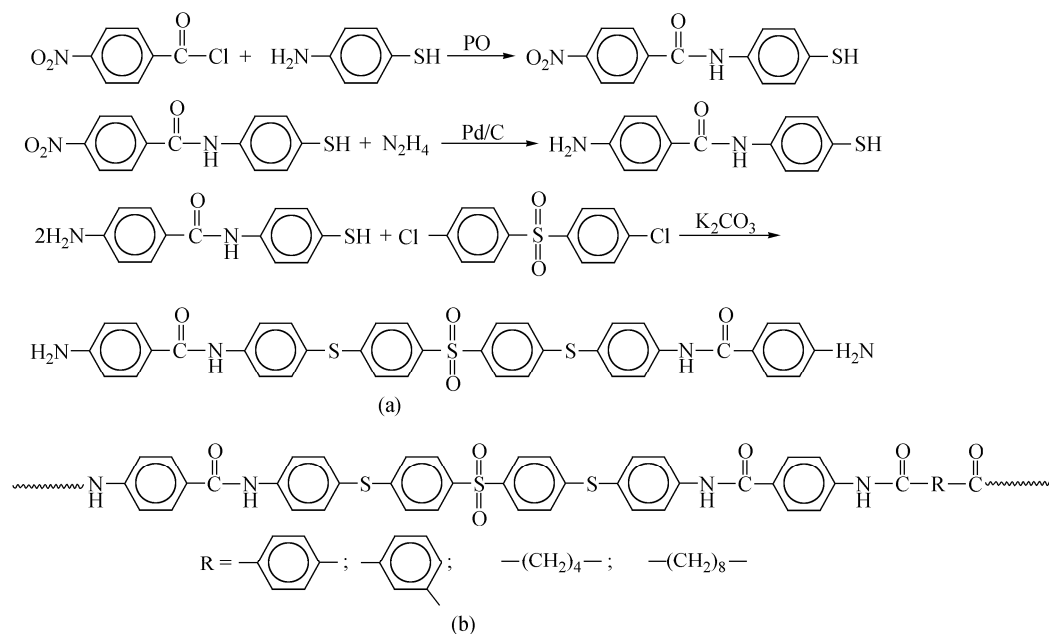
Polyamide Synthesis

The synthesis of polyamide typically was carried out as follows: A 100 mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube and calcium chloride drying tube was charged with 2 mmol of the diamine and 15 mL of dry NMP. The mixture was stirred at 0°C for 0.5 h. Then about 1 mL of propylene oxide was added, and after a few minutes 2 mmol of diacid chloride was added, and the mixture was stirred at 0°C for 0.5 h. The temperature was raised to room temperature, and the solution was stirred for 6 h. Polyamide was precipitated by pouring the flask content into water. Then it was filtered, washed with hot water and methanol and dried overnight under vacuum at 120°C (yields over 88 %).

RESULTS AND DISCUSSION

Generally, aromatic polymers that contain aryl sulfur linkages have lower glass transition temperatures, greater chain flexibility and tractability than their corresponding polymers without these groups in the chain^[18–20]. The enhanced solubility and lower glass transition temperatures are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation. Accordingly, engineering plastics containing sulfur derivatives such as poly(phenylene sulfide), poly(ether sulfone) and polysulfone have been placed into practical application due to their superior mechanical properties and good heat and chemical resistance^[21].

The main objective of this study was to produce modified polyamides with improved solubility and processability without too much sacrificing of their thermal and mechanical properties. Therefore a new diamine (SSAD) containing sulfone, sulfide and amide units was designed and used to prepare related polyamides. The synthetic route for the preparation of the diamine was comprised three steps: Nucleophilic substitution reaction of 4-aminothiophenol with 4-nitrobenzoyl chloride in the presence of propylene oxide (PO) yielded MPNB. Subsequently, AMPB compound was prepared *via* catalytic transformation of nitro groups to amino groups by using hydrazine monohydrate and Pd/C. Reaction of two moles of AMPB with bis(4-chlorophenyl) sulfone in the presence of K₂CO₃ resulted in preparation of SSAD diamine (Scheme 1a).

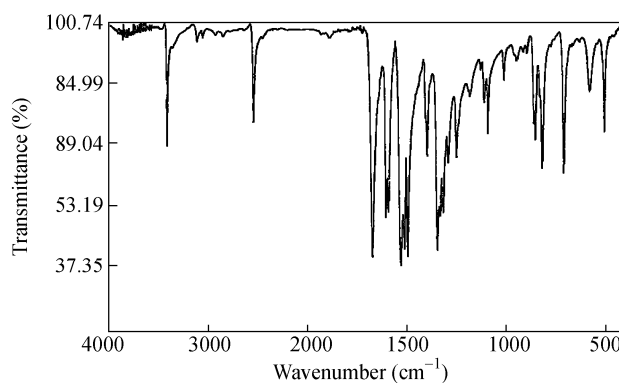
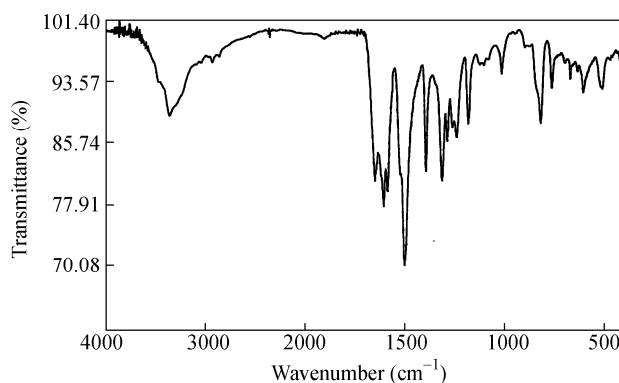


Scheme 1 Synthetic route for the (a) preparation of SSAD diamine and (b) poly(sulfone sulfide amide amide)s

All of the materials were characterized using common spectroscopic methods, and the results are collected in Table 1. The IR spectra of MPNB and SSAD were shown in Figs. 1 and 2, respectively.

Table 1. Characterization of substrates

Substrate	IR (KBr, cm^{-1})	$^1\text{H-NMR}$ (DMSO- d_6 , δ)	Elemental analysis						Yield (%)
			Calc. C	Calc. H	Calc. N	Found C	Found H	Found N	
MPNB	3210–3400 2544, 1672 1605, 1591 1512, 1398 1346, 1250 1092	10.52 (s, 1H, NH), 8.80 (s, 1H, SH), 8.34 (d, 2H, phenyl), 8.14 (d, 2H, phenyl), 7.67 (d, 2H, phenyl), 7.28 (d, 2H, phenyl)	56.93	3.65	10.22	56.21	3.43	10.95	82
AMPB	3295–3352 1649, 1605 1313, 1286 1180	9.88 (s, 1H, NH), 8.57 (s, 1H, SH), 7.82 (d, 2H, phenyl), 7.70 (d, 2H, phenyl), 7.47 (d, 2H, phenyl), 6.87 (d, 2H, phenyl), 5.77 (s, 2H, NH_2)	63.93	4.92	11.47	63.42	4.46	11.87	80
SSAD	3345–3425 1655, 1604 1585, 1497 1485, 1403 1358, 1228 1178, 1102	10.00 (s, 2H, NH), 7.89 (d, 4H, phenyl), 7.71 (d, 4H, phenyl), 7.51 (d, 4H, phenyl), 7.20 (d, 4H, phenyl), 7.08 (d, 4H, phenyl), 6.62 (d, 4H, phenyl), 5.81 (s, 4H, amine)	64.96	4.27	7.97	64.65	3.99	8.37	71

**Fig. 1** FT-IR spectrum of MPNB**Fig. 2** FT-IR spectrum of SSAD

The IR spectrum of SSAD showed absorption bands at 3345–3425 (NH_2), 1655 ($\text{C}=\text{O}$), 1604 (NH), 1358 (SO_2 symmetric), 1228 ($\text{C}-\text{S}$) and 1178 cm^{-1} (SO_2 asymmetric) confirming the prepared structure. Also $^1\text{H-NMR}$ spectrum of diamine confirmed the structure: A singlet at $\delta = 10.00$ was assigned to the amide protons. Peaks at about $\delta = 6.62$ –7.89 were related to the aromatic protons. A peak at $\delta = 5.81$ was attributed to the

amine protons (Table 1). Based on the structural features, the new diamine was expected to be a suitable monomer for preparing organosoluble, thermally stable polyamides. Under proper conditions, fully aromatic and semi-aromatic polyamides were prepared through polycondensation reaction of the SSAD with various diacid chlorides including TPC, IPC, AC and SC in the presence of propylene oxide as an acid scavenger (Scheme 1b).

All of the resulting polyamides were characterized by FTIR, $^1\text{H-NMR}$ and elemental analysis to confirm their chemical structures (Table 2), and a representative FTIR spectrum of the polyamides is shown in Fig. 3. As good evidences of polymer formation, two absorption peaks due to the two kinds of amide protons were observed in the $^1\text{H-NMR}$ spectra, and also amine protons disappeared.

Table 2. Polymer characterization

Polymer	IR (KBr, cm^{-1})	$^1\text{H-NMR}$ (DMSO- d_6 , δ)	Elemental analysis						η_{inh} (dL/g)	M_n^a	Yield (%)
			C	Calc. H	N	C	Found H	N			
SSAD-TPC	3410, 3120, 1655 1589, 1501, 1396 1313, 1238, 1180 1076	10.66/2H, 10.41/2H 8.11/4H, 8.07/4H, 8.01/4H, 7.94/4H, 7.77/4H, 7.53/4H, 7.20/4H	66.35	3.85	6.73	66.18	3.68	6.84	0.41	34100	93
SSAD-IPC	3395, 3112, 1654 1585, 1501, 1397 1315, 1242, 1180 1082	10.64/2H, 10.39/2H 8.51/1H, 8.10/2H, 8.06/4H, 8.02/1H, 7.99/4H, 7.90/4H, 7.72/4H, 7.50/4H, 7.18/4H	66.35	3.85	6.73	66.15	3.66	6.94	0.36	31300	88
SSAD-AC	3368, 3174, 2930 1665, 1585, 1501 1393, 1314, 1244 1150, 1071	10.22/2H, 10.13/2H 7.94/4H, 7.86/4H, 7.72/4H, 7.63/4H, 7.12/4H, 7.05/4H, 2.33/4H, 1.59/4H	65.02	4.43	6.90	64.89	4.55	6.72	0.37	32400	90
SSAD-SC	3366, 3145, 2924 1664, 1587, 1502 1396, 1313, 1242 1153, 1076	10.20/2H, 10.10/2H 7.91/4H, 7.82/4H, 7.70/4H, 7.59/4H, 7.09/4H, 7.01/4H, 2.28/4H, 1.52/4H, 1.28/8H	66.36	5.07	6.45	66.59	4.95	6.21	0.39	31100	91

^a According to GPC measurements

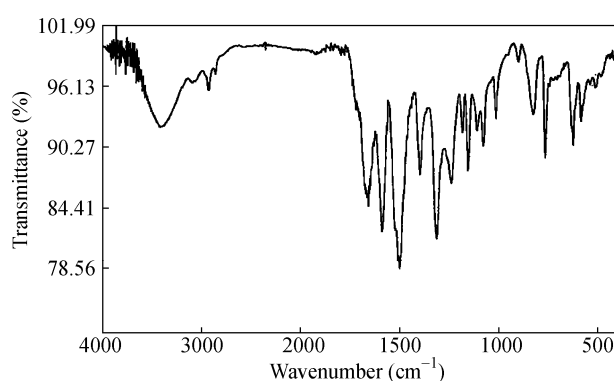


Fig. 3 FT-IR spectrum of SSAD-TPC polyamide

The solubility behavior of the polymers was studied in polar aprotic solvents. The polymers showed good solubility in dipolar aprotic solvents including DMF, DMAc, NMP and dimethylsulfoxide (DMSO). This was as

a result of introducing flexible sulfone and sulfide groups into the polymer backbone. Due to the presence of the flexible moieties on polyamide backbone, there was a considerable decrease in the rigidity of polymer chains which could be considered for reducing the crystallinity and improving the solubility of polymers. Presence of alkyl groups in the semi-aromatic polyamides derived from aliphatic acid chlorides increased the solubility of these polymers in comparison to fully aromatic polyamides.

The inherent viscosity of the polyamides was in the range of 0.36–0.41 dLg⁻¹ measured at a concentration of 0.5 g dL⁻¹ in NMP at 30°C. Also, evaluation of molecular weight was studied using GPC method from which moderate growth of molecular weight was concluded (Table 2).

According to the wide-angle X-ray diffraction measurements in the region of $2\theta = 5^\circ$ – 70° at room temperature, all of the polymers showed amorphous patterns. Presence of flexible groups in the polymer backbone might be responsible for this behavior.

Thermal properties of the polyamides were evaluated in air at a heating rate of 10 K/min using DSC and TGA techniques. According to the DSC curves, the polymers showed the glass transition temperatures in the range of 156–218°C. The SSAD-TPC polymer exhibited the highest T_g value, and the SSAD-SC polymer showed the lowest T_g value among the polyamides due to the fact that T_g was decreased by increasing the flexibility of the polymer backbones. The initial decomposition temperature (T_0) of the polyamides was about 184–265°C, temperature for 10% gravimetric loss (T_{10}) was in the range of 329–392°C, and also the char yield of polymers at 550°C was about 29%–45% based on the TGA analysis. The results are collected in Table 3, and a representative DSC curve and a TGA curve of the polyamides are shown in Figs. 4 and 5, respectively.

Table 3. Thermal characteristic data

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield at 550°C (%)
SSAD-TPC	218	265	392	460	45
SSAD-IPC	209	259	387	418	42
SSAD-AC	166	192	336	370	32
SEAD-SC	156	184	329	358	29

T_g : glass transition temperature; T_0 : initial decomposition temperature;

T_{max} : maximum decomposition temperature; T_{10} : temperature for 10% weight loss;

Char yield: weight of polymer remained

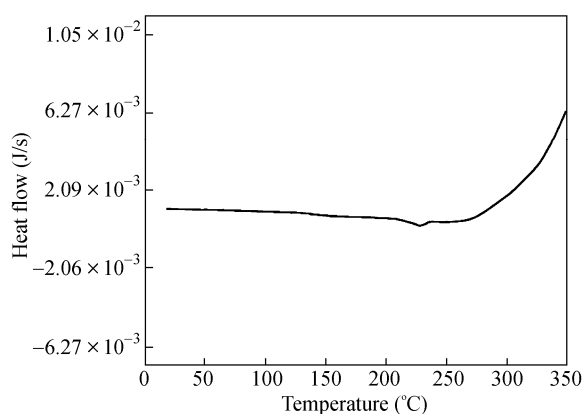


Fig. 4 DSC curve of SSAD-TPC polyamide

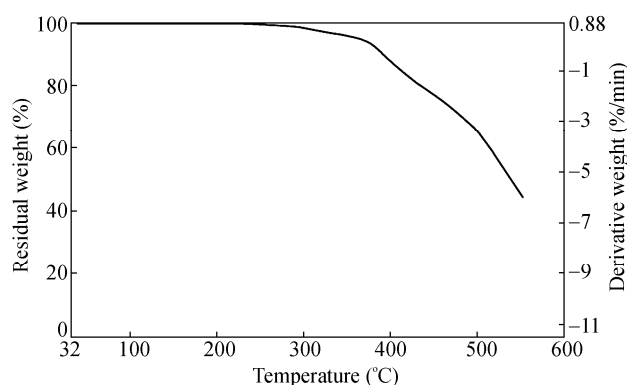


Fig. 5 TGA curve of SSAD-TPC polyamide

According to the obtained results the polymers showed good balance of properties including high thermal stability and improved solubility which was as a result of imparting certain structural units into the polymer backbones.

CONCLUSIONS

Aromatic diamines are valuable building blocks for the preparation of polyamides and induce specific properties to them. A novel diamine with built-in sulfone, sulfide, and amide units was prepared to produce organosoluble, thermally stable polyamides. A series of new polyamides was prepared by polycondensation of the diamine with aromatic and aliphatic diacid chlorides. Polymers showed good thermal stability due to the presence of preformed amide groups, phenylation of backbone and symmetry of the structure, and also they showed improved solubility due to the introduction of sulfone and sulfide flexible units.

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