

Novel Thermally Stable Arylene Sulphone Ether Poly(amide-imide)

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ABSTRACT

Nucleophilic aromatic substitution reaction of 5-amino-1-naphthol and also 4-aminophenol with bis(4-chlorophenyl)sulphone in *N*-methyl-2-pyrrolidone as solvent in the presence of K_2CO_3 resulted in preparation of two aromatic sulphone ether diamines. Polycondensation reaction of the prepared diamines with 4-chloroformylphthalic anhydride yielded thermally stable poly(sulphone ether amide-imide)s. The prepared polymers were characterized by conventional methods. Physical and mechanical properties of polymer including thermal behaviour, thermal stability, solution behaviour, solution viscosity, and modulus were studied. According to the obtained results, the prepared poly(sulphone ether amide-imide)s showed physical and thermal properties that lied between corresponding poly(sulphone ether amide)s and poly(sulphone imide)s. This was an important aspect of structure-property relationships.

Key Words: sulphone ether diamine, nucleophilic aromatic substitution, poly(sulphone ether amide-imide), thermally stable

INTRODUCTION

Thermostable polymers based on the recurring imide units are now being studied extensively for two purposes: to search for new methods of synthesis and to test the thermal and thermo-oxidative stability of those polymers, which are very promising for technical applications. Intensive developmental work in this field has been in progress for the last four decades, culminating in the preparation of various novel polyimides [1-3]. The demand for aromatic polyimides and other high temperature resistant polymeric materials is growing steadily due to their

superior performance characteristics that are increasingly expected from engineering polymers in the aerospace, automobile, electronics, and other industries. Aromatic, heterocyclic polyimides exhibit outstanding mechanical properties and excellent thermal and oxidative stability, and they are of major commercial and industrial importance.

However, the applications of the majority of polyimides are limited because of their infusibility and insolubility. Thus, for the processing of polyimides many copolyimides, such as poly(amide-imide)s, poly(ester-imide)s, poly(imide-carbonate)s, poly(amide-ester-imide)s have been prepared [4-7].

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By copolymerization, the solubilities of the polyimides were improved but the thermal stabilities were depressed. It seems that the synthesis of poly(amide-imide)s is more important than the other methods of copolymerization, because solubility and processibility can be improved without significantly sacrificing the thermal and mechanical properties.

For the preparation of poly(amide-imide)s various synthetic methods have been reported [8-13]. One of the most important of these methods is solution polymerization of a diamine with an acylchloride phenylanhydride.

On the other hand, aromatic polymers that contain aryl ether or aryl sulphone linkages generally have greater chain flexibility, lower glass transition temperatures, and greater tractibility than their corresponding polymers without any of these groups in the repeat units [14]. Polymers containing both aryl ether and aryl sulphone linkages generally are amorphous, have low glass transition temperatures, and show excellent mechanical properties [15,16]. Recently, there has been a great deal of interest in this field and much research has been conducted [17-19].

In our previous paper we reported the synthesis of sulphone ether polyimides and polyamides based on the prepared diamine [20]. The present paper deals with the preparation and characterization of novel poly(sulphone ether amide-imide).

The polymer was obtained by polycondensation reaction of the prepared sulphone ether diamine with 4-chloroformyl-phthalic anhydride.

Also for comparison, another sulphone ether diamine was prepared by the reaction of 4-aminophenol with bis(4-chlorophenyl) sulphone.

Reaction of the prepared diamine with 4-chloroformyl phthalic anhydride afforded the related poly(sulphone ether amide-imide).

EXPERIMENTAL

Materials

All needed chemicals were purchased from either Merck or Fluka Co. Bis(4-chlorophenyl)sulphone

was recrystallized from aqueous ethanol. NMP, toluene, and *N,N*-dimethylacetamide (DMAc), were purified by vacuum distillation over calcium hydride.

Instruments

Infra-red measurements were performed on a Bruker-IFS 48 FTIR spectrometer. The mass spectrum was recorded on a Shimadzu GC-MS-QP 1100 EX. The ¹H NMR spectra were recorded in DMSO-d₆ solution using a Bruker Avance DPX 250 MHz. Elemental analysis was performed by a CHN-O-Rapid Heraeus elemental analyzer (Tarbiat Modarres University, and Research Center of Defense Industries). The apparent molecular weights of the polymers were determined by gel permeation chromatography (GPC) using DMF at ambient temperature. A PL gel column with a DMF elution rate of 1.0 mL/min was used (Research Center of Jihad Engineering). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780. Differential thermogravimetric (DTG) trace was recorded on a Polymer Lab TGA-1500. The dynamic mechanical measurement was performed on a Polymer Laboratory Dynamic Mechanical Thermal Analyzer (DMTA) in the bending mode at 1 Hz and a heating rate of 5°C/min. Inherent viscosity was measured by using an Ubbelohde viscometer.

Monomer Synthesis

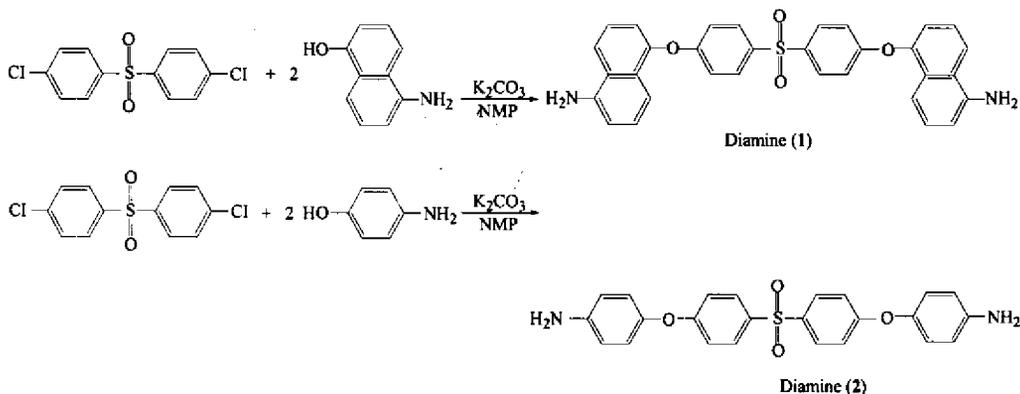
Sulphone ether diamine based on naphthyl group was prepared and fully characterized according to our paper [20]. IR (KBr): ν 3430, 1460-1600, 1310, 1160, and 1110 cm⁻¹. ¹H NMR (DMSO-d₆): δ 3.6 s (4H, amine), 6.65-7.85 m (16H, aromatic).

Another diamine was prepared similarly.

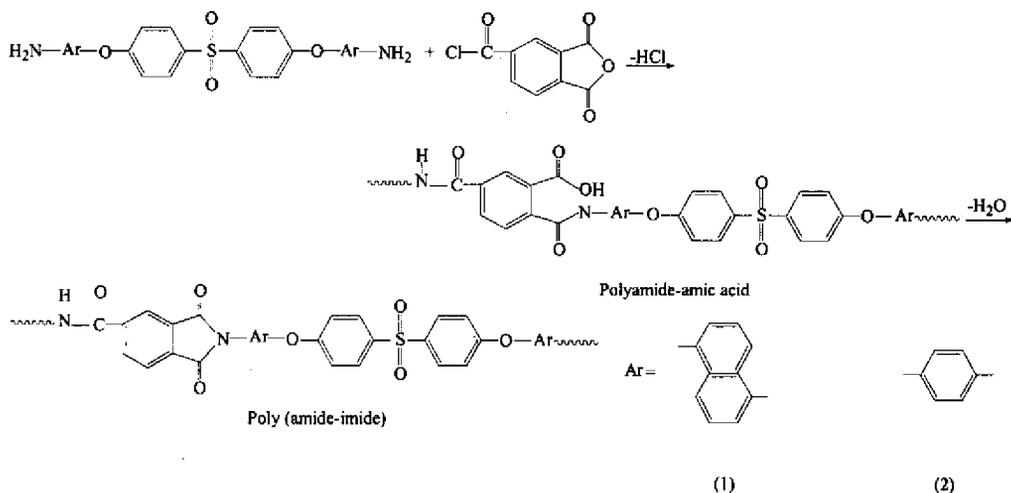
Poly(amide-imide) Synthesis

A typical procedure for the preparation of poly(amide-imide)s is as follows:

A 100-mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and a calcium chloride drying tube was charged with 1.5 mmol of the prepared diamine and 15 mL of dry NMP. The mixture was stirred and then 1.5 mmol of 4-chloroformylphthalic anhydride was added. The



Scheme I. Preparation of sulphone ether diamine.



Scheme II. Preparation of poly(sulphone ether amide-imide)s.

reaction temperature was maintained between 20–45°C by use of a water-ice bath and it was stirred for 1 h. Then about 1 mL of propylene oxide was added to act as the acid scavenger. The mixture was stirred at this temperature for about 6 h. Poly(amide-imide) was precipitated by pouring the flask content into methanol. Then it was filtered, washed with hot water and methanol, and finally it was dried

overnight under vacuum at 80°C. The yield of the reaction was about 86%.

RESULTS AND DISCUSSION

The sulphone ether diamines as a building block for the preparation of poly (amide-imide) were designed

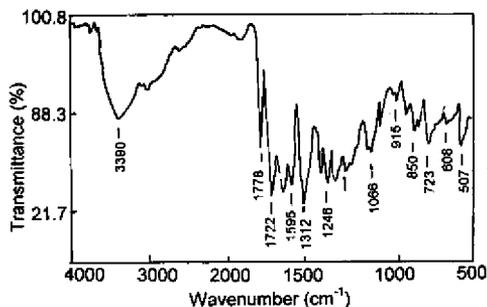


Figure 1. FTIR spectrum of polyamide-imide (1).

and prepared [20]. In fact, reaction of bis(4-chlorophenyl) sulphone with 5-amino-1-naphthol and also 4-aminophenol in presence of K_2CO_3 resulted in preparation of the desired diamines (Scheme I).

Since the objective of this research was to make a novel polyimide with improved solubility and processibility without remarkable decrease in the thermal and mechanical properties, some approaches were considered. The incorporation of flexible or kinked linkages in the backbone (sulphone and ether groups), the introduction of a large substituent along the polymer backbone (naphthyl group), the disruption of symmetry and regularity of the repeating unit (naphthyl group), and finally copolymerization of polyimide were achieved.

Accordingly, polycondensation-addition

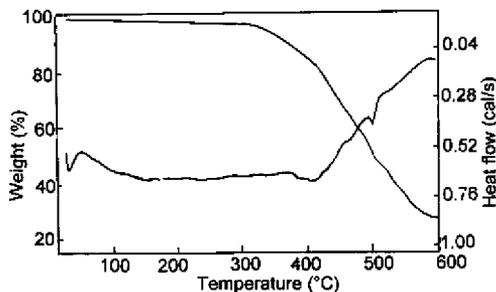


Figure 2. DSC-TGA curve of polyamide-imide (1).

reaction of the obtained diamines with 4-chloroformylphthalic anhydride in polar aprotic solvent (NMP) afforded polyamide-amic acid that, followed by chemical dehydration, the related poly(sulphone ether amide-imide)s were prepared (Scheme II). IR spectrum of the poly(amide-imide) showed characteristic bands at about 3380 cm^{-1} (N-H), 1775 , 1720 , 720 cm^{-1} (imide bands), 1660 cm^{-1} (carbonyl of amide), 1375 cm^{-1} (C-N of imide), 1315 and 1150 cm^{-1} (S=O), and 1110 cm^{-1} (-O-). The representative IR spectrum is shown in Figure 1.

The H NMR spectrum confirmed the proposed structure for polymer (1) by showing amide hydrogen (δ 10.5; 1H) and the aromatic hydrogens of imide ring (δ 7.89, 8.12, and 8.17; 3H) and the other aromatic hydrogens of phenyl rings (δ 6.85-8.27;

Table 1. Structure and properties of the polymers.

No.	Structure	Elemental analysis						Yield (%)	Inherent viscosity ^a (dL/g)
		Calculated			Found				
		C	H	N	C	H	N		
1		71.51	3.49	4.07	71.48	3.50	4.09	86	0.46
2		67.35	3.40	4.76	67.42	3.45	4.82	89	0.48

(a) Measured at a concentration of 0.5 g/dL in NMP at 30°C.

Table 2. Thermal properties of poly(amide-imide)s

Polymer	T _g (°C)	T ₀ (°C)	T _{5%} (°C)	T _{max} (°C)	Char yield (%)
1	240	300	335	540	32
2	250	320	350	545	43

T_g: Glass transition temperature; T_{5%}: Temperature for 5% weight loss; T_{max}: Maximum decomposition temperature. Char Yield: Weight of polymer remained.

20H). Also ¹H NMR showed the absorption of amide hydrogen (δ 10.75; 1H) and the aromatic hydrogens of imide ring (δ 7.75, 7.91, and 8.23; 3H) and the other aromatic hydrogens of phenyl rings (δ 6.90-7.90; 16H) for polymer (2). The results of polymerization reaction were brought in Table 1. The solubility of the polymer (1) was about 2.5 g/dL at ambient temperature in polar solvents such as NMP, DMAc, DMF, and DMSO. It was insoluble in less efficient solvents including THF, CHCl₃, toluene and xylene. The incorporation of a bulky pendent group and presence of flexible units (ether and sulphone) improved solubility of the polymer. The solubility behaviour of polymer (2) was similar, but smaller than polymer (1). This is a result of absence of bulky naphthyl group.

According to the GPC analysis $\bar{M}_n = 12,780$ and $\bar{M}_w/\bar{M}_n = 1.67$ for polymer (1) and also $\bar{M}_n = 13,330$ and $\bar{M}_w/\bar{M}_n = 1.48$ for polymer (2) were obtained. DSC and TGA techniques were used to study the thermal property and thermal behaviour of the polymers. There was not a transition related to softening or melting point of polymer in DSC traces. A step transition corresponding to a glass transition temperature (T_g) was observed at the range of 240-250°C in DSC curve.

TGA was used to determine the thermal stability of the polymers. It was carried out in air at a heating rate of 10°C/min. The results were collected in Table 2 and the representative DSC-TGA curve is shown in Figure 2. The polymers showed good thermal stability according to the results (T₅ is an important criterion for evaluation of thermal

stability). It is worth to mention that disruption of symmetry in polymer (1) caused lower stability in comparison with symmetrical polymer (2).

Thermal stability of the obtained poly(amide-imide)s was on the border of previously prepared polyimides and polyamides and it was comparable with similar polymer, which have been prepared earlier [20,21].

Film was obtained for mechanical measurement by casting from NMP and heating to 350°C and holding for 30 min. The storage modulus (E' Value) at 25 and 300°C was 5.76 and 1.89 GPa for polymer (1) and also 5.82 and 1.94 GPa for polymer (2), respectively.

CONCLUSION

A novel poly(sulphone ether amide-imide) was prepared by polycondensation-addition reaction of the sulphone ether diamine with 4-chloroformylphthalic anhydride. Introduction of sulphone and ether groups in the diamine and subsequently into the polymer backbone in companion with bulky pendent group and also disruption of symmetry led to nice balance of properties (thermal stability and solubility) in the prepared thermally stable poly(amide-imide).

Similarly, another poly(sulphone ether amide-imide) was prepared in which bulky, unsymmetrical naphthyl group was substituted by symmetrical phenyl group. It was observed that the presence of naphthyl group imposed more solubility by less stability in the final poly(amide-imide).

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