Synthesis and Characterization of Novel Soluble and Thermally Stable Polyamides Based on Pyridine Monomer

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SUMMARY: Nucleophilic aromatic substitution reaction of 4-aminophenol and also 5-amino-1-naphthol with 2,6-dichloropyridine in N-methyl-2-pyrrolidone (NMP) as solvent, in the presence of potassium carbonate, afforded two aromatic ether diamines. Eight soluble, thermally stable polyamides were prepared by polycondensation reaction of the obtained diamines with aromatic and aliphatic diacid chlorides including terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), adipoyl chloride (AC), and sebacoyl chloride (SC). The prepared monomers and polymers were characterized by conventional spectroscopic methods. Physical and thermal properties of the polymers, such as thermal behavior, thermal stability, solution viscosity, and solubility behavior were also studied.

Introduction

Aromatic polyamides are heat resistant polymers that generally exhibit outstanding mechanical properties and have excellent thermal and oxidative stability. Because of these properties they are of major commercial and industrial importance. Aromatic diamines are valuable building blocks for the preparation of polyamides. To extend the utility of these high performance materials, it has been a long desired goal to synthesize diamines which afford soluble and processable polymers. Aromatic polymers that contain an aryl ether linkage generally have greater chain flexibility, lower glass transition temperatures, and greater tractibility than the corresponding polymers without these groups in the repeat units.[1,2] The improved solubility and lower glass transition temperatures are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation.[3]

The choice of heterocyclic rings in the main chain of a synthetic polymer is to impart certain properties to the polymer.[4,5] The selection of a pyridine nucleus is based on its

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high thermal stability, derived from its molecular symmetry and aromaticity.[6,7]

In our continued interest to prepare thermally stable polymers [8-14], we wish now to describe the synthesis and characterization of 2,6-bis(4-aminophenoxy) pyridine and 2,6-bis(5-amino-1-naphthoxy) pyridine diamines. Polycondensation reactions of the prepared diamines with aromatic and also aliphatic diacid chlorides resulted in the preparation of eight soluble and thermally stable polyamides.

The use of 2,6-bis(4-aminophenoxy) pyridine diamine as a monomer for the preparation of some polymers has been reported[15,16], but here we wish to study a series of polyamides, based on two different diamines, and compare the structure-property relationships.

Experimental

Materials

The diacid chlorides, 2,6-dichloro pyridine, NMP, dimethylacetamide (DMAc), toluene, K_2CO_3, propylene oxide (PO), and methanol were purchased from Merck Chemical Co. 4-Aminophenol and 5-amino-1-naphthol were obtained from Aldrich Chemical Co. TPC and IPC were purified by sublimation. NMP, DMAc, and toluene were purified by vacuum distillation over calcium hydride.

Instruments

Infrared measurements were performed on a Bruker-IFS 48 FT-IR spectrometer. The ^{1}H-NMR spectra were recorded in dimethyl sulfoxide (DMSO-d_6) or chlorofom ($CDCl_3$) solution, using a Bruker Avance DPX 250-MHz instrument. A CHN-O-Rapid Heraeus elemental analyzer was used to perform elemental analyses.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780. Differential thermogravimetric (DTG) traces were recorded on a Polymer Lab TGA-1500. The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) over a temperature range of –100 to 200 °C at 1 Hz and a heating rate of 5 °C /min. The value of tan δ and the storage modulus versus temperature were

recorded for each sample. Inherent viscosities were measured by using an Ubbelohde viscometer.

Monomer Synthesis

Synthesis of 2,6-bis(4-aminophenoxy) pyridine diamine:

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 was placed in an oil-bath and charged with 0.01 mol of 2,6-dichloro pyridine , 25 mL of dry NMP, 15 mL of dry toluene and 0.021 mol of 4-aminophenol. Then 0.0315 mol of K_2CO_3 were 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 then kept at that 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% aqueous NaOH solution. The obtained diamine was dried in a vacuum oven at 60 °C. The yield of the reaction was about 88% (2.58). [IR (KBr): ν 3300-3450 (N-H); 1450-1600 (C=C); and about 1140 cm^{-1} (-O-); ^{1}H-NMR 8 (ppm) ($CDCl_3$): δ 3.60 s (4H, amine): 6.34 d (2H, pyridine ring); 6.63-6.66 m (4H, benzene ring); 6.90-6.93 m (4H, benzene ring); 7.51 t (1H, pyridine ring); elemental analysis calculated for $C_{17}H_{15}N_3O_2$: C, 69.62%; H, 5.12%; N, 14.33%, found: C, 69.49%; H, 5.19%; N, 14.42%].

Synthesis of 2,6-bis(5-amino-1-naphthoxy) pyridine diamine:

The above procedure was also used for the synthesis of the above diamine, but 5-amino-1-naphthol was used instead of 4-aminophenol. The yield of the reaction was about 92% (3.61g). [IR (KBr): ν 3300-3400 (N-H); 1460-1600 (C=C); and about 1150 cm^{-1} (-O-); ^{1}H-NMR (DMSO-d_6): δ 5.83s (4H, amine): 6.50 d (2H, naphthyl ring); 6.71 d (2H, pyridine ring); 7.01-7.29 m (8H, naphthyl ring); 7.75 t (1H, pyridine ring); 7.94 d (2H, naphthyl ring); elemental analysis calculated for $C_{25}H_{19}N_3O_2$: C, 76.33%; H, 4.83%; N, 10.69%, found: C, 76.24%; H, 4.79%; N, 10.74%].

Polyamide synthesis

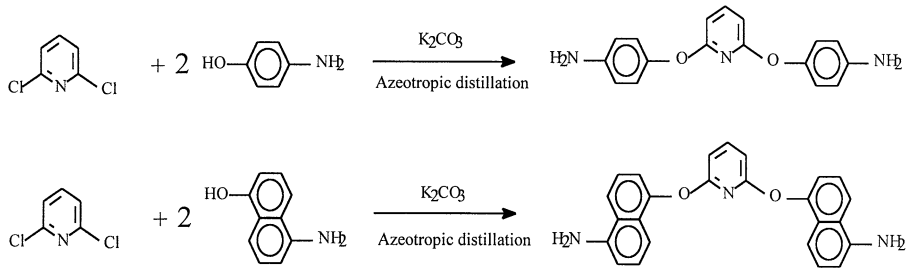
The synthesis of a polyamide was typically carried out as follows: A 100-mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and a calcium chloride drying tube was charged with 1.5 mmol of the prepared diamine and 12 mL of dry NMP and the mixture stirred at 0 °C for 0.5h. About 1mL of propylene oxide was then added, and after a few minutes 1.5 mmol of diacid chloride was added. This mixture was then stirred first at 0 °C for 0.5h and then at room temperature for 6h. The polyamide product was precipitated by pouring the contents of the flask into water. It then was filtered, washed with hot water and methanol, and finally dried overnight under vacuum at 120 °C. Yields of > 87% were obtained.

Results and Discussion

The main objective of this study was to prepare modified polyamides with improved solubility and processability without sacrificing their thermal and mechanical properties.

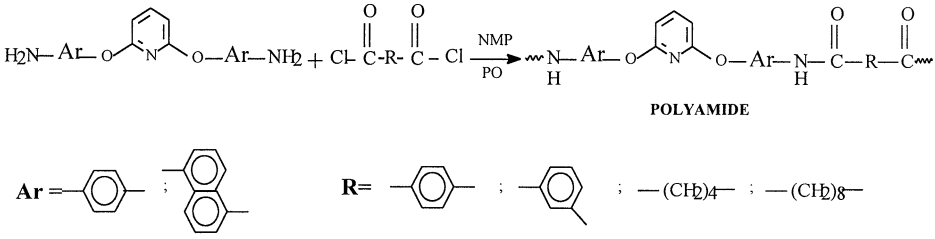
Towards this objective, the following structural modifications were considered: (1) the incorporation of flexible or kinked linkages in the backbone; (2) the introduction of heterocyclic rings into the polymer backbone; (3) the disruption of symmetry and regularity of the repeating unit. Accordingly, diamine building blocks for the synthesis of such polyamides were prepared.

2,6-bis(4-aminophenoxy) pyridine and 2,6-bis(5-amino-1-naphthoxy) pyridine diamines were prepared by the nucleophilic aromatic substitution reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloro pyridine, respectively. The reactions were performed in the presence of anhydrous potassium carbonate in NMP as solvent (Scheme 1).



Scheme 1. Synthesis of ether diamines

The prepared diamines was fully characterized by conventional spectroscopic methods and their structures confirmed. Polycondensation reaction of the obtained diamines with aromatic diacid chlorides resulted in the preparation of fully aromatic polyamides. Also, aliphatic diacid chlorides were used to prepare, and then compare, the properties of semi-aromatic polyamides (Scheme 2).



Scheme 2. Preparation of poly(ether amide)s

Structures of the prepared polyamides were determined by common spectroscopic methods and the results are tabulated in Table 1.

Table 1. Reactants and properties of the poly(ether amide)s

Reactants	IR (KBr) (cm^{-1})	NMR(DMSO-d_6) (δ)	Elemental Analysis Calc. C H N	Elemental Analysis Found C H N	Yield (%)	$\eta_{Inh.}$ [c] (dL/g)
AP[a]-TPC	3314 1653 1126	10.19/2H,8.02/4H,7.86 /1H,7.63/4H,7.01/4H, 6.65/2H	70.92/4.02/9.93	70.85/3.99/9.98	98	0.502
AP-IPC	3310 1664 1128	10.15/2H,8.69/1H,8.26 /2H,7.82/1H,7.68/1H, 7.65/4H,7.03/4H,6.67/ 2H	70.92/4.02/9.93	70.82/4.06/9.97	93	0.495
AP-AC	3352 1663 1122	9.92/2H, 7.75/1H, 7.58 /4H,7.00/4H,6.48/2H, 2.32/4H,1.62/4H	68.49/5.21/10.42	68.54/5.27/10.38	87	0.486
AP-SC	3418 1657 1115	9.87/2H, 7.72/1H, 7.53 /4H,7.00/4H,6.43/2H, 2.71/4H,1.68/4H,1.35/ 8H	70.59/6.32/9.15	70.52/6.36/9.08	98	0.525
AN[b]-TPC	3318 1663 1129	10.67/2H,8.04/4H,7.87 /2H,7.80/2H,7.71/1H, 7.68/2H,7.55/2H,7.47/ 2H,7.22/2H, 6.73/2H	75.72/4.01/8.03	75.65/3.97/8.09	98	0.498
AN-IPC	3321 1663 1121	10.65/2H,8.76/1H,8.28 /2H,7.89/2H,7.83/1H, 7.79/2H,7.69/1H,7.66/ 2H,7.53/2H,7.45/2H, 7.21/2H,6.72/2H	75.72/4.01/8.03	75.59/4.07/7.97	92	0.478
AN-AC	3256 1663 1120	9.92/2H,7.88/2H,7.69/ 2H,7.65/1H,7.60/2H, 7.39/2H,7.37/2H,7.14/ 2H,6.68/2H,2.34/4H, 1.63/4H	73.96/4.97/8.35	73.82/5.02/8.30	88	0.479

AN-SC	3404 1659 1123	9.90/2H,7.85/2H,7.68/ 2H,7.64/1H,7.60/2H, 7.38/2H,7.35/2H,7.12/ 2H,6.66/2H,2.69/4H, 1.69/4H,1.38/8H	75.13/5.90/7.51 75.08/5.94/7.46	95	0.507

[a] 2,6-bis(4-aminophenoxy) pyridine
[b] 2,6-bis(5-amino-1-naphthoxy) pyridine
[c] measured at a concentration of 0.5 g/dL in DMAc at 30 °C

The inherent viscosities of the polyamides measured in DMAc were about 0.478-0.525 dL/g, indicating a moderate-high molecular weight (Table 1).

Thermal behavior of the polymers was studied by recording DMTA traces. The softening point of the polyamides was not detected. However, the storage modulus of the polymers decreased and the tan δ went through a maximum in the 185-229 °C range for fully aromatic polyamides and 138-161 °C for semi-aromatic ones. This property is attributed to the T_g of the polymers.

Also, all the polymers showed an exotherm transition, starting at about around 190 to 290 °C, and assigned to thermal degradation. DSC traces were also recorded and the obtained results confirmed the results of DMTA analysis.

The thermal stabilities of the polyamides were evaluated by TGA analysis. The polyamides started to lose weight, because of thermal degradation, between 190-290 °C. A 10% polymer weight loss, as a criterion for the thermal stability of the polyamides, was in the 345-465 °C range indicating that the prepared polymers had good thermal stability. The obtained results are tabulated in Table 2.

Table 2. Thermal stability data of the polyamides

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield at 600 °C (%)
AP-TPC	229	290	465	484	50
AP-IPC	196	282	450	472	53
AP-AC	161	230	410	460	35
AP-SC	151	216	405	466	19
AN-TPC	202	245	425	454	56
AN-IPC	185	236	415	453	55
AN-AC	146	200	370	442	25
AN-SC	138	190	345	408	15

The thermal stability of the polyamides derived from 2,6-bis(4-aminophenoxy) pyridine diamine was higher than that of corresponding polyamides based on 2,6-bis(5-amino-1-naphthoxy) pyridine diamine. It could be attributed to the symmetry of 2,6-bis(4-aminophenoxy) pyridine diamine. This factor also affected the solubility of the obtained polymers. Although all the polymers were soluble in common organic solvents such as NMP, DMAc, DMF, and dimethyl sulfoxide (DMSO) and less sufficient solvents such as m-cresol, the aminonaphthoxy pyridine derived polyamides were more soluble than the corresponding aminophenoxy pyridine derived polymers.

Conclusions

The synthesis of two diamines containing flexible ether linkages and heterocyclic moieties was carried out by the nucleophilic aromatic substitution reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloropyridine. The diamines were polycondensed with aromatic and aliphatic diacid chlorides to provide eight different polyamides, all with good thermal stability. The introduction of ether linkage and the

presence of the heterocyclic pyridine ring in the polymers backbone improved the solubility of the polyamides without sacrificing thermal stability too much. The synthesis and study of properties of the polyimides from the prepared diamines is in progress.

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