

Polyisophthalamides with phenoxy pendant groups

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Polyisophthalamides containing phenoxy pendant groups were prepared from 5-phenoxyisophthaloyl chloride and aromatic diamines, and their properties were compared with those of unsubstituted polyisophthalamides. The incorporation of one phenoxy group per repeating unit brought about a decrease in the glass transition temperatures of 20–30°C, while the thermal resistance (t.g.a.) remained unchanged for those polymers with aliphatic or ether linkages in the main chain, and slightly diminished for the fully aromatic polymers. Other properties investigated were mechanical resistance, solubility and water absorption.

(Keywords: aromatic polyamides; synthesis; glass transition; thermal degradation; mechanical resistance; water absorption)

INTRODUCTION

In previous papers we have reported on polyisophthalamides containing voluminous pendant groups, synthesized by polycondensation of aromatic diamines and 5-substituted isophthaloyl chlorides^{1–3}. This work is concerned with the synthesis and evaluation of new polyisophthalamides where phenoxy groups were incorporated as pendant groups. The good thermal stability of polyphenylene oxides, as well as the relative flexibility of the C–O–C linkage have been recognized and tested in many instances^{4,5}. On the other hand, diphenylether pendant groups have been claimed to improve the solubility of aromatic polyheterocycles^{6,7}, and groups which encompass phenoxy moieties have been successfully incorporated as side substituents in sulphone ester polymers⁸. Consequently, it was expected that the incorporation of pendant phenoxy groups would give rise to aromatic polyamides with a favourable balance of properties. Such properties as solubility, thermal transitions, heat resistance, mechanical strength, and moisture absorption were studied and compared with those of the unsubstituted homologous polyisophthalamides.

EXPERIMENTAL

Materials and monomers. Pyridine was refluxed on KOH for 12 h, distilled and stored on molecular sieves. *N,N*-Dimethylacetamide (DMA) and *N*-methyl-2-pyrrolidinone (NMP), were distilled twice on P₂O₅ and stored in a dark bottle on molecular sieves. 3,5-Dimethylphenol and bromobenzene were commercially available and they were used as received. Aromatic diamines were commercially available and were purified by recrystallization under N₂ from suitable solvents. 2,2-Bis(4-aminophenyl)propane (DDP) was prepared by the method reported elsewhere⁹.

Synthesis of 5-phenoxyisophthaloyl chloride. A mixture of 106 g (0.90 mol) of 3,5-dimethylphenol and 44.3 g (0.80 mol) of KOH was refluxed for 2 h, and then water and excess phenol were removed by vacuum. To the molten phenolate, 124 g (0.80 mol) of bromobenzene and 0.4 g of active copper were added and the mixture was heated to 220°C for 4 h. After cooling, the product was extracted with ether. The ethereal solution was washed with 10% aqueous KOH, then several times with water, and finally dried on CaCl₂. The ether was removed and the residue vacuum distilled. Phenoxy-3,5-dimethylbenzene (100 g, 63%) was collected at 85–90°C/1 mm.

Phenoxy-3,5-dimethylbenzene (0.2 mol) was oxidized to 5-phenoxyisophthalic acid with potassium permanganate (1.6 mol) in a 1:1 mixture of water/pyridine heated to gentle reflux for 8 h. After cooling, the black precipitate of MnO was filtered off, the filtrate washed with ether (2 × 200 ml), and the pyridine separated by azeotropic distillation. The diacid was precipitated from the solution by adding 2M HCl and recrystallized from water/ethanol. The yield was 73% (m.p. 306°C).

5-Phenoxyisophthaloyl chloride was prepared by refluxing the diacid in excess thionyl chloride for 4 h. Once the thionyl chloride was removed, benzene was added and in turn distilled. The residue was recrystallized from *n*-hexane. The yield was 82% (m.p. 52°C).

Synthesis of polymers. All the polymers were prepared by the low-temperature procedure in a solution of DMA under N₂. For example, polymer VIII was prepared by adding 2.9512 g (10.00 mmol) of 5-phenoxyisophthaloyl chloride to a stirred solution of 1.9829 g (10.00 mmol) of bis(4-aminophenyl) methane in 25 ml of DMA at –10°C. The solution was maintained at this temperature for 1 h, and at room temperature for an additional hour. The viscous solution was poured into water and the polyamide separated in the form of white pearls, which were thoroughly washed with water, extracted with

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acetone in a Soxhlet for 12 h, and dried in a vacuum oven at 60°C overnight (yield 97%).

Characterization and measurements. Elemental analysis, i.r. and ¹H n.m.r. spectroscopy, were used to identify precursors and polymers. The viscosities were measured in a 0.4 mm i.d. Ostwald viscometer at 25 ± 0.1°C and 0.5% w/v polymer concentration in NMP.

The thermal properties were measured by dynamic t.g.a. and differential scanning calorimetry (d.s.c.). All the samples were tested under N₂ at a heating rate of 10°C min⁻¹. Wide angle X-ray diffractograms were obtained at room temperature using a Ni-filtered Cu Kα radiation from a rotating anode source (40 kV, 200 mA). For the measurement of mechanical properties, strips 5 mm wide and 80 mm long were cut from polymer films and tested on an Instron dynamometer at 20°C. Pneumatic clamps were used, and an extension rate of 2 mm min⁻¹ was applied with a gauge length of 10 mm.

To determine the equilibrium water absorption, polymer samples were previously conditioned at 120°C in vacuum over P₂O₅ for 24 h. Then they were placed in a desiccator where 65% r.h. was maintained by means of an oversaturated aqueous solution of NaNO₂ at 20°C, and were periodically weighed. The equilibrium was reached before 24 h in every case.

RESULTS AND DISCUSSION

Polyisophthalamides with phenoxy pendant groups were prepared from aromatic diamines and a new monomer, 5-phenoxyisophthaloyl chloride, following the scheme shown in Figure 1.

All the polymers were obtained in yields over 95%, and had medium to high inherent viscosities (Table 1). The new polymers were identified by i.r. and n.m.r. spectroscopy. As an example, the ¹H n.m.r. spectrum of one of them has been reproduced in Figure 2.

Polymer properties

The results of the solubility tests for *N,N*-dimethylformamide, *m*-cresol and cyclohexanone are listed in Table 1. From the data it could be concluded that the incorporation of pendant phenoxy groups brings about a general increase in the solubility. Surprisingly,

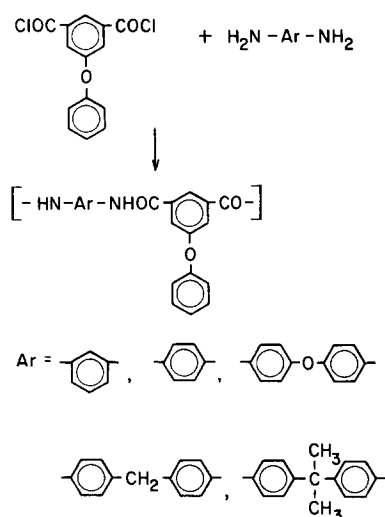


Figure 1 Synthesis of poly(5-phenoxyisophthalamides)

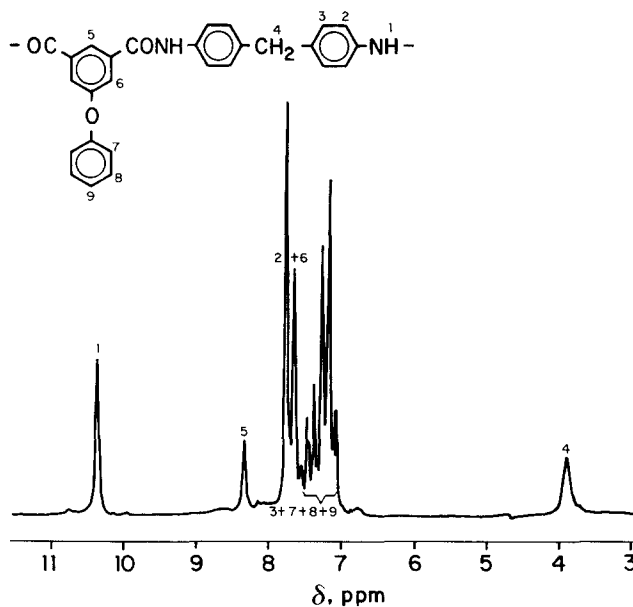


Figure 2 ¹H n.m.r. spectrum of a phenoxy-modified polyisophthalamide

solubility of the polymer with *m*-phenylene units in the main chain did not seem to be greatly affected by the presence of the side bulky groups (polymer VI). A feasible explanation for this behaviour is that the polymer developed a certain degree of order that allowed a dense packing of the chains.

Glass-transition temperatures were measured by the calorimetric method. The *T_g* values of the polymers are listed in Table 1.



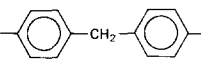
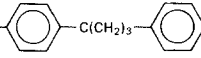
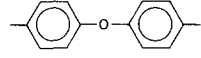
The modification of the polyisophthalamides caused a general depression of the *T_g* values estimated at 20–30°C. Although the voluminous aromatic side groups generally work by hindering the free segmental motions, and hence increasing the polymer *T_g* values, the effect of chain separation seems to be dominant in our case, and eventually the lower hydrogen bridge density should account for the observed decreasing *T_g*.

On the other hand, the chemical structure of the diamines played the main role to establish the order of *T_g* values in both series of polyamides. The trend *p*-phenylene > isopropylidenediphenylene ≥ *m*-phenylene > oxydiphenylene > methylenediphenylene was consistent with results previously reported^{2,3}. The *T_g* found for polymer VI from *m*-phenylenediamine was somewhat lower than expected, and this may be due to its lower molecular weight (lower viscosity).

No endothermic melting peak was observed by d.s.c. in any case up to 420°C, which was the temperature at which the polymers began to decompose. Crystallization exotherms over the *T_g* values were also not detected in any case.

As to the thermal stability, measured by t.g.a., some significant differences were observed between the reference and the modified polyamides (Table 1). The initial degradation temperature, *T_d*, of unmodified polyamides depended on the diamine rest, the *T_d* decreasing in the order *p*-phenylene > *m*-phenylene > oxydiphenylene > methylenediphenylene > isopropylidenediphenylene. However, in the series of polyamides containing phenoxy pendant groups,

Table 2 Water absorption of poly(5-phenoxyisophthalamides)

Amine	Water absorption (%)	Mol H ₂ O per repeat unit	Mol H ₂ O/eq. amide
	4.1 (9.3)	0.76 (1.23)	0.38 (0.61)
	4.9 (8.6)	0.92 (1.14)	0.46 (0.57)
	2.5 (5.4)	0.59 (0.99)	0.30 (0.50)
	2.4 (5.3)	0.60 (1.06)	0.30 (0.53)
	2.7 (6.1)	0.64 (1.12)	0.32 (0.56)

The values for the homologous unmodified polyamides are in parentheses

with the amide-water bonds, can account for the decrease in water absorption.

The irregularity of the water uptake of polyamide VI with *m*-phenylene moieties, unexpectedly lower than that of polyamide VII with *p*-phenylene moieties, suggested a difference in crystallinity of the samples. Consequently, they were studied by wide angle X-ray diffraction, but the results indicated the polymers to be substantially amorphous in both cases. Nevertheless, a plausible explanation for this irregular behaviour seems to relate to a certain degree of order somehow developed by polymer VI, which would also be consistent with its comparatively poor solubility.

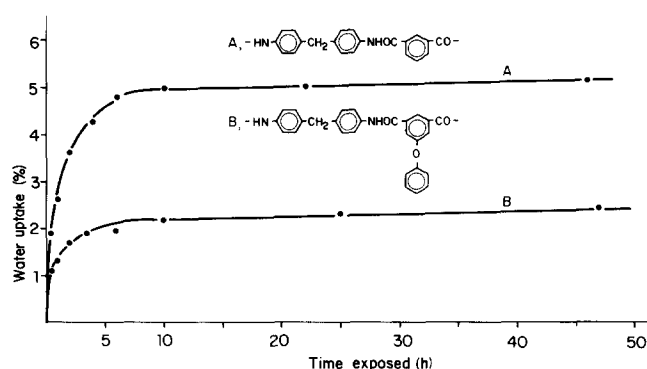


Figure 4 Water absorption (%) versus time for polyamides III (A) and VIII (B)

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