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Polyisophthalamides with pendent heterocyclic groups: 3. Pyridine pendent groups

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A series of polyisophthalamides (PIPAs) containing pendent isonicotinamido groups has been prepared from six aromatic diamines and a novel monomer, 5-(isonicotinoylamino)isophthalic acid. These polymers, which should be considered as modified PIPAs, have high inherent viscosities (about 1.0 dl g^{-1}) and are synthesized in high yields by the phosphorylation polycondensation method. They show a better solubility in organic polar solvents than the parent unmodified polyisophthalamides, and their glass transition temperatures are 20–30°C higher. However, the thermal stability, as measured by thermogravimetric analysis, is lower, showing initial thermal decomposition temperatures of about 400°C. These novel PIPAs can take up approximately twice as much water by weight as conventional PIPAs. Equilibrium water absorption of up to 17% can be measured for some samples.

(Keywords: aromatic polyamides; synthesis; pyridine pendent groups)

Introduction

Aromatic polyamides have been the object of many studies to determine the relationship between their outstanding properties and their morphology and chemical structure[1,2]. Due to the stiffness of the polymer chains and the strong molecular interactions through hydrogen bonding of amide groups, aromatic polyamides show limited solubility in organic solvents. The incorporation of bulky pendent groups has been accepted as a convenient approach to modify the properties of aromatic polyamides and other aromatic polymers[3,4] because it produces beneficial changes in solubility while maintaining the inherent thermal resistance[5,6].

Within the framework of a systematic study of modified polyisophthalamides (PIPAs), the present work was aimed at the synthesis and characterization of novel aromatic polyamides with pyridine pendent groups. Pyridine-containing aromatic condensation polymers have been studied previously, but most of the examples reported are limited to polymers with pyridine moieties in the main chain[7–9]. From these antecedents, it is known that the presence of pyridine units does not impart remarkable loss of thermal resistance, whereas additional advantages could be observed in chain flexibility and solubility.

In the present paper the pendent group introduced is a combination of a pyridyl ring and an amide group (thus, an isonicotinamide unit) joined to the 5-position of the isophthaloyl moiety, with the main purposes of enhancing solubility and water uptake. Furthermore, an evaluation of the properties of the new (modified) PIPAs was made in comparison to their unmodified counterparts and to those bearing an iminobenzoyl pendent group, described previously[10].

Experimental

Synthesis of 5-(isonicotinoylamino)isophthalic acid (INIA). A stirred mixture of isonicotinic acid (0.4 mol) and freshly distilled thionyl chloride (118 ml, 1.6 mol), surrounded by a slow stream of dry nitrogen, was heated to reflux for 12 h. Excess thionyl chloride was removed by distillation under reduced pressure and the resulting crystalline powder of isonicotinoyl chloride hydrochloride was used as prepared.

Isonicotinoyl chloride hydrochloride (0.30 mol) was added portion-wise to a solution of 5-aminoisophthalic acid (0.30 mol) and *N*,*N*-dimethylaminopyridine in 125 ml dimethylacetamide (DMAc) cooled to 10°C. Next, the temperature was slowly raised to 40°C and the reaction was maintained at this temperature for 6 h. The reaction mixture was poured into water, the precipitate filtered off, extracted with hot water several times and dried in vacuum at 120°C. The product was recrystallized twice from dimethylformamide/H_2O (3/2). Yield: 71%; m.p. = 355°C (d). Analysis: calculated for $C_{14}H_{10}O_5N_2$ (286.25), C 58.75, H 3.52, N 9.79. Found, C 58.64, H 3.45, N 9.63. ^1H n.m.r. (200 MHz, δ, ppm, dimethylsulfoxide-d_6): 10.80 (s, 1H); 8.80 (dd, 2H, $J_1 = 4.42$ Hz, $J_2 = 1.65$ Hz); 8.66 (d, 2H, $J = 1.52$ Hz); 8.25 (t, 1H, $J = 1.52$ Hz); 7.90 (dd, 2H, $J_1 = 4.42$ Hz, $J_2 = 1.65$ Hz).

Polymer syntheses. A flask equipped with a mechanical stirrer and condenser was charged with a mixture of INIA (10.0 mmol), diamine (10.0 mmol), pyridine (6 ml), lithium chloride (1.4 g) and *N*-methylpyrrolidone (NMP) (20 ml). The mixture, surrounded by nitrogen, was stirred and heated to 105°C. Triphenyl phosphite (TPP) (20.0 mmol) was then added to the solution and the reaction was maintained at that temperature for 4 h. The viscous reaction mixture was poured into methanol and the collected polymer was washed thoroughly in water

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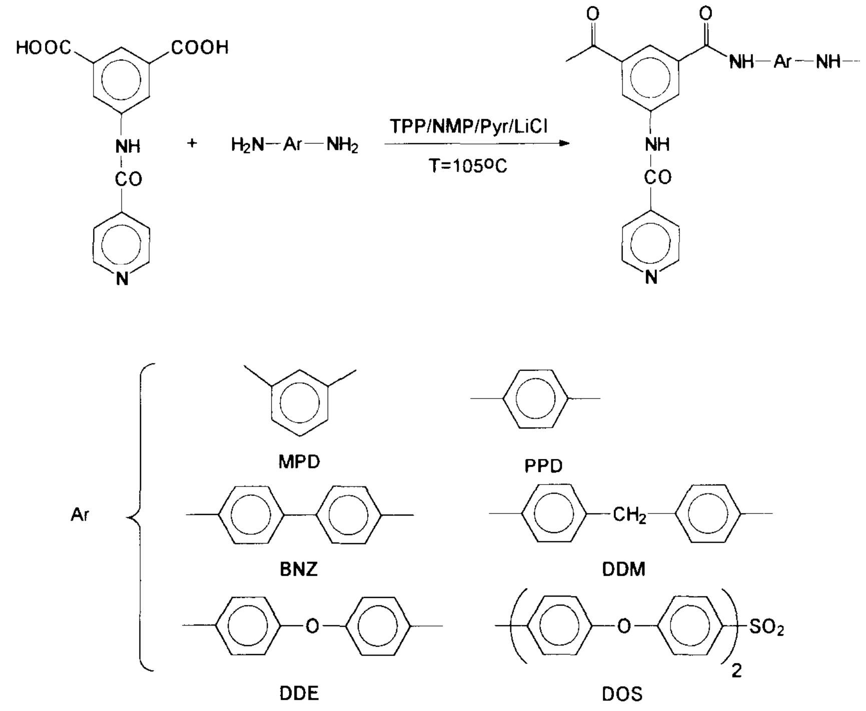

Scheme 1 Synthesis of the series of modified polyisophthalamides (PIPAs)

Table 1 Properties of PIPAs with pyridine pendent groups

Polymer	η_{inh} (dl g^{-1})^a	T_g (°C)^b	T_d (°C)^c	Y_c (%)^d
MPD-INI	0.56	321 (276)	390	67
PPD-INI	1.34	327 (295)	410	64
BNZ-INI	1.29	339 (303)	415	69
DDM-INI	0.95	302 (264)	390	63
DDE-INI	0.99	305 (267)	390	68
DOS-INI	0.67	283 (260)	370	54

[a] Measured on solutions of 0.5 g dl^{-1} in NMP at 30°C
[b] Values in parentheses are for unsubstituted polyisophthalamides
[c] Onset temperature of initial decomposition
[d] Char yield at 700°C in nitrogen atmosphere

and methanol. The polymer was finally extracted in a Soxhlet apparatus with acetone and dried in a vacuum oven at 110°C overnight. Yields of over 96% were obtained.

Results and discussion

The synthesis of the diacid INIA, containing an isonicotinamido pendent group, was carried out by means of a typical low temperature condensation reaction in high yield. The presence of an amide function in the monomer did not allow for synthesis of the acid chloride by conventional methods. Consequently, the direct polycondensation between INIA and aromatic diamines in a typical Yamazaki reaction[11] was chosen for the synthesis of the aromatic polyisophthalamides with pendent isonicotinamide groups (*Scheme 1*).

Very high yields were always achieved and relatively high inherent viscosities (η_{inh}) in the range 0.56–1.34 dl g^{-1} were obtained (see *Table 1*). All of the polymers gave transparent, tough films when cast from DMAc solutions. The polymers were characterized by ^1H and ^{13}C n.m.r. Peaks attributable to chain ends were not observed in the n.m.r. spectra of any polymer.

The data summarized in *Table 1* prove that the incorporation of bulky isonicotinamide groups did cause a significant increase (~30–40°C) in the glass transition temperatures (T_gs) of the polymers compared to the unmodified PIPAs. The T_gs are also higher, by 20–30°C, than those of the polymers with iminobenzoyl pendent groups[10]. Since the benzene and the pyridine rings are very similar in size, and the conformation and rotational barriers of bonds involved in both pendent groups are very similar (both involving a linking amide group), the cause of this increase in the T_g values may be attributed to the higher polarity of the pyridine ring compared to the phenyl ring.

The thermal stability of the polymers was evaluated by thermogravimetric analysis (t.g.a.) in N_2. The values of the onset of thermal degradation temperature (T_d), presented in *Table 1*, show a clear decrease compared to the parent, unmodified polymers[10]. In addition, the T_d value is almost the same for all polymers (390–410°C), except for INI-DOS. This coincidence is probably associated with the breakdown of the bonds joining the side groups to the main chain, as a previous step in the degradation of the main chain. The T_d values are also slightly lower than those corresponding to the polymers with iminobenzoyl pendent groups[10], which suggests that the electronic effects caused by the present of the pyridine ring lower the strength of the linkage to the main chain, and make the breaking of the side groups easier. The presence of two steps in the t.g.a. curves, which are clear when the derivatives of the curves are considered, confirms the existence of two different degradation processes, as illustrated in *Figure 1* for polymer DDE-INI. In the second step, the onset of weight loss, which corresponds to homolytic polymer degradation, varies depending on the structure of the diamine. It is maximal for PPD and minimal for DDM. It is also noteworthy that the char yields at 700°C in nitrogen are very high, giving values between 54 and 69%.

The incorporation of pendent pyridine groups causes a general increase in the solubility. All of the polymers are soluble in H_2SO_4 and in highly polar aprotic organic solvents. In less polar solvents, e.g. pyridine, cresol and cyclohexanone, the polymers show a lower degree of solubility; yet, except for the most rigid PIPAs (PPD and BNZ), all of the novel PIPAs are soluble in *m*-cresol. As expected, the flexible diamine DOS gave the most soluble polymer. Thus, DOS-INI showed good solubility in pyridine, *m*-cresol, and even in cyclohexanone.

Polyamides take up considerable amounts of water, mainly due to their relatively high polarity, and the possibility of establishing hydrogen bonds. The water uptake is generally proportional to the number of amide groups present in the repeating unit. Thus, the isothermal

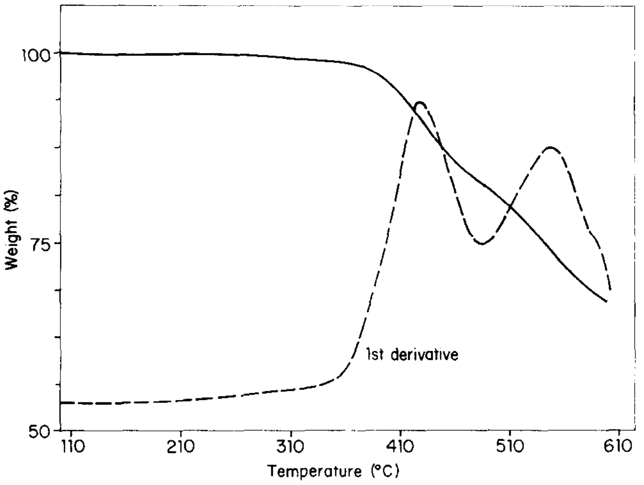

Figure 1 T.g.a. and derivative of t.g.a. curves for polymer DDE-INI. Curves determined under nitrogen at a rate of 10°C min^{-1}

Table 2 Moisture absorption of PIPAs with pyridine pendent groups^a

Polymer	Water absorption (%)	Mol H_2O/ repeat unit	Mol H_2O/ eq. amide
MPD-INI	16.7 (9.3) [11.1]	3.3 (1.2) [2.2]	1.1 (0.6) [0.7]
PPD-INI	17.3 (8.8) [10.5]	3.4 (1.1) [2.1]	1.1 (0.6) [0.7]
BNZ-INI	14.2	3.4	1.1
DDM-INI	12.1 (5.4) [7.2]	2.9 (1.0) [1.8]	1.0 (0.5) [0.6]
DDE-INI	11.7 (6.1) [7.8]	3.0 (1.1) [2.0]	1.0 (0.5) [0.6]
DOS-INI	8.1	3.1	1.0

^{a} Values in parentheses correspond to unsubstituted PIPAs; values in square brackets correspond to iminobenzoyl pendent PIPAs

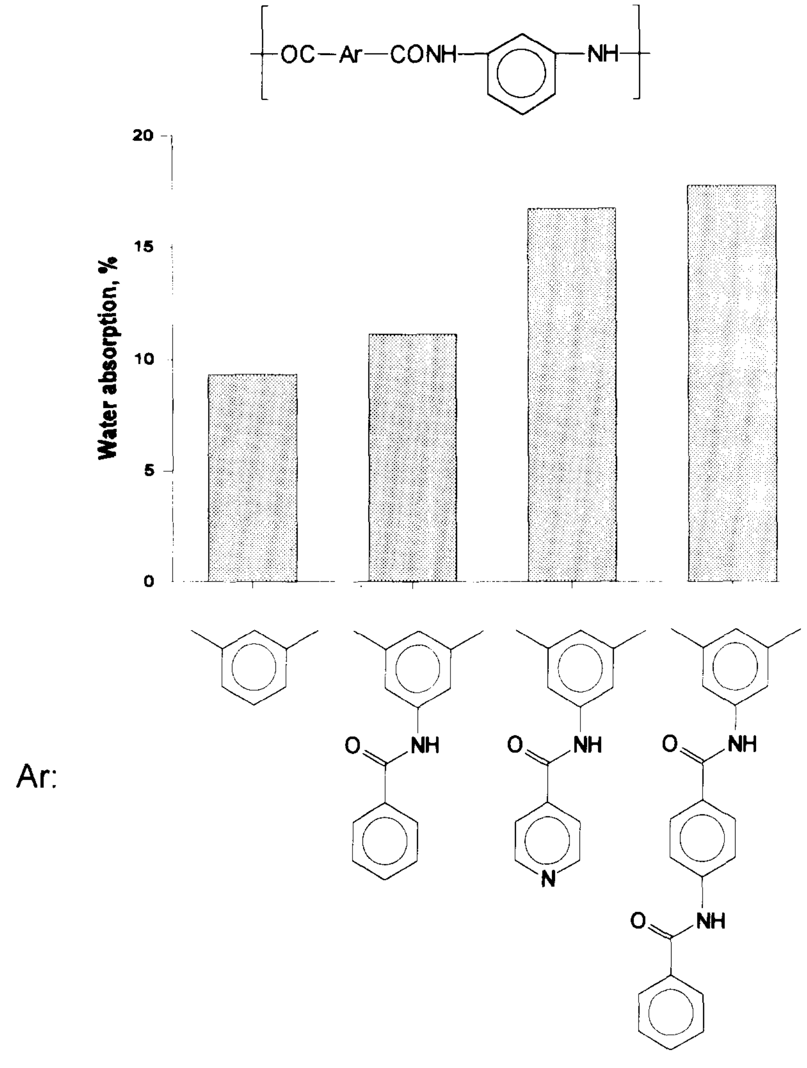

Figure 2 Comparison of water absorption (%, w/w) for selected aromatic polyamides

sorption of water by films of the polymers was measured and compared to the proportion of amide groups in each polymer. The data obtained are shown in *Table 2*, along with those corresponding to the reference unmodified polyamides and to the homologous PIPAs with iminobenzoyl pendent groups. The values of water uptake, measured at equilibrium in a conditioned atmosphere (~65% relative humidity), were very high, corresponding to amorphous structures with a high density of polar amide groups. Moreover, the pyridine group seems equivalent to an additional amide group in its ability to pick up water, as can be seen in the third column of *Table 2*, which summarizes the moles of absorbed water per repeating unit for the three series of polymers. This is confirmed in *Figure 2*, where the water sorption of a new PIPA having a pendent oligomeric group is compared to those previously indicated[12]. All of the PIPAs containing pendent isonicotinamide groups absorbed approximately twice as much water as the corresponding unmodified PIPAs having the same diamine moieties.

In conclusion, INIA has proved to be a suitable condensation monomer for the preparation of high molecular weight PIPAs by combining it with aromatic diamines in a typical Yamazaki polycondensation process. The presence of the pendent groups greatly changed the general properties of the polymers compared to those of the parent unmodified PIPAs. The solubility in polar solvents and the T_g values were improved, while the thermal resistance (t.g.a.) was negatively affected by the presence of the pendent groups. The hydrophilic character (water uptake) was greatly enhanced, to such an extent that, excluding those PIPAs containing ionic groups, these novel PIPAs must be considered among the most hydrophilic described so far.

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