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Aromatic Polyamides

A New Direct Condensation Reaction

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Summary

Aromatic polyamides are prepared by a direct condensation reaction using phenyldichlorophosphite as reagent at 80-90°(2h) and 95-100°(4h) in N-methyl-2-pirrolidone and pyridine as acceptor for hydrochloric acid.

Introduction

Polyamides are usually prepared by melt polycondensation from dicarboxylic acids and diamines at high temperatures (1). Dehydration of aromatic amino acids by thermal means has generally led to low molecular weight polymer. For example when p-aminobenzoic acid is heated at 250-300°, polymer with low molecular weight results (2). A paper by Iwakura reports the preparation of poly-p-benzamide with inherent viscosity 1.5, by thermal polymerisation at 300-350° of p-(phenoxycarboxylaminobenzamide) benzoic acid (3). Recently,it was found that diphenyl and triphenyl phosphite reacted with carboxylic acids in the presence of pyridine to give the acyloxy-N-phosphonium salt of pyridine accompanied by dephenoxylation which produced the corresponding amides on aminolysis (4). We used the same reaction with triphenyl phosphite prepared "in situ" from phenol and phosphorus trichloride in pyridine as solvent and acceptor for hydrochloric acid (5).

Results and discussion

In a previous paper, we showed that phenyldichlorophosphite is a new reagent for synthesis of aromatic amides (6).

In this work, we have investigated if the phenyldichlorophosphite is a good reagent for the synthesis of aromatic polyamides. The phenyldichlorophosphite has two reactive groups (two atoms of chlorine), which participate in the synthesis of aromatic amides at 110-120°(6). At lower temperatures, only one atom of chlorine is reactive. For the synthesis of the polyamides, we used 1 mole reagent for 1 mole monomer. For example, in the case of p-aminobenzoic acid, we used phenyldichlorophosphite (1 mole), p-aminobenzoic acid (1 mole) and lithium chloride in N-methyl-2-pyrrolidone (NMP) as solvent and pyridine as acceptor for hydrochloric acid. The obtained mixture was heated, when the solution became viscous, resulting the corresponding polymer. When we used only 0.5

mole phenyldichlorophosphite for 1 mole p-aminobenzoic acid, a polymer with low viscosity was formed. As acceptor for hydrochloric acid we tried many tertiary amines, but the pyridine was found to be the most suitable base. In the case of reaction between aromatic dicarboxylic acids (1 mole) and aromatic diamines (1 mole), we used 2 moles phenyldichlorophosphite.

As a result of these investigations and similar with other cases (6), we propose the following mechanism of reaction:

$$HOOC - Ar - COOH + 2C_6H_5OPCl_2 \xrightarrow[0 - 20^\circ]{Py}$$

(I)

$$H_5C_6O(Cl)POOC{-}Ar{-}COOP(Cl)OC_6H_5 + 2PyH^+Cl^-$$

(II)

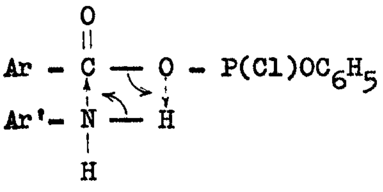
$$(II) + H_2N - Ar' - NH_2 \xrightarrow[80 - 100^\circ]{}$$

(III)

$$(-OC - Ar - CONH - Ar'{-}NH-)_n + 2C_6H_5OP(Cl)OH$$

(IV)

We supposed, similar as in other cases (6-9), that this reaction involves a four-centre transition state (V):



(V)

Experimental

The following materials were used: p-aminobenzoic acid was recrystallized from water, 4,4'-diaminodiphenyl ether and benzidine were recrystallized from ethanol, while 4;4'-diaminodiphenylmethane was recrystallized from benzene. Izophthalic acid was recrystallized from ethanol and terephthalic acid from acetic acid. NMP was freshly distilled from P_2O_5 and pyridine from KOH.

Polycondensation reaction of p-aminobenzoic acid

A solution of LiCl (2g) and p-aminobenzoic acid (2.74 g, 0.02 moles) in dried NMP (40 ml) and dried pyridine (7 ml) was stirred till it became clear. To the obtained solution, under stirring and cooling to 0-5°, 2.8 ml (0.02 moles) phenyldichlorophosphite (10) was added very slowly (the reaction is exothermic).The mixture was stirred for 1 h at room temperature. Then it was heated gradually to 80-90°(2h) and at 95-100°(4h), under nitrogen and stirring. At the end of reaction, the hot solution (60-80°) was slowly poured into a large volume of methanol (300 ml) with vigorous stirring. The fibrous polymer was collected by filtration,washed well with methanol (3-4 times) and dried at 100° under reduced pressure.

General procedure for the preparation of polyamides 1-6

A solution of isophthalic or terephthalic acid (1.661 g, 0.01 mole), lithium chloride (1.6 g) and 0.01 mole of aromatic diamine in 20 ml NMP and 20 ml pyridine, was treated as above with 2.8 ml (0.02 mole) phenyldichlorophosphite. The polymers were precipitated by the work-up described above.

Table 1 shows the aromatic polyamides obtained in this way.

TABLE 1

Aromatic polyamides obtained by means of the phenyldichlorophosphite as reagent.

Diamine	Dicarboxylic acid.	Aromatic polyamide[a)] Inherent viscosity[b)]
1.p,p'-Diaminodiphenylmethane.	Isophthalic acid	0.89
2.p,p'-Diaminodiphenyl ether.	Isophthalic acid	0.73
3.p-Phenylenediamine.	Isophthalic acid	0.81
4.Benzidine	Isophthalic acid	0.3
5.p,p'-Diaminodiphenylmethane	Terephthalic acid	0.42
6.p,p'-Diaminodiphenyl eter	Terephthalic acid	0.36
7. p-Aminobenzoic acid		1.4

a) The products were identified by elementary analysis and IR spectra.

b) H_2SO_4 at 25°.

By this new direct synthesis we obtained aromatic polyamides with high inherent viscosities, which are difficult to obtain by the heating of aromatic diamines with aromatic dicarboxylic acids.

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