Synthesis of Polyamides *via in-situ* Polycondensation

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It is well known¹ that polyamides can be obtained under mild conditions by using active diesters such as phenyl esters. In this case, the isolation of the active diesters is necessary because of the purification. On the other hand, aryl sulfites are found² to be effective for synthesizing the active diesters in a quantitative yield by reacting aryl sulfites with carboxylic acids in the presence of a base such as pyridine or imidazole. Therefore, it is expected that

polyamides may form under mild conditions when nylon salts from dicarboxylic acids and diamines are subjected to the reaction in the presence of pyridine or imidazole together with a stoichiometric amount of aryl sulfites, since active diesters may form *in-situ* in the solution and the polycondensation of the active diesters may follow. This paper describes the synthesis of polyamides *via in-situ* polycondensation by using aryl sulfites.

EXPERIMENTAL

Diphenyl, di-(*p*-nitrophenyl) or catechol sulfites were prepared by reacting thionyl chloride with corresponding phenols in refluxing monochlorobenzene.^{3,4} Nylon salts from dicarboxylic acids and diamines were prepared by mixing methanol solutions of dicarboxylic acids and diamines, followed by filtration and recrystallization in aqueous methanol solution. Polycondensation reaction was carried out as follows: nylon salts or amino acids were suspended in dimethylformamide (DMF) in a desired concentration and a given amount of diphenyl sulfite and imidazole was added to the solution. When pyridine was used as a solvent, imidazole was not added. The whole solution was kept at room temperature or 60°C with a vigorous

stirring in a given period. Then, the solution was poured into excess acetone and precipitated polymers were collected by filtration, washed with water and acetone and dried.

The polymers obtained were identified as corresponding polyamides by infrared and elemental analyses. Solution viscosities of the polyamides were measured in the concentration of 0.5 g/100 ml of 96% sulfuric acid at 30°C.

RESULTS AND DISCUSSION

Table I summarizes results of the polycondensation of various nylon salts or amino acids in the presence of diphenyl sulfite in dimethylformamide (DMF) or pyridine (Py). It is seen in Table I that imidazole was superior to pyridine as a base since an insoluble polymer was

Table I. Polycondensation of nylon salts or amino acids in the presence of phenyl sulfite^a

Nylon salt or amino acid		Base	Temp, °C	Time, day	Polymer	
HOOC—R—COOH (NH ₂ —R—COOH)	NH ₂ —R'—NH ₂				Yield, %	η_{sp}/C
—(CH ₂) ₄ —	—(CH ₂) ₆ —	Im	Room	3	69	0.13
"	"	" ^b	"	3	66	0.15
"	"	"	60	6	35	0.29
"	"	Py ^c	60	6	25	Insoluble
"		Im	Room	5	81	0.12
"	"	"	60	1	75	0.13
"		"	Room	5	43	0.09
—(CH ₂) ₈ —	—(CH ₂) ₆ —	"	60	1	50	0.16
"		"	60	1	77	0.07
"	Room	5	0	—
—(CH ₂) ₄ —	—NHCO— —CONH—	"	"	5	79	0.10
"	"	"	60	1	57	0.07
HOOC—CH ₂ —NH ₂	"	"	Room	5	0	—
HOOC—(CH ₂) ₅ —NH ₂	"	"	"	5	12	0.14
HOOC— —NH ₂	"	"	60	1	0	—

^a Polycondensation was carried out by using 0.0025 mol of nylon salts or amino acids in the presence of 0.005 mol of phenyl sulfite and imidazol in 10 ml of DMF.

^b The amount of imidazole was reduced to 0.0025 mol.

^c 10 ml of pyridine was used as a solvent.

formed in pyridine. Higher temperatures rather reduced polymer yields and thus room temperature was preferable. The combination of adipic acid and hexamethylenediamine produced a corresponding polyamide in about 70-% yield and the solution viscosity of the polyamide was not satisfactory. This might be ascribed to an insufficient conversion of carboxylic acid to a corresponding active ester. Aromatic diamines such as *p*- or *m*-phenylenediamines also produced the corresponding polyamides in a good yield in comparison with hexamethylenediamine, while aromatic dicarboxylic acids such as isophthalic acid did not yield any polyamides at all. Isophthalic acid dihydrazide could also produce a corresponding polyhydrazide from adipic acid by means of the same method. On the other hand, amino acids did not produce polyamides in the presence of phenyl sulfite and imidazole.

Therefore, the acidity or reactivity of carboxylic acid may be related to the formation of the active diesters by phenyl sulfite.

It is well known that *p*-nitrophenyl ester is easily subjected to a nucleophilic replacement by amine, in comparison with phenyl ester. Therefore, various sulfites including di-(*p*-nitrophenyl) sulfite, catechol sulfite, or benzenesulfonyl chloride were investigated in terms of the catalytic activity for the polycondensation of nylon salts or amino acids. Table II summarizes the results of the polycondensation by these sulfites. As was expected, di-(*p*-nitrophenyl) sulfite initiated the polycondensation of nylon 66 salt (adipic acid/hexamethylenediamine) to form polyamide in higher yield than diphenyl sulfite. However, fully aromatic polyamides were not obtained even by di-(*p*-nitrophenyl) sulfite. Catechol sulfite did not initiated the

Table II. Polycondensation of nylon salts or amino acids by various sulfites

Sulfite	Monomer		Base	Solvent	Temp, °C	Time, hr	Polymer	
	HOOC—R—COOH (NH ₂ —R—COOH)	NH ₂ —R'—NH ₂ (NH ₂ —R—COOH)					Yield, %	η _{sp} /C
(NO ₂ — —O) ₂ SO	—(CH ₂) ₄ —	—(CH ₂) ₆ —	Im	DMF	Room	20	87	0.10
"	"	"	"	"	60	24	50	0.07
"	"	—NHCO— —CONH—	"	"	60	24	60	0.04
"	"	NH ₂ — —COOH	"	"	60	24	0	—
SO	—(CH ₂) ₄ —	—(CH ₂) ₆ —	"	"	60	24	0	—
"	"	"	"	"	60	24	0	—
SO ₂ Cl	"	"	Py	Py	Room	41	77	0.22
"	"	"	Im	THF ^b	Room	40	0	—
"	—(CH ₂) ₈ —	"	H ₃ PO ₄	Py	Room	24	90	0.06
"	"	NH ₂ —CH ₂ —COOH	Py	Py	Room	14	16	—
"	"	"	Py	Py	Room	41	75	0.08

^a Polycondensation was carried out by using 0.0025 mol of nylon salts in the presence of 0.005 mol of sulfites and base in 10 ml of solvent.

^b Tetrahydrofuran.

^c 20 ml of pyridine was used.

polycondensation at all, since catechol sulfite is stable enough to react with carboxylic acid, while benzenesulfonyl chloride could initiate the polycondensation in pyridine but not in tetrahydrofuran (THF). It was found that glycine was subjected to a polycondensation reaction in the presence of benzenesulfonyl chloride in pyridine to form polypeptide having a low solution viscosity. More detailed investigations on the optimum conditions to form a high molecular weight polyamide are being carried out and results will be published in the near future.

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