SHORT COMMUNICATION

Synthesis of Polyester by Direct Polycondensation with Triphenylphosphine

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(Received April 18, 1981)

KEY WORDS Direct Polycondensation / Polyester / Triphenylphosphine /
Polyhalo-Compound / Hydroxyl Benzoic Acid / Pyridine / 2,5-Pyridine
Dicarboxylic Acid /

Various methods have been developed^{1–5} for synthesizing polyamides by the direct polycondensation of monomers under mild conditions through phosphorylation reactions. However, very few papers have been published on this method of synthesis. The difficulty in polyester synthesis under mild conditions may be ascribed to the low nucleophilicity of hydroxyl groups which are not sufficiently high enough to form ester linkages by these phosphorylation reactions, compared with amino group reactivity. Aromatic polyesters have been obtained⁶ by heating mixtures of dicarboxylic acids and diols at temperatures above 100°C in the presence of triaryl phosphine.

It was recently found⁷ that an aromatic polyamide with a high molecular weight could be obtained in a quantitative yield under mild conditions by the reaction of *p*-aminobenzoic acid in the presence of triphenylphosphine with polyhalo-compounds such as carbon tetrachloride in a pyridine solution. This reaction has now been extended to the direct polycondensation of monomers such as *m*-hydroxybenzoic acid to form polyesters. Polyesters can be obtained very rapidly at room temperature. So far, this is the first report dealing with the synthesis of polyesters by the direct polycondensation under mild conditions.

The following general procedure was employed for synthesizing an aromatic polyester from *m*-hydroxybenzoic acid: 0.01 mol of *m*-hydroxybenzoic acid and triphenylphosphine was dissolved in 10 cm³ of pyridine and then 0.01 mol of hexachloroethane added to the solution with stirring at room temperature. As soon as the hexachloroethane was added, an exothermic reaction took place immediately and the solution became heterogeneous with a separation of a solid polymer and the whole solution solidified within 5 minutes. Excess methanol was added to remove the polymer which was isolated by filtration. The polymer was repeatedly washed with water and methanol, and dried under reduced pressure. The solution viscosity of the polymer was determined in *m*-cresol at 30°C. The polymer was identified as the corresponding polyester derived from *m*-hydroxybenzoic acid by means of elemental analysis and infrared spectrum where absorptions owing to ester groups appeared at 1720 and 1230 cm^{–1}.

Table I summarizes the results of the polycondensation of various monomers in the presence of triphenylphosphine and polyhalo-compounds.

It can be seen in Table I that polyesters were obtained in good yields by using carbon tetra-

Table I. Synthesis of polyester in the presence of triphenyl-phosphine and various halo-compounds at room temperature

Monomer	Halo-compound	Solvent	Concn.	Polymer yield	η_{sp}/c^a
			mol/dm ⁻³	%	
BPA ^b -2,5-Py ^c	CCl ₄	NMP ^d -Py ^e (1:1)	0.25	33	0.19
	CBr ₄	"	0.25	74	0.23
	Cl ₃ CCCl ₃	"	0.25	87	0.31
	Cl ₃ CCCl ₃	"	0.5	64	0.20
	Cl ₃ CCOO- -OCCCCl ₃	"	0.25	57	0.24
	Cl ₃ CCOCCl ₃	"	0.25	0	—
<i>m</i> -Hydroxybenzoic acid	Cl ₃ CCCl ₃	Py	1.0	82	0.12
	Cl ₃ CCCl ₃	"	0.5	23	0.10
<i>p</i> -Hydroxybenzoic acid	Cl ₃ CCCl ₃	"	1.0	100	—
BPA/ADA ^f	Cl ₃ CCCl ₃	"	0.5	100	0.12

^a 0.1 g 10 cm⁻³ in *m*-cresol at 30°C.^b Bisphenol A.^c 2,5-Pyridinedicarboxylic acid.^d *N*-Methyl-2-pyrrolidone.^e Pyridine.^f Adipic acid. **Figure 1.** Effect of molar ratios of hexachloroethane to *m*-hydroxybenzoic acid on the polycondensation. Ph₃P-monomer, 1.2:1.0; solvent, pyridine 10 cm³; temp, room temp; time, 1 h. Monomer concn: O, 1.0 mol dm⁻³; ●, 0.5 mol dm⁻³.

bromide or hexachloroethane in concurrence with triphenylphosphine. The combination of triphenylphosphine as the initiator yielded a polyester of

Figure 2. Rate of the polycondensation of *m*-hydroxybenzoic acid in the presence of triphenylphosphine and halo-compound at room temperature. Monomer concn, 1.0 mol dm⁻³; Ph₃P-halo-compound-monomer, 1.2:1.5:1.0; ●, stirring; O, non-stirring; solvent, pyridine 10 cm⁻³.

relatively high solution viscosity.

Figure 1 indicates the results of the polycondensation of *m*-hydroxybenzoic acid by the combination of triphenylphosphine and hexachloroethane in terms of the effect of the molar ratio of hexachloroethane on the monomers. The yield of

the polyester reached a maximum at the molar ratio of triphenylphosphine–hexachloroethane–monomer = 1.2:1.5:1.0. The yield of the polyester was found susceptible to the molar ratio among the initiators and monomer.

Figure 2 indicates the conversion rate of *m*-hydroxybenzoic acid to the corresponding polyester and it can be seen that the polycondensation took place very rapidly and was completed within 20 minutes to yield the polyester.

A study in greater detail on the direct polycondensation for the polyester synthesis is being carried out to find out the optimum reaction conditions and the reaction mechanism involved. The results will be

published in the near future.

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