

Synthesis of Poly(*p*-benzamide) with Triphenylphosphine and Hexachloroethane Reagents—Reaction Conditions

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ABSTRACT: The polycondensation reaction of *p*-aminobenzoic acid with the reagent of triphenylphosphine and hexachloroethane was investigated in order to establish the optimum reaction conditions for direct polycondensation. Reaction conditions, such as the molar ratios of triphenylphosphine and hexachloroethane to the monomer, the concentrations of monomer and reagents, the reaction temperature and the kinds of acid acceptor and solvent, had considerable influence on the yield and the molecular weight of the resulting polyamide. The poly(*p*-benzamide) having the highest molecular weight was obtained with the molar ratio of triphenylphosphine–hexachloroethane–monomer = 1.2 : 1.5 : 1.0 in the mixed solvent of tetramethylurea and pyridine at room temperature.

KEY WORDS Poly(*p*-benzamide) / Polycondensation / Triphenylphosphine / Hexachloroethane / Polyamide /

It has been found¹ recently that polyamides can be prepared rapidly from dicarboxylic acid and a diamine by a direct polycondensation reaction with a reagent of triphenylphosphine and polyhalo-compounds under conditions so mild that polycondensation can be carried out at room temperature. In particular, the polyamide having a relatively high molecular weight was obtained with a combination of triphenylphosphine and hexachloroethane or hexachloroacetone. The polymer obtained with hexachloroacetone had a violet color, while the polymer obtained with hexachloroethane colored light yellow. This paper deals with the reaction conditions for direct polycondensation, using a combination of triphenylphosphine and hexachloroethane in order to establish the optimum reaction conditions for obtaining a high molecular weight polyamide.

EXPERIMENTAL

Polycondensation

A given amount of *p*-aminobenzoic acid (4-ABA) and triphenylphosphine (Ph₃P) was dissolved in 10 cm³ of solvent, and a given amount of hexachloro-

ethane (C₂Cl₆) was added to the solution with stirring at room temperature. As soon as the hexachloroethane was added, the reaction solution became yellow and an exothermic reaction took place. Then, the reaction solution became heterogeneous with the separation of a solid polymer, and at times the entire solution solidified within 2 min. Excess methanol was added to remove the solvent and by-products from the resulting polymer which was then isolated by filtration. The polymer was repeatedly washed with water and methanol, and dried under reduced pressure.

Characterization

The structures of the obtained polymers were identified by infrared and elemental analyses. The values of the elemental analyses for aliphatic polyamides were in close agreement with calculated values.

Anal. Calcd for C₆H₁₁NO (Nylon 6): C, 63.7%; H, 9.7%; N, 12.4%. Found: C, 62.6% H, 9.7%; N, 11.0%.

Elemental analyses of the aromatic polyamides did not agree with the calculated values since the high thermal stabilities of these samples prevented

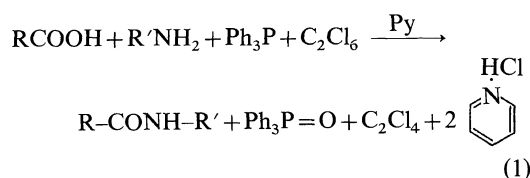
accurate analyses. Also, the aromatic polyamides had no distinct melting points. The structures of the aromatic polyamides were identified by the absorption band at 1640 cm^{-1} (amide I) in the infrared spectra.

The solution viscosities of the polymers were determined at a concentration of 0.01 g cm^{-3} in concentrated sulfuric acid at 30°C .

RESULTS AND DISCUSSION

The solution viscosities and yield of the resulting polyamides varied with the molar ratios of the reagent to the monomer 4-ABA. The polyamides was obtained in a quantitative yield in pyridine when molar ratios of Ph_3P and C_2Cl_6 ranged from 1 to 2. The optimum molar ratio among Ph_3P , C_2Cl_6 , and 4-ABA was 1.2:1.5:1.0 as can be seen from Figure 1, and the polyamide having a solution viscosity as high as 3 was obtained in a quantitative yield in pyridine at room temperature.

It can be considered that the polycondensation reaction proceeds stoichiometrically as shown by following equations:



It can be seen from equation 1 that the amount of reagent required for the polycondensation reaction seems to be a stoichiometric amount of monomer in a molar amount. However, the experimental amount of reagent required for the polycondensation exceeded the equivalent amount of monomer possibly because some side reactions such as the decomposition of reagent in pyridine to form triphenylphosphine oxide took place. Moreover, other undesirable side reactions, such as a reaction of an amine with reagent which forms unreactable phosphoramidate possibly occurred, causing a decrease in the molecular weight of the polyamide.

The monomer concentration was also found to have a significant effect on the molecular weight of the resulting polyamide, as shown in Figure 2.

The polyamide having the highest solution viscosity of 3 was obtained at a monomer concentration of 0.4 mol dm^{-3} in pyridine. Subsequently,

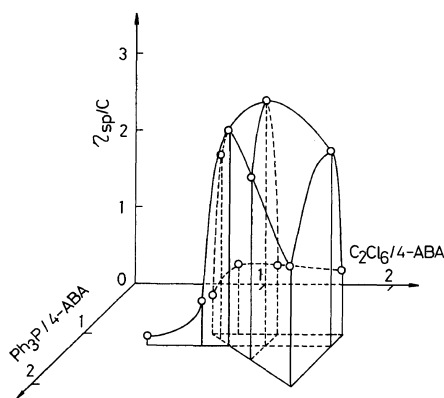


Figure 1. Effect of molar ratios of triphenylphosphine, hexachloroethane, and monomer on the solution viscosities of poly(*p*-benzamide). Monomer concn, 0.4 mol dm^{-3} ; temp, room temp; time, 30 min; solvent, pyridine.

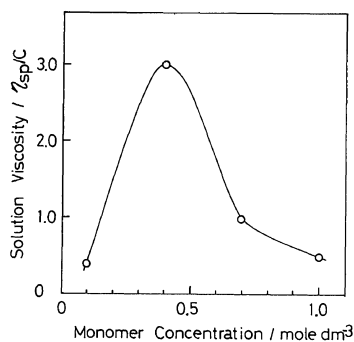


Figure 2. Effect of monomer concentrations on the polycondensation of 4-ABA. Molar ratios of C_2Cl_6 - Ph_3P -4-ABA = 1.5 : 1.2 : 1.0; temp, room temp; time, 30 min; solvent, pyridine.

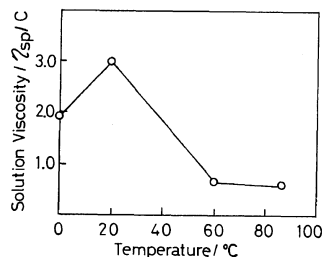


Figure 3. Effect of reaction temperature on the polycondensation of 4-ABA. Monomer concn, 0.4 mol dm^{-3} ; molar ratios of C_2Cl_6 - Ph_3P -4-ABA = 1.5 : 1.2 : 1.0; time, 30 min; solvent, pyridine.

the solution viscosity of polyamide decreased with increasing monomer concentration. The decrease in solution viscosity can be explained by the entangle-

ment of growing polymer chains with each other, with increasing monomer concentration, leading to low reactivity of the polymer end groups.

Solution viscosity of resulting polyamide was greatly dependent on reaction temperature as evident from Figure 3, which indicates that the maximum solution viscosity was observed at 20°C. With increasing reaction temperatures, the resulting polyamide became violet, and the solution viscosity of the resulting polyamide decreased, presumably owing to significant side reactions such as the formation of P-N linkage.

The results of the direct polycondensation reaction carried out in various solvents are summarized in Table I. It can be seen from this Table that the solvent had an important influence on the molecular weight of the polyamide and that pyridine had a specific effect on the polycondensation reaction in terms of solution viscosities of the polyamide.

The results of the polycondensation reaction of 4-ABA carried out in various pyridine derivatives, triethylamine and *N,N*-dimethyltoluidine as an acid acceptor are summarized in Table II. No polyamide was obtained in triethylamine.

The highest polymer solution viscosity of 5 was obtained in a mixed solvent of tetramethylurea and pyridine of 30% content in volume. This was preferable from the standpoint of solution viscosities as can be seen from Figure 4.

The effect of these solvents on polycondensation reactions was related to both the polarities of the solvents and the solubilities of the resulting poly-

amides. As shown in Table II, pyridine had a specific effect on the direct polycondensation reaction with triphenylphosphine and hexachloroethane in preparing poly(*p*-benzamide) with a high molecular weight. Pyridine functioned not only as an acid acceptor but also as a reagent. If pyridine

Table II. Solvent effect on the polycondensation of 4-ABA^a

Solvent	pK _a ^b	Polymer			
		Yield/%		η _{sp} /c	
		S ^c	M ^d	S ^c	M ^d
2-Chloropyridine	0.49	21		0.09	
Quinoline	4.81	88		0.17	
Pyridine	5.25	100	100	2.99	5.16
3-Picoline	5.63	87	89	0.71	0.69
<i>N,N</i> -Dimethyl- <i>o</i> -toluidine	5.86	4		—	
2-Picoline	5.94	89	81	0.26	0.26
4-Picoline	6.03	96	83	0.37	1.27
2,6-Lutidine	6.60	79	100	0.25	0.30
Triethylamine	10.75	0		—	

^a Monomer concn, 0.4 mol dm⁻³; molar ratios of C₂Cl₆-Ph₃P-4-ABA = 1.5 : 1.2 : 1.0; temp, room temp; time, 30 min.

^b Cited from "CRC Handbook of Tables for Organic Compound Identification, 3rd edition."

^c S, solvent only.

^d M, mixed solvents containing 70% tetramethylurea.

Table I. Solvent effect on the polycondensation of 4-ABA^a

Solvent	Dielectric constants	Polymer	
		Yield/%	η _{sp} /c
Triethylamine	2.42	0	—
Quinoline	9.0	88	0.17
Pyridine	13.3	100	2.70
Tetramethylurea	23	96	0.33
<i>N</i> -Methyl- α -pyrrolidone	32.2	100	0.15
Hexamethylphosphortriamide	34	0	—

^a Monomer concn, 0.4 mol dm⁻³; molar ratios of C₂Cl₆-Ph₃P-4-ABA = 1.5 : 1.2 : 1.0; temp, room temp; time, 30 min.

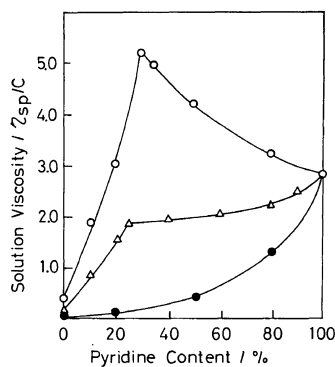
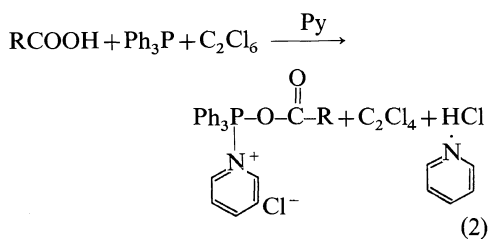
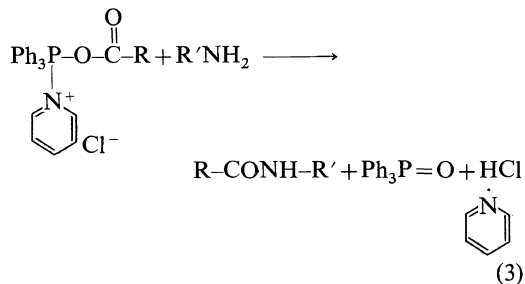


Figure 4. Solvent effect on the polycondensation of 4-ABA. Monomer concn, 0.4 mol dm⁻³; molar ratios of C₂Cl₆-Ph₃P-4-ABA = 1.5 : 1.2 : 1.0; temp, room temp; time, 30 min. Mixed solvent: (O), tetramethylurea-pyridine; (Δ), *N*-methyl- α -pyrrolidone; (●), hexamethylphosphortriamide-pyridine.

played a role only as an acid acceptor, then the amount of pyridine requiring for the reaction should be twice as much moles as monomer. Nevertheless, the amount of pyridine actually used to obtain the polymer having the highest solution viscosity was 8 times the number of moles of monomer. This suggests that pyridine might participate in the reaction process directly. Probably, pyridine forms an active intermediate along with the carboxylic acid and reagent according to the following reaction:



The formation of this intermediate might be related to the basicity and structure of carboxylic acid and pyridine derivatives. The *N*-phosphonium pyridine complex of carboxylic acid has an active acyl group which may react with an amine to form an amide linkage as follows:



REFERENCE

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