Reaction Mechanism of Direct Polycondensation with Triphenylphosphine and Hexachloroethane

Guo-chuang WU, Hozumi TANAKA, Kohei SANUI,
and Naoya OGATA

*Department of Chemistry, Sophia University,
7–1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan*

ABSTRACT: The reaction mechanism of direct polycondensation with triphenylphosphine and hexachloroethane was investigated by gas chromatography, infrared and NMR spectroscopic analyses. It was found that pyridine participated in the reaction process of the direct polycondensation of dicarboxylic acid and diamine in the presence of triphenylphosphine and hexachloroethane in addition to serving as solvent and acid acceptor. The polyamide formation passed through an active acyl intermediate of carboxylic acid formed from triphenylphosphine and hexachloroethane in the presence of pyridine, followed by an aminolysis reaction with amine to form an amide linkage.

KEY WORDS Polyamide / Polycondensation / Triphenylphosphine / Hexachloroethane / Pyridine /

Polyamides have been prepared in good yield by direct polycondensation reactions with triphenylphosphine and polyhalo-compounds under mild conditions such as room temperature. The reaction conditions of direct polycondensation were investigated with regard to the synthesis of poly(p-benzamide).[1]

Much investigation has been carried out on the mechanism of the reaction of triphenylphosphine (Ph_3P) with tetrachloromethane (CCl_4),[2-7] but the system of Ph_3P and hexachloroethane (C_2Cl_6) had been investigated only by Appel.[8] For example, Appel synthesized polypeptides by using Ph_3P and C_2Cl_6 and indicated in his report that an intermediate Ph_3PCl_2, formed from Ph_3P and C_2Cl_6, might possibly lead to an amide linkage from the acid and amine.

We found, however, that phosphorane Ph_3PCl_2 prepared from Ph_3P and C_2Cl_6 in acetonitrile did not initiate the polycondensation of p-aminobenzoic acid (4-ABA) in pyridine. When the monomer 4-ABA was added to a previously mixed solution of Ph_3P and C_2Cl_6 in pyridine, the yield of polyamide was 100% although the solution viscosity of the resulting polyamide was very low, as shown in Table I. Moreover, pyridine was found to play

a specific role in forming a high molecular weight polyamide by this direct polycondensation reaction.

This paper reports on some of the model reactions investigated by gas chromatography, infrared and NMR analyses in order to determine the role of pyridine in the reaction process. The reaction mechanism for direct polycondensation is discussed.

EXPERIMENTAL

Polycondensation

1) Poly(p-benzamide). 0.54 g (0.004 mol) of p-aminobenzoic acid and 1.26 g (0.0048 mol) of Ph_3P were dissolved in 10 cm³ pyridine, and 1.42 g (0.006 mol) C_2Cl_6 were added to the solution with stirring at room temperature. As soon as the C_2Cl_6 was added, the reaction solution became yellow and an exothermic reaction took place. The entire reaction solution solidified within 2 min. After 30 min, 100 cm³ of methanol was added to remove by-products from the polymer which was isolated by filtration. The polymer was washed 3 times with water and 2 times with methanol and finally dried under reduced pressure for 12 hours.

2) Poly(p-phenylene terephthalamide). 0.356 g (0.002 mol) of terephthalic acid and 1.26 g (0.0048

mol) of Ph_3P were dissolved in $5 cm^3$ pyridine, and 0.2341 g (0.002 mol) of *p*-phenylenediamine and 1.42 g (0.006 mol) of C_2Cl_6 were dissolved in another $5 cm^3$ of pyridine. As soon as the two solutions were mixed with stirring at room temperature, an exothermic reaction took place and a yellow precipitate was obtained. After 30 min, the reaction solution was treated in the same manner indicated above.

3) Solution Viscosities of Polyamides. Solution viscosities of the polyamides were measured at a concentration $0.1 g/10 cm^3$ in concentrated sulfuric acid at 30°C.

Model Reaction

All model reactions of aniline ($C_6H_5NH_2$) with either acetic acid (CH_3COOH) or pivalic acid (($CH_3)_3CCOOH$) were carried out by the same method mentioned in 2) of the polycondensation. The concentrations of the carboxylic acid and amine were $0.4 mol dm^{-3}$, respectively.

The model reaction for the gas chromatographic measurement was carried out using $C_6H_5NH_2$ and CH_3COOH in tetrahydrofuran.

The chemical shifts of α-H of pyridine under various conditions were determined by a Hitachi model R-22 (90 MHz) spectrometer at 25°C in *N*-methyl-2-pyrrolidone (NMP) using hexamethyl-disiloxane (HMS) as the internal standard.

The ^{31}P NMR spectra of model reaction products were determined with a JEOL FX 90 Q (36.27 MHz) spectrometer using phosphoric acid as the standard at 25°C.

RESULTS AND DISCUSSION

Reaction of Ph_3P and C_2Cl_6

Appel[8] reported that Ph_3PCl_2 was produced from Ph_3P and C_2Cl_6 in acetonitrile, as shown:

$$Ph_3P + C_2Cl_6 \rightarrow Ph_3PCl_2 + C_2Cl_4 \qquad (1)$$

In our investigation, C_2Cl_4 was also identified in the reaction mixture of Ph_3P and C_2Cl_6 in tetrahydrofuran by gas chromatography but no other chloroderivatives could be detected. Moreover, the amount of C_2Cl_6 reacted was equal to the amount of C_2Cl_4 produced. The ^{31}P NMR spectrum of the reaction mixture of Ph_3P and C_2Cl_6 in chloroform showed a peak at 63.5 ppm, which could be assigned to the phosphorane Ph_3PCl_2 (Table III). These

results are consistent with those reported by Appel. Nevertheless, polyamide could not be obtained when monomer 4-ABA was added to phosphorane prepared from Ph_3P and C_2Cl_6 in acetonitrile. However, a polyamide with high solution viscosity was obtained by adding C_2Cl_6 to the previously mixed solution of 4-ABA and Ph_3P in pyridine.

Table I. Effect of addition order of reagents on polycondensation[a]

Addition order	Yield %	η_{sp}/c
C_2Cl_6 to $(4\text{-}ABA + Ph_3P)$	100	2.73
4-ABA to $(Ph_3P + C_2Cl_6)$	100	0.08
TPA to $(PhDA + Ph_3P + C_2Cl_6)$	0	—
PhDA to $(TPA + Ph_3P + C_2Cl_6)$	100	0.12

[a] Solvent, pyridine $10 cm^3$; temp, room temp. Concn of monomer: 4-ABA, $0.4 mol dm^{-3}$; TPA, PhDA $0.2 mol dm^{-3}$. Concn of reagent: Ph_3P, $0.48 mol dm^{-3}$; C_2Cl_6, $0.6 mol dm^{-3}$. TPA, terephthalic acid; PhDA, *p*-phenylenediamine.

Table II. Chemical shifts of α-H of pyridine under various conditions

Condition	Solvent	Chemical shift ppm
Py	NMP	8.76
Py + Ph_3P	NMP	8.51
Py + Ph_3PO	NMP	8.51
Py + $Ph_3PO + C_2Cl_4$	NMP	8.50
Py + $Ph_3P + C_2Cl_6$	NMP	8.98
Py + HCl	NMP	8.50
Py + CH_3COOH	NMP	8.67
Py + $CH_3COOH + Ph_3P$ + C_2Cl_6	NMP	9.08

Table III. Chemical shifts of P in the ^{31}P NMR spectra of various compounds

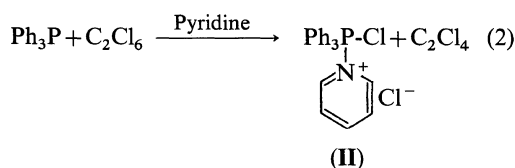| Compound	Solvent	Chemical shift ppm		
Ph_3P	Py		−6.0	
Ph_3PO	Py	25.1		
$Ph_3P + C_2Cl_6$	Py	25.2	−5.9	−16.7
$Ph_3P + C_2Cl_6$	$CHCl_3$	63.5	29.3	−5.3
Ph_3PCl_2[7]	CH_2Cl_2	61.5		

When 4-ABA was added to the previously mixed solution of Ph$_3$P and C$_2$Cl$_6$, the polyamide had a very low solution viscosity, as can be seen from Table I.

The above findings all indicate that the reaction products formed from Ph$_3$P and C$_2$Cl$_6$ in pyridine should be different from the phosphorane formed in acetonitrile or chloroform.

Thus, in order to determine the role of pyridine in direct polycondensation, the ^{1}H NMR spectra of pyridine were measured under various conditions. The results are summarized in Table II.

Table II shows that the chemical shift of α-H of pyridine determined in NMP was 8.76 ppm and that in the presence of either Ph$_3$P or Ph$_3$PO and C$_2$Cl$_4$ was about 8.51 ppm. However, the chemical shift of α-H of pyridine shifted to 8.98 ppm when C$_2$Cl$_6$ was added with Ph$_3$P. Furthermore, the ^{31}P NMR spectra of the reaction solution of Ph$_3$P and C$_2$Cl$_6$ in pyridine showed a peak at -16.7 ppm, as can be seen from Table III.

These results suggest that pyridine participates in the reaction process of Ph$_3$P and C$_2$Cl$_6$, and forms an intermediate as follow:

$$Ph_3P + C_2Cl_6 \xrightarrow{\text{Pyridine}} \underset{\substack{\displaystyle \overset{+}{N} \\ Cl^-}}{Ph_3P\text{-}Cl} + C_2Cl_4 \quad (2)$$

(II)

The peak at -16.7 ppm in the ^{31}P NMR spectrum of the reaction products from Ph$_3$P and C$_2$Cl$_6$ in pyridine can be assigned to complex **II** as shown

above.

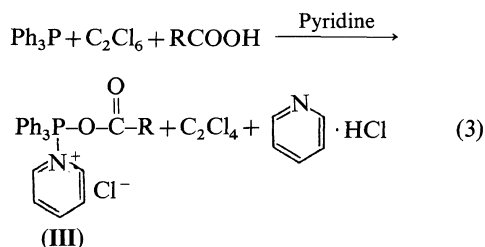*Reaction of Carboxylic Acid with the Phosphine Complex*

The ^{31}P NMR spectrum of the reaction solution of pivalic acid and Ph$_3$P/C$_2$Cl$_6$ in chloroform in the absence of pyridine showed a peak at 39.1 ppm.

However, when pyridine was present along with other reagents at beginning, the peak at 39.1 ppm disappeared and a new peak appeared at 65.2 ppm as shown in Table IV. The peak at 65.2 ppm could be assigned to a complex formed from pivalic acid and the Ph$_3$P/C$_2$Cl$_6$ reagent in the presence of pyridine.

Furthermore, the infrared spectrum of the reaction solution of pivalic acid and Ph$_3$P/C$_2$Cl$_6$ showed an absorption at 1630 cm^{-1}, assignable to the band of P–N=C.[9]

These results suggest that a new intermediate III might possibly be formed from carboxylic acid and the Ph$_3$P/C$_2$Cl$_6$ reagent in the presence of pyridine as follows:

$$Ph_3P + C_2Cl_6 + RCOOH \xrightarrow{\text{Pyridine}}$$

$$\underset{\substack{\displaystyle \overset{+}{N} \\ Cl^-}}{Ph_3P\text{-}O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}R} + C_2Cl_4 + \underset{}{\bigodot}\cdot HCl \quad (3)$$

(III)

However, evidence for the formation of complex **III** could not be detected in the model reaction of acetic acid with Ph$_3$P/C$_2$Cl$_6$ by ^{31}P NMR measure-

Table IV. Chemical shifts of P in the ^{31}P NMR spectra of various model reaction products

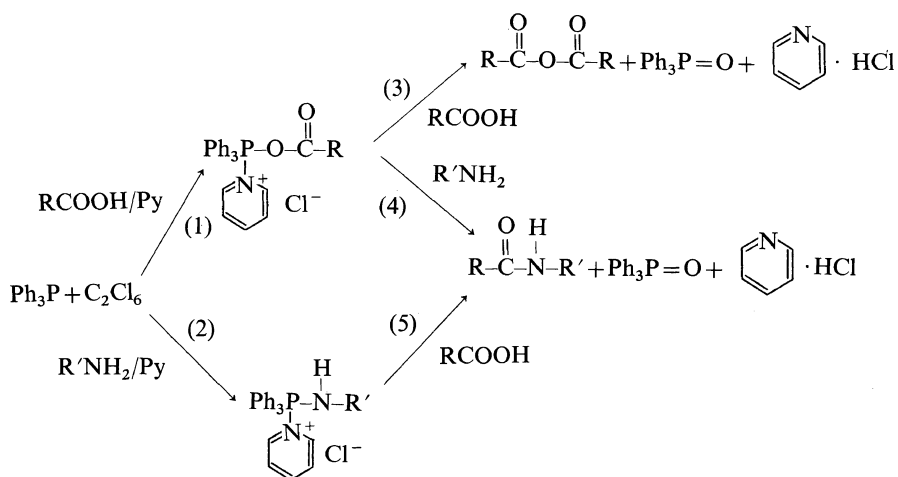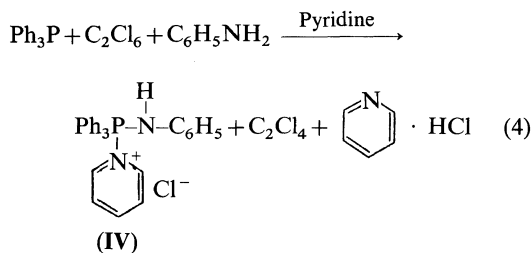| Condition	Solvent	Chemical shift		
		ppm		
Ph$_3$P/CH$_3$COOH/C$_6$H$_5$NH$_2$	Py			-6.0
Ph$_3$P/C$_2$Cl$_6$/CH$_3$COOH	Py		25.2	-5.8
Ph$_3$P/C$_2$Cl$_6$/(CH$_3$)$_3$CCOOH	CHCl$_3$	39.1		-5.4
Ph$_3$P/C$_2$Cl$_6$/(CH$_3$)$_3$CCOOH/Py	CHCl$_3$	65.2	28.8	-5.4
Ph$_3$P/C$_2$Cl$_6$/(CH$_3$)$_3$CCOOH/Py	CH$_3$CN		25.4	-5.6
Ph$_3$P/C$_2$Cl$_6$/C$_6$H$_5$NH$_2$/Py	CH$_3$CN	31.1	25.1	-6.2
Ph$_3$P/C$_2$Cl$_6$/(CH$_3$)$_3$CCOOH/C$_6$H$_5$NH$_2$/Py	CH$_3$CN	31.4	25.5	-6.2
Ph$_3$P/C$_2$Cl$_6$/CH$_3$COOH/C$_6$H$_5$NH$_2$	Py	31.9	26.1	-5.6
Ph$_3$P/C$_2$Cl$_6$/CH$_3$COOH/C$_6$H$_5$NH$_2$/Py	NMP	31.4	25.5	-6.2

Table V. Effects of amine addition time
on the resulting polymer composition

Amine addition time	Component[a]	
	Anhydride	Amide
s		
	%	%
0	100	0
15	6.3	93.7
60	31.3	68.7
90	39.6	60.4

[a] The percentage of each component was estimated by
the infrared analysis.

ment. Probably, this intermediate is much more
reactive in the presence of pyridine and is converted
immediately into Ph$_3$PO and an acid anhydride.
Evidence for the formation of acid anhydride was
found through infrared spectroscopic analysis, as
shown in Table V.

Furthermore, the reagent Ph$_3$P/C$_2$Cl$_6$ reacted
with amine to form a phosphonium salt:

$$Ph_3P + C_2Cl_6 + C_6H_5NH_2 \xrightarrow{\text{Pyridine}}$$

$$\text{Ph}_3\overset{H}{\underset{\underset{\text{Cl}^-}{N^+}}{\overset{|}{P}-N-C_6H_5}} + C_2Cl_4 + \underset{}{\text{pyridine}} \cdot \text{HCl} \quad (4)$$

(IV)

The peak at 31.1 ppm (Table IV) was assignable
to complex **IV**. As can be seen from Table I,
however, the polyamide could not be obtained when
terephthalic acid was added to the previously mixed
solution of *p*-phenylenediamine and the reagent
Ph$_3$P/C$_2$Cl$_6$. This suggests that phosphonium salt
was formed from diamine and the reagent, but the
polycondensation reaction could not take place
because the phosphonium salt **IV** was compara-
tively less reactive with carboxylic acid.

Amide Formation Reaction

Model reactions of Ph$_3$P with C$_2$Cl$_6$, carboxylic
acids, and aniline in various solvents were carried
out both in the presence and absence of pyridine.
Table IV summarizes the chemical shifts of P in the
^{31}P NMR spectra of various model reaction prod-
ucts and shows that carboxylic acid does not react
with the amine in the absence of C$_2$Cl$_6$.

The various reactions mentioned above might
occur competitively during the polycondensation
process. In fact, there are three peaks in the ^{31}P
NMR spectra and the peak at 31.4 ppm can be
assigned to the phosphonium salt **IV**.

Furthermore, the acid anhydride formation
would occur simultaneously with amide formation.

These results lead us to consider the following
reaction paths:

(reaction scheme)

It is evident from Table I that the polyamide can be obtained by the addition of p-phenylenediamine to a reaction mixture of terephthalic acid, Ph_3P, and C_2Cl_6, whereas the polyamide is not obtainable when terephthalic acid is added to a reaction mixture of p-phenylenediamine, Ph_3P, and C_2Cl_6.

Consequently, the reaction path (1)—(4) may be considered the main course for the formation of an amide linkage from carboxylic acid and an amine in the presence of Ph_3P and C_2Cl_6 in pyridine.

Competitive reactions among paths (1) to (5) prevent the formation of a polyamide having a high molecular weight because of the loss in molar valances of functional groups; also an exclusive reaction passing through path (1) followed by path (4) would be required for the formation of a polyamide of high molecular weight.

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