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SHORT COMMUNICATION

Synthesis of Polyamide by Phosphorylation. IV.

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It was reported in previous papers[1-3] that polycondensation of dicarboxylic acids with diamines takes place at room temperature in suspension state by a phosphorylation reaction with triphenyl phosphite and imidazole. Similar polycondensation was found[4] by using di- or triphenyl phosphites and pyridine and aromatic polyamide having a high molecular weight was obtained under mild conditions.

The phosphorylation reaction using phosphorus trichloride or oxychloride and pyridine is well known[5] as a means of obtaining peptide from α-amino acids. Polyamides are usually obtained by melt polycondensation of dicarboxylic acids and diamines at elevated temperatures. However, it is very difficult to obtain polyamides having high melting points, such as aromatic polyamides, by means of the melt polycondensation method because of the thermal decomposition of the resulting polyamides at high temperatures. Therefore, this phosphorylation reaction was applied to initiate the polycondensation of dicarboxylic acids with diamines so as to yield polyamide under mild conditions.

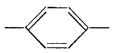
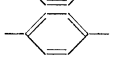
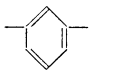
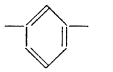
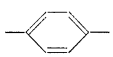
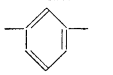
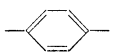
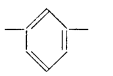
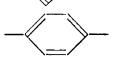
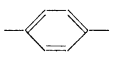
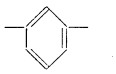
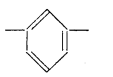
$$NH_2\text{—}R\text{—}NH_2 + HOOC\text{—}R'\text{—}COOH \xrightarrow[\text{Pyridine}]{PCl_3 \text{ or } POCl_3} \text{-[-NH—R—NHCO—R'—CO-]-} + HCl + O{=}POH\ (Cl_2POH)$$

A portion of 0.005 mol of PCl_3 or 0.01 mol of $POCl_3$ was dissolved in 20 m*l* of pyridine or organic solvents containing an equimolar amount of pyridine. To this solution was added 0.005 mol of nylon salt (salt of dicarboxylic acid and diamine) and the suspension was stirred at room temperature. The suspension developed a red-brown color and changed gradually to a gel-like state. After a given period, the gel was poured into excess acetone and the precipitated polymers were filtered; this was followed by repeated washing with water and drying. Results of the polycondensation are summarized in Table I, where it is clearly seen that pyridine was necessary to initiate the polycondensation with PCl_3.

Yields of polyamide from aliphatic dicarboxylic acids and hexamethylenediamine (HMD) were much inferior to those from aromatic diamines, although the yield of polyamide from sebacic acid and HMD was high. The inherent viscosities of the polyamides from aromatic diamines were higher than those from HMD. Yields of polyamide from aromatic dicarboxylic acids and aromatic diamines were almost quantitative and the inherent viscosities of those aromatic polyamides were relatively high. Particularly, the combination of isophthalic acid and *p*-phenylenediamine yielded a high molecular weight polyamide. The superior polymerizability of the aromatic diamines resulting from the phosphorylation with PCl_3 coincided with the results using di- or triphenyl phosphites and pyridine reported by Yamazaki.[4] However, the phosphite—pyridine system was not able to yield a high molecular weight polyamide from aromatic dicarboxylic acids. Therefore, the PCl_3—pyridine system was found to be better for obtaining fully aromatic polyamides.

Phosphorus oxychloride initiated the polycondensation of nylon salts. However, polyamides obtained from HMD did not dissolve

Table I. Polycondensation of various nylon salts by PCl_3 or $POCl_3$ and pyridine[a]

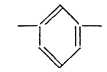
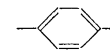
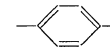
Initiator	Nylon salt		Solvent	Acid acceptor	Time, hr	Polymer	
	HOOC—R—COOH	NH_2—R—NH_2				Yield, %	η_{inh}[b]
	—$(CH_2)_4$—	—$(CH_2)_2$—	DMF[c]	None	21	0	—
	〃	〃	HMPA[d]	None	21	0	—
	〃		DMF	Py[e]	23	10	—
	〃		HMPA	Py	23	100	0.18
	〃		DMF	Py	23	0	—
	〃		HMPA	Py	23	100	0.16
	—$(CH_2)_2$—	—$(CH_2)_6$—	Py	Py	17	34	0.05
PCl_3	—$(CH_2)_4$	〃	Py	Py	23	11	—
	—$(CH_2)_8$—	〃	Py	Py	20	99	0.08
	—$(CH_2)_4$—		Py	Py	22	100	0.18
	〃		Py	Py	22	71	0.12
			Py	Py	64	97	0.42
			Py	Py	64	97	0.20
			Py	Py	64	100	0.13
			Py	Py	64	94	0.12
	—$(CH_2)_4$—	—$(CH_2)_6$—	Py	Py	41	60	Insoluble
	—$(CH_2)_8$—	〃	Py	Py	41	127	Insoluble
$POCl_3$	—$(CH_2)_4$—		Py	Py	26	44	—
	〃		Py	Py	26	10	—

[a] Nylon salt 0.25 mol/*l*, room temperature.
[b] Measured in H_2SO_4 at 30°C.
[c] Dimethylformamide.
[d] Hexamethylphosphortriamide.
[e] Pyridine.

in *m*-cresol or surfuric acid and a cross-linking reaction occured. The yield of polyamides from aromatic diamines by the initiation with $POCl_3$ were also poor. Therefore, $POCl_3$ was much inferior to PCl_3 in terms of the initiation activity for the polycondensation of nylon salt.

Since the phosphorylation reaction of both amine and carboxylic and occurs simultaneously as a competitive reaction,[3] the low inherent viscosities of the resulting polyamides might be ascribed to the molar balance loss of amino and carboxyl groups during the polycondensation. Therefore, the reaction of diamine with PCl_3 was carried out at first in pyridine and then the addition of dicarboxylic acid to the solution was made. Results are summarized in Table II,

Table II. Polycondensation of diamine-phosphorus trichloride complex with dicarboxylic acid[a]

HOOC—R—COOH	H_2N—R—NH_2	Time, hr	Polymer	
			Yield, %	η_{inh}[b]
—$(CH_2)_4$—	—$(CH_2)_6$—	16+24	62	0.10
—$(CH_2)_8$—	—$(CH_2)_6$—	16+24	74	0.13
—$(CH_2)_4$—		16+24	100	0.32
—$(CH_2)_4$—		16+24	100	0.36
—$(CH_2)_4$—		17+47	100	0.26

[a] Monomer concn. 0.25 mol/*l* in pyridine, room temperature.
[b] Measured in H_2SO_4 at 30°C.

which indicate that the inherent viscosities of the resulting polyamides increased as expected.

The reaction mechanism of the polycondensation initiated by PCl_3 and pyridine might be the same phosphorylation reaction as the polycondensation with triphenyl phosphite and pyridine. Since the phosphite—pyridine system yielded polyurea from carbon dioxide and diamine, as reported by Yamazaki, it was expected that the PCl_3—pyridine system might yield polyurea from carbon dioxide and diamine. A portion of 0.005 mol of *m*- or *p*-phenylenediamine was dissolved in 20 m*l* of pyridine containing 0.005 mol of PCl_3 and the solution was kept at 60°C. Carbon dioxide gas was bubbled into the solution for 6 hr. After the solution was poured into acetone, polyurea was obtained in 26—29-% yields. The inherent viscosities of the polyurea from *m*- or *p*-phenylene—diamine were 0.11—0.15.

Further detailed results of the polyamide or polyurea syntheses by the PCl_3—pyridine system will be reported in a later paper.

REFERENCES

1. N. Ogata and H. Tanaka, *Polymer J.*, **2**, 672 (1971).
2. N. Ogata and H. Tanaka, *ibid.*, **3**, 365 (1972).
3. N. Ogata and H. Tanaka, *ibid.*, **6**, 461 (1974).
4. N. Yamazaki and F. Higashi, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 185 (1974).
5. W. Grassmann and E. Wünsch, *Chem. Ber.*, **91**, 449 (1958).

Errata

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Vol.	No.	Page	Line	Printed	Should read
7	2	202	10th (left column) from the bottom	···spheres of	···spheres or
〃	〃	203 (Table I.)	No. 48	2/1 b	2/1 b[b]
〃	〃	205	12th (left column) from the bottom	"steric factor"[15]	"steric factor"
〃	〃	206	Ref. 18	L. L. Slonimskii	G. L. Slonimskii