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High-Energy Phosphonium Compounds and Their Application to Polymer Synthesis

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High-Energy Phosponium Compounds and Their Application to Polymer Synthesis

NOBORU YAMAZAKI and FUKUJI HIGASHI

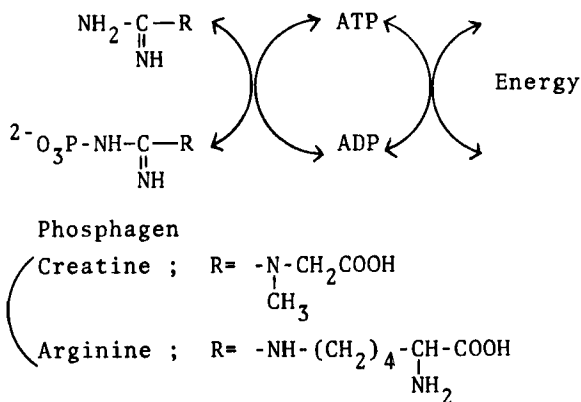
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ABSTRACT

High-energy phosponium compounds, the N-phosponium salts of pyridines, were prepared by the oxidation of phosphorous acid and its esters with mercuric salts or halogens in pyridines, or by a hydrolysis-dehydration reaction of diphenyl and triaryl phosphites or phosphonites. These salts are very reactive to nucleophiles, activating carboxyl, amino, or hydroxyl compounds via the corresponding N-phosponium salts to yield carboxylic amides and esters in high yields on further aminolysis, alcoholysis, and acidolysis. These reactions, especially the hydrolysis-dehydration reactions with phosphites, were successfully extended to the direct polycondensation reaction of dicarboxylic acids with diamines, of free α -amino acids or dipeptides, and of carbon dioxide and disulfide with diamines under mild conditions, yielding linear polymers of high molecular weight (polyamides, polypeptides, polyureas, and polythioureas).

INTRODUCTION

Adenosine triphosphate (ATP), a typical high-energy compound in living cells, plays an important role as an energy source in the production of lipids, proteins, and carbohydrates, and it is consumed and regenerated via a coupling to the phosphagen-ATP system [1]:



Thus energies obtained from reactions such as the oxidative breakdown of glucose are transferred to (adenosine diphosphate) ADP, resulting in ATP, and the energies in ATP, in turn, are reserved in the phosphate bond of phosphagens.

During the course of studying chemical reactions via a process similar to the energy transfer in living cells described above, we have developed a new process like the phosphagen-ATP system which involved the oxidation of phosphorous acid and its esters with mercuric salts or halogens, or dephenoxylation of phosphites, giving rise to the high-energy phosphonium compounds, N-phosphonium salts of pyridines.

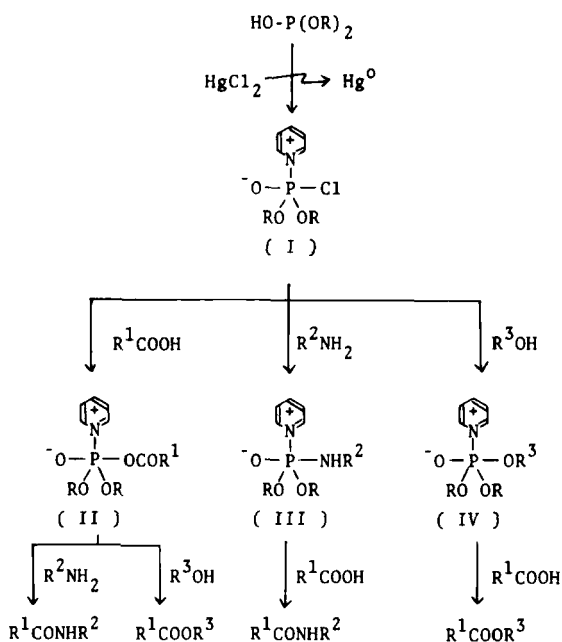
This paper describes studies on the reactions of the N-phosphonium salts of pyridines, and the application of the reactions to polymer synthesis.

RESULTS AND DISCUSSION

Reactions of the N-Phosphonium Salts of Pyridines

The N-phosphonium salts of pyridines given by the oxidation of phosphorous acid and its esters are very reactive to nucleophiles, activating carboxyl, amino, or hydroxyl compounds to yield the corresponding carboxylic amides and esters in high yields on further aminolysis, alcoholysis, and acidolysis [2].

These reactions were studied in terms of steric effect, acidity and basicity of carboxylic acids, amines, and tertiary amines such as pyridine by using phosphorous acid and its mono-, di-, and tri-esters, as proposed in Scheme 1 for the case of the reaction with diesters. These N-phosphonium salts (I-IV) were

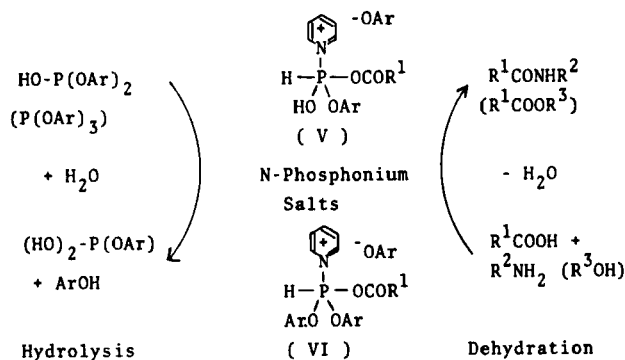


SCHEME 1.

separated and characterized on the bases of the IR spectra, acid-base titration, and their reactions.

These reactions were successfully used for the preparation of peptides and active esters of amino acids, with no detectable amounts of racemization (Table 1) [3].

We also showed that phosphites, especially diphenyl and triaryl phosphites, reacted nonoxidatively with carboxylic acids in the presence of pyridine to give the acyloxy-N-phosphonium salt of pyridine (V and VI in Scheme 2) accompanied by dephenoxylation,



SCHEME 2.

which produced the corresponding amides and esters on aminolysis and alcoholysis. The N-phosphonium salts such as II were presumed from the stoichiometric relationship among phosphites, pyridine, and the carboxyl component [4].

In these reactions, hydrolysis of diphenyl and triaryl phosphites to monoaryl phosphites and phenol was coupled by dehydration between carboxylic acids and amines or alcohols to the corresponding amides and esters. Therefore, the reaction was generalized as a hydrolysis-dehydration reaction (Scheme 2).

The proposed concept of the hydrolysis-dehydration reaction using phosphites was shown to be applicable also to reactions with other phosphorous compounds, such as phosphonites, phosphinites, and phosphonates [5]. The aryl esters of these phosphorus compounds were effective for producing amides and esters, whereas alkyl esters were ineffective (Eqs. 1-3).

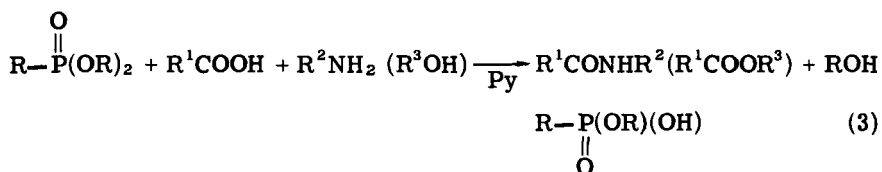
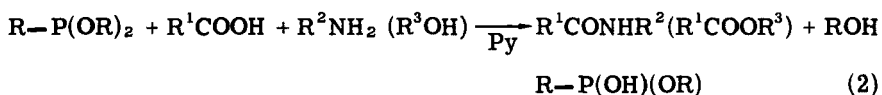
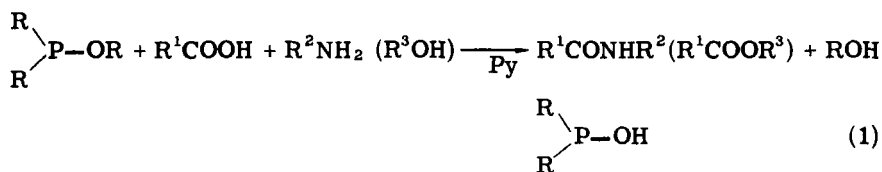


TABLE 1. Peptide Synthesis by Means of Oxidation of Diphenyl Phosphite with Mercuric Chloride in Pyridine^a

Peptide	Yield (%)	Method ^b
Z-Gly-Gly.OEt	84	A
	92	B
	95	C
Z-Phe-Gly.OEt	90	B
Z-Gly-Tyr.OEt	90	B
Z- α -Glu-Gly.OEt	70	B
Z-Glu(NH ₂)-Gly.OEt	79	C
Z-Met-Gly.OEt	93	C

^aThe coupling reaction was carried out at 45°C for 12 hr.

^bMethod A: Activation of carboxyl components.

Method B: Activation of amino components.

Method C: Activation and coupling reaction in the presence of both components.

These reactions with phosphites, phosphinites and phosphonites were employed for the preparation of peptides and active esters of amino acids in good yields (Tables 2 and 3).

TABLE 2. Peptide Synthesis via the Hydrolysis-Dehydration Reaction with Phosphites and Phosphonite in Pyridine^a

Peptide	Yield (%) of peptide		
	HO-P(OPh) ₂	P(OPh) ₃	Et-P(OPh) ₂
Z-Gly-Gly.OEt	91	92	92
Z-Phe-Gly.OEt	90	85	90
Z-Gly-Tyr.OEt	88	96	86
Z-Glu(NH ₂)-Gly.OEt	85	-	78
Z-Met-Gly.OEt	91	95	93

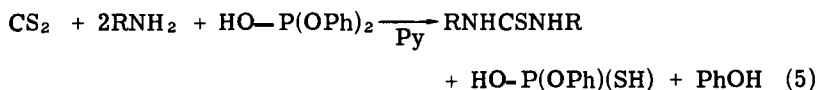
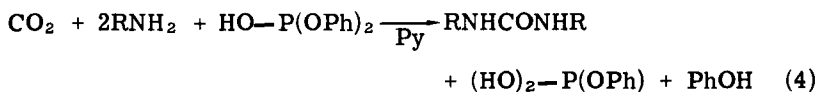
^aThe reaction was carried out at 40°C for 6 hr using diphenyl phosphite (1 equiv), and for 12 hr using triphenyl phosphite (0.5 equiv) and diphenyl ethylphosphonite (1 equiv).

TABLE 3. Preparation of Active Esters via the Hydrolysis-Dehydration Reaction with Phosphites and Phosphonite in Pyridine^a

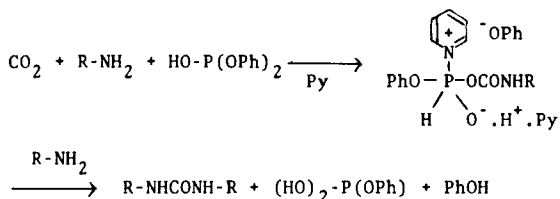
Active ester	Yield (%) of active ester		
	HO-P(OPh) ₂	P(OPh) ₃	Et-P(OPh) ₂
Z-Gly-O-C ₆ H ₄ -NO ₂	77	83	74
Z-Gly-O-C ₆ H ₄ -COOCH ₃	69	70	75
Z-Gly-S-C ₆ H ₄	89	64	74
Z-Phe-O-C ₆ H ₄ -NO ₂	73	73	71
Z-Glu(NH ₂)-O-C ₆ H ₄ -NO ₂	45	48	-

^aThe reaction was carried out at 40°C for 12 hr using diphenyl phosphite (1 equiv), triphenyl phosphite (0.5 equiv), and diphenyl ethylphosphonite (1 equiv).

Considering that the chemical reactivity of carboxylic acids is similar to that of carbonic acid, as is observed in amide and ester formation, we have attempted the substitution of carbon dioxide for carboxylic acids in the coupling reaction with amines by using phosphite in pyridine or imidazole, and found that ureas are, in fact, produced in good yields (Eq. 4) [6]. Similarly, carbon disulfide reacted with amines to yield the thioureas (Eq. 5):

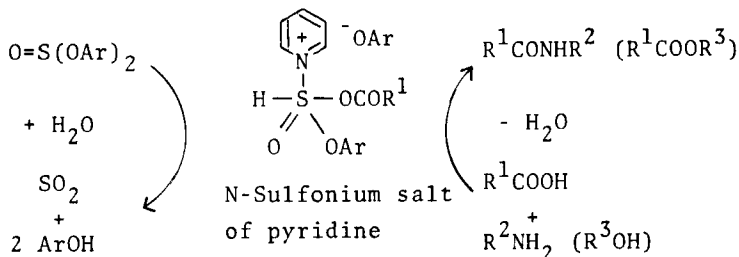


Based on the stoichiometric involvement of phosphites and pyridine in the reaction, the reaction was proposed to proceed via a carbamyl N-phosphonium salt of pyridine (Scheme 3).



SCHEME 3.

In addition, we successfully applied the concept of the hydrolysis-dehydration reaction with phosphorus compounds to the reaction with sulfur compounds such as diaryl sulfites [7]:



The Polycondensation Reactions

The reactions with phosphorus compounds were extended to the direct polycondensation reactions of dicarboxylic acids with diamines, of free α -amino acids or dipeptides, and of carbon dioxide and disulfide with diamines under mild conditions.

Polyamides

Direct polycondensations of aromatic diamines with dicarboxylic acids have generally been described as a poor route to high molecular linear polyamides. Recently, high molecular weight polyamides have been obtained with limited success by a melt polymerization of 4,4'-diaminodiphenylmethane with aliphatic dicarboxylic acids [8].

Surprisingly, by using the reactions via V and VI in Scheme 2, polyamides of high molecular weight were obtained directly from dicarboxylic acids and diamines in NMP solutions containing pyridine (Table 4) [9]. A combination of aromatic diamines with aliphatic dicarboxylic acids gave polymers of higher viscosity than an aliphatic diamine. On the other hand, 4,4'-diaminodiphenylsulfone yielded low viscous polymer, probably because of the lower basicity. Aromatic dicarboxylic acids, even with aromatic diamines and aromatic amino acids, did not form high viscous polymers. Isophthalic acid gave higher viscous polymer than terephthalic acid. This result led us to consider that higher solubility of polymer favors the polycondensation.

The difficulty of obtaining aromatic polyamides as shown above was overcome to a large extent by carrying out the polycondensation reaction in the presence of metal salts capable of improving the dissolution power of the polyamides [10].

As Table 5 shows, the addition of LiCl or CaCl₂ to the reaction mixture favored the polycondensation of *p*-aminobenzoic acid (*p*-ABA), giving poly-*p*-benzamide of high molecular weight in quantitative yield.

There are observed maxima of molecular weight of polymer at a concentration of about 4 wt% of LiCl or 8 wt% of CaCl₂ in the reaction mixture. Further addition retarded the reaction, and almost no polymer was obtained in the presence of more than 12 wt% LiCl or 20 wt% CaCl₂, where the reaction mixtures were deeply colored.

Considering that the presence of 2 wt% LiCl and 5 wt% CaCl₂, corresponding to an equivalent of phosphite and *p*-ABA, was very effective, the salts might participate in the reaction itself.

TABLE 4. Direct Synthesis of Polyamides by Using Phosphites and Phosphonite in NMP-Py Solution^a

Dicarboxylic acid	Diamine	HO-P(OPh) ₂		P(OPh) ₃		Et-P(OPh) ₂	
		Yield (%)	η_{inh}	Yield (%)	η_{inh}	Yield (%)	η_{inh}
HOOC-(CH ₂) ₄ -COOH	$\left\{ \begin{array}{l} \text{NH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \\ \text{NH}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{NH}_2 \end{array} \right.$	94	1.22	100	0.63	97	0.97
		100	0.95	100	0.74	97	1.65
	$\left\{ \begin{array}{l} \text{NH}_2-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-\text{NH}_2 \\ \text{NH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{NH}_2 \end{array} \right.$	86	0.28	78	0.18	62	0.22
		73	0.22	85	0.31	85	0.26
HOOC-(CH ₂) ₈ -COOH	$\left\{ \begin{array}{l} \text{NH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \\ \text{NH}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{NH}_2 \end{array} \right.$	97	1.45	100	1.07	96	1.12
		-	-	100	1.84	98	1.57
HOOC-C ₆ H ₄ -COOH	$\left\{ \begin{array}{l} \text{NH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \\ \text{NH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \end{array} \right.$	100	0.23	100	0.34	98	0.30
		100	0.12	-	-	-	-
HOOC-C ₆ H ₃ (COOH)-COOH	$\left\{ \begin{array}{l} \text{NH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \\ \text{NH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \end{array} \right.$	-	-	100	0.54	98	0.43
		84	0.26	-	-	-	-
	NH ₂ -C ₆ H ₄ -COOH	98	0.16	100	0.22	97	0.21

^a[Monomer] = 0.25 mole/liter; [HO-P(OPh)₂] = [P(OPh)₃] = [C₂H₅-P(OPh)₂] = 1.0 mole/mole of monomer; solvent = NMP/Py = 40/10(ml/ml); temperature = 100°C; time = 6 hr.

TABLE 5. Polycondensation Reaction of p-ABA in the Presence of Several Metal Salts^a

Metal salt	Polymer	
	Yield (%)	η_{inh}^b
LiCl	100	1.27
Li(AcAc)	0	-
CaCl ₂	98	1.07
CaCl ₂ ·2H ₂ O	71	0.04
KSCN	46	0.12
MgCl ₂	100	0.31
ZnCl ₂	97	0.20
None	100	0.22

^a[Monomer] = 0.4 mole/liter; [P(OC₆H₅)₃] = 1.0 mole/mole of monomer; [Metal salt] = 4 wt% in the solvent; solvent = NMP/Py = 40/10(ml/ml); temperature = 100°C; time = 6 hr.

^bMeasured in H₂SO₄ at 30°C.

Therefore, metal salts may contribute to the improvement of the dissolution power of the resulting polyamide and also to the depression of the side reaction owing to the formation of complexes between phenol derived from phosphite with metal salts, such as those of CaCl₂ with alcohols and phenols.

It was expected that the polycondensation reaction at high temperatures might favor the solubility of the resulting polymer, but be undesirable for the stability of the complexes of phenol with metal salts. As a consequence, an optimum of the reaction temperature might be observed in the polycondensation reaction.

An optimum of viscosity ($\eta_{inh} = 1.71$) was observed at a reaction temperature at around 80°C in the polycondensation of p-ABA. Above this temperature the viscosity decreased gradually with the temperature. Only low-viscosity polymer was obtained at a temperature of 60°C.

Solvents and the amount of pyridine in the NMP-pyridine mixed solvent affected the polycondensation of p-ABA in the presence of 4 wt% LiCl. Of the solvents tested, NMP was most effective and DMAC, in which the reaction mixture became light yellow, gave moderate results, whereas DMF largely retarded the reaction, probably because of a side reaction of DMF with LiCl at high temperatures, as indicated by deep colorization of the reaction mixture.

The viscosity of polymer varied with the amount of pyridine in the NMP-pyridine mixed solvent, showing the highest value in the solvent of relatively high pyridine content (40%) in spite of unfavorable results in pyridine alone. This result suggests that the solvent of this composition has a strong solvating power, as a combination of NMP and HMPA containing LiCl, each of which could not dissolve poly-p-benzamide, was a very powerful solvent.















Several wholly aromatic polyamides were prepared by using triphenyl phosphite in NMP-pyridine solution containing 4 wt% LiCl (Table 6). The combination of isophthalic acid with diamines gave a polymer of high viscosity, whereas terephthalic acid with pK_a values similar to those of isophthalic acid did not give high-viscosity polymers. The unfavorable results from terephthalic acid may be due to the lower solubility of polymers with a rigid structure. m-ABA of lower acidity than p-ABA did not yield a polymer with a high viscosity, although higher solubility was expected from polymer from m-ABA with a flexible structure.

Polypeptides

Though the preparation of polypeptides directly from free amino acids is very difficult because of their tendency to give cyclic dimers (diketopiperazines) by ordinary methods [11], we have succeeded in obtaining linear polypeptides with relatively high molecular weight by the direct polycondensation of α -amino acids through the use of diphenyl and triaryl phosphites in pyridine. We have also obtained polypeptides with ordered sequences by the indirect polycondensation of activated derivatives of peptides, such as their active esters by ordinary methods, directly from unactivated dipeptides (Table 7) [12].

The polycondensation of amino acids was affected significantly by the solvent. Interestingly, nonpolar solvents (such as n-hexane) and haloalkanes (such as chloroform) gave polymers of relatively higher viscosity than highly polar aprotic solvents (such as DMF) in spite of heterogeneity of the system in these nonpolar solvents (Table 8).

TABLE 6. Preparation of Aromatic Polyamides by Means of Triphenyl Phosphite in NMP-Pyridine Solution Containing 4 wt% LiCl^a

Dicarboxylic acid ^b	Diamine	Polymer η_{inh}^c
HOOC-  -COOH (3.72, 4.40)	NH ₂ -  -NH ₂	1.14
	NH ₂ -  -O-  -NH ₂	1.34
	NH ₂ -  -CH ₂ -  -NH ₂	0.93
HOOC-  -COOH (3.54, 4.46)	NH ₂ -  -NH ₂	0.19 (0.21) ^d
	NH ₂ -  -O-  -NH ₂	0.32
	NH ₂ -  -CH ₂ -  -NH ₂	0.33
	NH ₂ -  -COOH (3.07, 4.70)	1.32
	NH ₂ -  -COOH (2.28, 4.89)	0.43

^a[Monomer] = 0.6 mole/liter; [P(OC₆H₅)₃] = 1.0 mole/mole of monomer; solvent = NMP/Py = 20/15(ml/ml); temperature = 100°C; time = 3 hr.

^bValues in parentheses are pK₁ and pK₂.

^cPolymers were obtained in quantitative yields, and the viscosity was measured in H₂SO₄ at 30°C.

^dCaCl₂ (8 wt%) was used in lieu of LiCl.

Polyureas and Polythioureas

The results of the preparation of polyureas under mild conditions (a pressure of less than 40 atm of carbon dioxide and a temperature around 40°C) and of polythioureas (using diphenyl phosphite in pyridine) are given in Table 9 [13]. Although the preparation of

TABLE 7. Direct Polycondensation of Amino Acids and Dipeptides by Using Phosphites and Phosphonite in Pyridine^a

Amino acid and peptide	HO-P(OPh) ₂		P(OPh) ₃		Et-P(OPh) ₂	
	Yield (%)	η_{inh}	Yield (%)	η_{inh}	Yield (%)	η_{inh}
Glycine	77	0.13	70	0.15	70	0.17
L-Alanine	45	0.12	100	0.14	73	0.18
L-Leucine	75	0.12	68	0.17	60	0.25
L-Phenylalanine	72	0.09	90	0.08	46	0.11
Glycylglycine	76	0.12	100	0.19	-	-
Glycyl-L-leucine	29	0.14	-	-	-	-

^a[Monomer] = 1.25 mole/liter; [HO-P(OC₆H₅)₂] = 1.5 mole/mole of monomer; [P(OC₆H₅)₃] = [C₂H₅-P(OC₆H₅)₂] = 1.0 mole/mole of monomer; temperature = 40°C; time = 18 hr.

TABLE 8. Polycondensation of L-Leucine in Various Solvents^a

Solvent	Yield (%)	η_{inh}^b
n-Hexane	79	0.24
Dichloroethane	87	0.17
Chloroform	82	0.17
Benzene	78	0.16
Acetonitrile	82	0.16
Dioxane	87	0.13
Dimethoxyethane	90	0.13
Diisobutyl ketone	83	0.11
DMF	70	0.11
DMAc	70	0.11
NMP	65	0.10




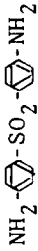

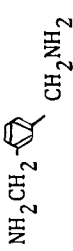
^a[L-Leu] = 1.25 mole/liter; [Py] = 2.0 mole/mole of the phosphite; [HO—P(OC₆H₅)₂] = 1.5 mole/mole of monomer; temperature = 40°C; time = 18 hr.

^bMeasured in dichloroacetic acid at 30°C.

polyureas from carbon dioxide under drastic conditions (high temperatures and high pressures) or from carbon oxysulfide has been reported, neither preparative methods are operative under moderate conditions, nor have the methods for the synthesis of polythiureas from carbon disulfide been described.

As Table 9 shows, aromatic diamines, from which polymers with good solubility in pyridine were formed, gave polymers of higher molecular weight, whereas polymers from 4,4'-diaminodiphenylsulfone and p-phenylenediamine were insoluble even in HMPA and showed low viscosity in sulfuric acid. On the other hand, an aliphatic diamine with high basicity afforded a polymer of low

TABLE 9. Direct Polycondensation of Carbon Dioxide and Disulfide with Diamines by Using Diphenyl Phosphite in Pyridine^a

Diamine	Polyurea					
	Ordinary pressure			20 atm		
	Yield (%)	η_{inh}^b	η_{inh}^d	Yield (%)	η_{inh}^b	η_{inh}^d
	100	0.32	2.24	100	2.24	0.18
	98	0.22	0.51	100	0.51	0.25
	95	0.44	1.87	100	1.87	0.15
	13	0.09 ^c	0.14 ^c	86	0.14 ^c	0.07
	100	0.08 ^c	0.09 ^c	100	0.09 ^c	0.12 ^c
	33	0.08	0.13	46	0.13	-

^a[Monomer] = 0.26 mole/liter; [HO-P(OC₆H₅)₂] = 2.0 mole/mole of monomer; temperature = 40°C; time = 4 hr with CO₂ and 6 hr with CS₂.

^bMeasured in HMPA at 30°C.

^cMeasured in H₂SO₄ at 30°C.

^dMeasured in DMSO at 30°C.

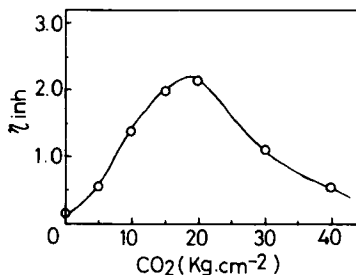


FIG. 1. Effect of the pressure of carbon dioxide upon the viscosity of polyurea from 4,4'-diaminodiphenylmethane at 40°C for 4 hr.

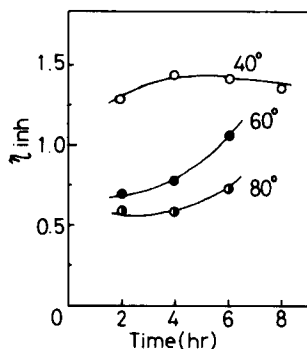


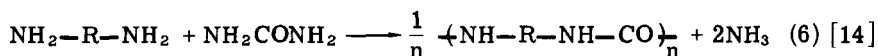
FIG. 2. Effect of the reaction temperature and time upon the viscosity of polyurea from carbon dioxide (10 atm) and 4,4'-diaminodiphenylmethane.

viscosity in low yield because of retardation by the formation of pyridine-insoluble and unreactive ammonium carbamate. These were also the results in the case of polythioureas.

The initial pressure of carbon dioxide and the reaction temperature affected the molecular weight of the resulting polyurea, a viscosity maxima being given by the reaction at around 40°C under a pressure of 20 atm of carbon dioxide. Above this pressure, the viscosity decreased with the pressure, dropping at 40 atm to one-fifth of that at 20 atm (see Figs. 1 and 2).

The unfavorable effects of both high temperature and high pressure upon the molecular weight may be caused by a depolymerization reaction or by an intermolecular or intramolecular exchange reaction

between polymers, as observed in the Eqs. (6) and (7). These side reactions may be promoted by higher reaction temperatures and higher pressures of carbon dioxide, and also in the presence of carbon dioxide and/or diphenyl phosphite.



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