Synthesis of Polyamides by Direct Polycondensation with Diphenyl 2,3-Dihydro-2-oxo-3-benzothiazolyl Phosphate as a New Activating Agent

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ABSTRACT: A new activating agent for amide condensations, diphenyl 2,3-dihydro-2-oxo-3-benzothiazolyl phosphate, was prepared by the reaction of 2(3*H*)-benzothiazolone with diphenyl phosphorochloridate in the presence of triethylamine in acetonitrile at room temperature. The new activating agent was found to be useful for the preparation of amides from carboxylic acids and amines. The direct polycondensation of dicarboxylic acids with aromatic diamines using the activating agent in the presence of triethylamine proceeded at room temperature to produce polyamides with inherent viscosities up to 1.1 dl g⁻¹. Furthermore, the activating agent was used for the synthesis of polyamides from bis(oxo carboxylic acids) or 2,6-pyridinedicarboxylic acid and 4,4'-oxydianiline.

KEY WORDS Polyamide / Direct Polycondensation / Activating Agent / Dicarboxylic Acid / Diamine /

A direct polycondensation has attracted a considerable attention due to its simplicity and efficiency of this procedure as a synthetic method.

As a part of our program directed toward the synthesis of new activating agents for the preparation of polyamides from dicarboxylic acids and diamines, we have recently demonstrated that 3,3'-(phenylphosphinylidene)-

bis[2(3*H*)-benzothiazolone] (**1**) is very useful as an activating agent for the formation of high molecular weight polyamides.¹ However, a disadvantage is that only one of the two benzothiazolone group in the activating agent **1** can be used as a leaving group, so that the other benzothiazolone group is wasted (eq 1).

To circumvent this problem, we decided to undertake the synthesis of an alternative activating agent containing one benzothiazolone ring.

Thus, we herein describe the successful synthesis of polyamides from dicarboxylic acids and aromatic diamines by the direct polycondensation using the new activating agent,

diphenyl 2,3-dihydro-2-oxo-3-benzothiazolyl phosphate (2).

EXPERIMENTAL

Materials

Diphenyl 2,3-Dihydro-2-oxo-3-benzothiazolyl Phosphate (2). 2(3*H*)-Benzothiazolone (3) was synthesized by the same procedure used in a previous paper.²

To a solution of 2(3*H*)-benzothiazolone (24.2 g, 0.16 mol) and triethylene (TEA) (22.4 ml, 0.16 mol) in acetonitrile (30 ml) was added dropwise with stirring a solution of diphenyl phosphorochloridate (33.0 ml, 0.16 mol) in acetonitrile (10 ml). The addition was complete in 1 h, and stirring was continued at room temperature for 20 h. The solvent was removed *in vacuo* to give a white paste. Then, water (500 ml) was added to the residue to remove TEA-hydrochloride. The precipitate was collected by filtration and dried *in vacuo*. Recrystallization from *n*-hexane gave white needles. The yield was 50 g (82%). mp 90–91°C. IR (KBr) ν 1670, 1710 (C=O), 1170, 1190 (P=O, P–O–C), 960 cm⁻¹ (P–O–C). MS (*m/e*) 383.4 (M⁺). *Anal.* Calcd for C₁₉H₁₄NO₄PS: C, 59.53%; H, 3.68%; N, 3.65%. Found: C, 59.7%; H, 3.7%; N, 3.8%.

Diamines. 4,4'-Oxydianiline (ODA) (supplied by Mitsui Toatsu Chemical Industries Ltd.) and 4,4'-methylenedianiline (MDA) (supplied by Mitsubishi Chemical Industries Ltd.) were purified by recrystallization from tetrahydrofuran and cyclohexane, respectively.

Dicarboxylic Acids. Isophthalic acid, adipic acid, and sebacic acid were purified by recrystallization. 4,4'-Oxybis(benzoic acid) and 4,4'-(*p*-phenylenedioxy)dibenzoic acid were prepared through oxidation of the corresponding dimethyl compounds with potassium permanganate in pyridine–water. These dicarboxylic acids were purified by recrystallization from acetic acid and dioxane, respectively.^{3,4} *p,p'*-Oxybis(3-benzoyl propionic acid), and 7,16-dioxodocosanedioic acid were prepared

by literature procedures.^{5,6}

Solvents and Reagents. *N*-Methyl-2-pyrrolidone (NMP) (supplied by Mitsubishi Chemical Industries Ltd.), and hexamethylphosphoramide (HMPA) were purified by vacuum distillation and stored over 4Å molecular sieves. The other reagents and solvents were obtained commercially and used as received.

Model Reaction

Typical examples of the model reaction are as follows.

Benzanilide (5a). Activating agent 2 (0.422 g, 1.1 mmol) was added to a stirred solution of benzoic acid (0.122 g, 1.0 mmol), aniline (0.09 ml, 1.0 mmol), and TEA (0.14 ml, 1.0 mmol) in NMP (2 ml) at room temperature. The solution was stirred for 3 h, and poured into 1*N*-NaOH aqueous solution. The precipitate was filtered, washed with water, and dried. The yield was 0.181 g (92%). mp 162°C (lit.⁷ 162°C).

Isophthalamide (6a). To a solution of isophthalic acid (0.166 g, 1.0 mmol), aniline (0.18 ml, 2.0 mmol), and TEA (0.29 ml, 2.0 mmol) in NMP (2 ml), was added the activating agent 2 (0.805 g, 2.1 mmol). The mixture was stirred at room temperature for 3 h. The product was isolated as described above. The yield was 0.297 g (94%). mp 294–295°C (lit.⁸ 295–296°C).

Polycondensation

Typical examples of the polycondensation are as follows.

Polyamide (9a) from isophthalic acid (8a) and ODA. The activating agent 2 (0.843 g, 2.2 mmol) was added to a solution of isophthalic acid (0.166 g, 1.0 mmol), ODA (0.200 g, 1.0 mmol), and TEA (0.29 ml, 2.0 mmol) in NMP (1 ml). The mixture was stirred at room temperature for 5 h. The resulting viscous solution was diluted with NMP (9 ml) and poured into methanol (500 ml). The polymer that precipitated was filtered and refluxed in meth-

anol for 2 h. The fibrous polymer was collected and dried *in vacuo* at 100°C. It weighed 0.330 g (99%). Inherent viscosity of the polymer in concentrated sulfuric acid was 1.1 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30°C IR (film) ν 1660 (C=O), 3240 cm⁻¹ (N-H). *Anal.* Calcd for C₂₀H₁₄N₂O₃: C, 59.53%; H, 3.68%; N, 3.65%. Found: C, 59.7%; H, 3.7%; N, 3.8%.

Polyamide (9f) from *p,p'*-oxybis(3-benzoylpropionic acid) (8f) and ODA. A mixture of the activating agent **2** (0.843 g, 2.2 mmol), dicarboxylic acid **8f** (0.370 g, 1.0 mmol), ODA (0.200 g, 1.0 mmol), TEA (0.29 ml, 2.0 mmol), and lithium chloride (0.085 g, 2.0 mmol) in HMPA (2 ml) was stirred at room temperature for 16 h. The polymer solution was worked up as described above.

The yield was essentially quantitative. The inherent viscosity of the polymer in NMP was 0.77 dl g⁻¹ ($c=0.5$ g dl⁻¹ at 30°C). IR (film) ν 1660 (C=O), 3240 cm⁻¹ (N-H).

RESULTS AND DISCUSSION

Preparation of the Activating Agent (2)

We already reported that 1,3-benzisoxazole-3-yl diphenyl phosphate is useful for the formation of high molecular weight polyamides.⁹ This finding prompted us to develop a new activating agent containing one benzothiazolone ring. The new activating agent **2** was readily prepared by the reaction of 2(3*H*)-benzothiazolone (**3**) and diphenylphosphorochloridate (**4**) in the presence of TEA in acetonitrile at room temperature (eq 2).

Table I. Preparation of amides **5** and diamides **6** using activating agent **2**^a

Carboxylic acid	Amine	Product	Yield/%
Benzoic acid	Aniline	Benzanilide (5a)	92
Benzoic acid	Benzylamine	<i>N</i> -Benzylbenzamide (5b)	70
Cinnamic acid	Aniline	<i>N</i> -Phenylcinnamamide (5c)	94
Cinnamic acid	Benzylamine	<i>N</i> -Benzylcinnamamide (5d)	96
Cinnamic acid	Cyclohexylamine	<i>N</i> -Cyclohexylcinnamamide (5e)	88
<i>o</i> -Nitrobenzoic acid	Aniline	<i>N</i> -Phenyl- <i>o</i> -nitrobenzamide (5f)	76
Isophthalic acid	Aniline	Isophthalanilide (6a)	94
Isophthalic acid	Benzylamine	<i>N,N'</i> -Dibenzylisophthalamide (6b)	98
Adipic acid	Aniline	Adipanilide (6c)	94
Adipic acid	Benzylamine	<i>N,N'</i> -Dibenzyladipamide (6d)	94
Sebacic acid	Benzylamine	<i>N,N'</i> -Dibenzylsebacamide (6e)	96

^a Reaction was carried out with 1 mmol of each reactants in the presence of TEA in NMP (2 ml) for 3 h at room temperature.

Phosphorylation of **3** might be expected to give either the *N*- or *O*-phosphoryl product because of its well-known tautomerism. The above reaction conditions gave preferentially the more thermodynamically stable *N*-phosphoryl

product **2**. The structure of **2** was assigned on the basis of elemental analysis, IR and mass spectroscopy. The IR spectrum showed carbonyl absorptions at 1690 and 1710 cm⁻¹ and P=O bond absorptions at 1170 and

1190 cm^{-1} .*Model Reaction*

In order to determine the optimum conditions for condensations, we first studied the synthesis of benzanilide (**5a**) from benzoic acid and aniline in NMP in the presence of activating agent **2** by the direct procedure. This procedure consists of adding activating agent **2** to a solution of carboxylic acid and amine in NMP that contains a tertiary organic base to form carboxylate anion.

The condensations proceeded rapidly at room temperature to give the corresponding amides (**5**) in good yields. Furthermore, the reaction of dicarboxylic acids in the presence of the

activating agent **2** was carried out to determine if the method gave the desired model compounds in high enough yield to give promise as a polymer-forming reaction (eq 4).

The desired diamides (**6**) were obtained in excellent yields. The results are summarized in Table I.

The most probable reaction pathway similar to that using a phosphorus-based activating agent, is as follows (eq 5):

Activating agent **2** first reacts with carboxylic acids to form mixed carboxylic-phosphoric anhydride **7**, a highly activated acylating agent. Active intermediate **7** is less stable and its enhanced reactivity causes it to react ra-

pidly with amines to give amides.

Polycondensation

To determine the optimum conditions for the polycondensation, we examined the

amount of activating agent **2** on the direct polycondensation of isophthalic acid with 4,4'-oxydianiline (ODA) in the presence of TEA. The results are summarized in Table II. A 10 mol% excess of reagent **2** based on each monomer was appropriate.

On the basis of these results, the direct polycondensation of various dicarboxylic acids with aromatic diamines was carried out with activating agent **2** in the presence of TEA in polar aprotic solvents (eq 6).

Table II. Effects of amount of the activating agent **2** on the polycondensation of isophthalic acid and ODA^a

Molar equivalent of 2 relative to monomer	Polymer $\eta_{inh}/dl\ g^{-1}\ ^b$
2.1	0.48
2.2	1.1
2.3	1.1

^a Polycondensation was carried out with 1 mmol of each monomers using the activating agent in NMR (2 ml) for 5 h at room temperature.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

Table III indicates that polyamides from aromatic dicarboxylic acids were easily produced in quantitative yields with inherent viscosities up to 1.1 dl g^{-1} . The polycondensation of aliphatic dicarboxylic acids with diamines yielded low molecular weight polyamides in which polycondensation proceeded in heterogeneous solution in NMP but in homogeneous solution in HMPA.

To improve the solubility of polymers in NMP, lithium chloride known to increase the solvating power of aprotic solvents, was added to the polycondensation system. However, the addition of LiCl showed little effect either on the solubility or on the molecular weight of polyamides obtained. Then, to improve the solubility of the resulting polymers, polycondensation was conducted at 80°C. The reaction temperature was found to be effective on the molecular weight of the polyamides obtained.

On the other hand, the addition of LiCl on the polycondensation in HMPA showed a favorable effect on the molecular weight of polymer, where polyamides with inherent viscosities up to 1.1 dl g^{-1} were obtained in the presence of two molar equivalents of LiCl relative to each monomer at room temperature. As described above, polycondensation in HMPA proceeded in a homogenous solution in the absence of LiCl. Therefore, the effects of LiCl cannot be explained simply by increasing the solubility of polymer. Another explanation must be considered such as the formation of a

Table III. Polycondensation of dicarboxylic acids with diamines using activating agent **2**^a

Dicarboxylic acid 8	Diamine	Solvent/ml	Time h	Polymer		
				Type	Yield	η_{inh}^b
					%	dl g ⁻¹
8a	ODA	NMP (1.0 ml)	5	9a	99	1.1
8a	MDA	HMPA (1.0 ml)	5	9a'	99	0.55
8a	MDA	HMPA (1.0 ml)	24	9a'	99	0.82
8b	ODA	NMP (1.5 ml)	16	9b	99	0.54
8b	ODA	HMPA (1.5 ml)	9	9b	99	0.86
8c	ODA	NMP (1.5 ml)	13	9c	98	0.89
8c	ODA	HMPA (1.5 ml)	4	9c	99	0.72
8d	ODA	NMP (1.5 ml)	5	9d	98	0.38
8d	ODA	HMPA (1.5 ml)	18	9d	94	0.30
8e	ODA	HMP (1.5 ml)	5	9e	99	0.31
8e	ODA	HMPA (1.5 ml)	24	9e	99	0.41

^a Polycondensation was carried out with 1 mmol of the monomers using the activating agent (2.2 mmol) in a solvent at room temperature.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

Table IV. Polycondensation of aliphatic dicarboxylic acids with ODA using activating agent **2**^a

Dicarboxylic acid 8	Reaction condition				Polymer	
	Solvent	LiCl	Temp	Time	Yield	η_{inh}^b
		mmol	°C	h	%	dl g ⁻¹
8d	NMP	2.0	80	4	99	0.71
8e	NMP	2.0	25	2	91	0.39
8e	NMP	0.1	80	4	99	0.70
8e	NMP	2.0	80	4	99	0.92
8e	HMPA	2.0	25	18	99	1.1

^a Polycondensation was carried out with 1.0 mmol of the monomers using the activating agent (2.2 mmol) in the solvent (1.5 ml).

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

complex between the reactants and LiCl. These results are summarized in Table IV.

Our method was extended to the synthesis of polyamides from bis(oxo carboxylic acids) and pyridinedicarboxylic acid. The direct polycondensation of bis(oxo carboxylic acids), *p,p'*-oxybis(3-benzoylpropionic acid) (**8f**) and 7,16-dioxodocosanedioic acid (**8g**) with ODA was carried out under conditions similar to those described for the preparation of polyamides from aliphatic dicarboxylic acids. Table V

indicates that poly(keto-amide) (**9f**) was easily produced in quantitative yield with an inherent viscosity of 0.77 dl g⁻¹. On the other hand, the synthesis of poly(keto-amide) (**9g**) with a high molecular weight required heating. The formation of a Schiff's base as a side reaction was not observed.

Next, the synthesis of polyamide (**9h**) from **8h** and ODA was carried out in NMP at room temperature. The polycondensation proceeded in homogeneous solution and resulted in an

Table V. Polycondensation of bis(oxo carboxylic acid)s with ODA using activating agent **2**^a

Dicarboxylic acid 8	Reaction condition					Polymer		
	Solvent/ml	LiCl	Temp	Time	Type	Yield	η_{inh}	
		mmol	°C	h		%	dl g ⁻¹	
8f	NMP (2.0)	None	25	24	9f	99	0.38 ^b	
8f	HMPA (2.0)	None	25	24	9f	99	0.41 ^b	
8f	HMPA (1.5)	2.0	25	20	9f	99	0.58 ^b	
8f	HMPA (2.0)	2.0	25	18	9f	99	0.77 ^b	
8g	HMPA (1.5)	None	25	24	9g	93	0.25 ^c	
8g	HMPA (1.5)	2.0	25	10	9g	97	0.38 ^c	
8g	NMP (1.5)	None	25	24	9g	95	0.33 ^c	
8g	NMP (1.5)	None	60	5 min	9g	97	0.53 ^c	
8g	NMP (1.5)	2.0	80	5 min	9g	97	0.73 ^c	

^a Polycondensation was carried out with 1.0 mmol of the monomers using the activating agent (2.2 mmol) in the solvent.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

^c Measured at a concentration of 0.5 g dl⁻¹ in HMPA at 30°C.

Table VI. Polycondensation of pyridine-2,6-dicarboxylic acid **8h** with ODA using activating agent **2**^a

Solvent	Polymer
ml	$\eta_{inh}/\text{dl g}^{-1}$ ^b
0.5	0.40
1.0	0.53
1.5	0.70
2.0	0.52

^a Polycondensation was carried out with 1.0 mmol of the monomers using the activating agent (2.2 mmol) in NMP for 24 h at room temperature.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

inherent viscosity up to 0.70 dl g⁻¹ (Table VI).

The polymers obtained were identified as desired polyamides by comparing their IR spectra with those of authentic polyamides.

In conclusion, our studies indicate that the new activating agent **2** is very useful for the preparation of amides and high molecular weight polyamides under mild conditions. The

reactivity of reagent **2** is nearly equal to that of **1**.

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