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Isao Furukawa[a]; Motohiro Hashiyama[a]; Shizunobu Hashimoto[a]
[a] Department of Applied Chemistry, Doshisha University Karasuma-imadegawa, Kyoto, Japan

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SYNTHESIS OF POLYAMIDES WITH [(1,2,3-BENZOTRIAZINE-4-ONE)-3-YL] DIPHENYL PHOSPHATE AS A NEW ACTIVATING AGENT

ISAO FURUKAWA,* MOTOHIRO HASHIYAMA, and
SHIZUNOBU HASHIMOTO

Department of Applied Chemistry
Doshisha University
Karasuma-imadegawa, Kamigyo-ku, Kyoto 602, Japan

ABSTRACT

A new activating reagent for amide condensation [(1,2,3-benzotriazine-4-one)-3-yl] diphenyl phosphate (BTDP), was prepared in good yield (88%) by the reaction of 3-hydroxy-1,2,3-benzotriazine-4-one with diphenyl phosphorochloridate in the presence of triethylamine (TEA) in tetrahydrofuran. Benzanilide was readily prepared with this reagent from benzoic acid and aniline at room temperature in a model reaction. The polycondensation of several aromatic dicarboxylic acids with aromatic diamines that have electron-donating substituents with BTDP in the presence of TEA in *N*-methyl-2-pyrrolidone proceeded at room temperature to form polyamides with inherent viscosities of 0.33-1.14 dL/g. However, polyamides from aliphatic dicarboxylic acids and diamines that carry electron-withdrawing substituents showed lower inherent viscosities than those from aromatic acids and amines with electron-donating substituents.

INTRODUCTION

Aromatic polyamides, which exhibit excellent mechanical properties as well as thermal and chemical stability, are widely utilized in numerous fields as engineering plastics. These are usually prepared by solution or interfacial reaction between dicarboxylic acid chlorides and aromatic diamines. They can also be prepared by reaction between dicarboxylic acids and aromatic diamines under severe conditions because aromatic amines are less active than aliphatic ones. Thus, a number of activating agents were recently developed for synthesis of polyamides under mild conditions [1-17].

In this paper we report the preparation of [(1,2,3-benzotriazine-4-one)-3-yl] diphenyl phosphate (BTDP) as a new activating agent for synthesis of polyamides from aromatic diamines and dicarboxylic acids under mild conditions.

EXPERIMENTAL

Materials

Amines. Aniline was purified by distillation under reduced pressure. 4,4′-Diaminodiphenyl ether (DDE), 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl sulfone (DDS), and benzidine (BEN) were purified by recrystallization from tetrahydrofuran (THF), benzene, methanol, and water, respectively.

Carboxylic Acids. Benzoic acid, isophthalic acid (IPA), adipic acid (ADP), and sebacic acid (SEA) were purified by recrystallization from water, methanol, ethyl acetate, and acetone, respectively. 2,6-Pyridine-dicarboxylic acid (PDA) was purified by recrystallization from water, and then the water was removed by azeotropic distillation with toluene. The terephthalic acid (TPA) was a special-grade reagent.

Solvents and the Other Reagents. 3-Hydroxy-1,2,3-benzotriazine-4-one was prepared from 2-aminobenzhydroxamic acid by the procedure described by Ahern et al. [18], mp 193-194°C. Diphenyl phosphorochloridate, *N*-methyl-2-pyrrolidone (NMP), hexamethylphosphoric triamide (HMPA), *N*,*N*′-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and the other reagents were purified by distillation under reduced pressure.

Preparation of BTDP

To a mixture of 0.186 g (5.0 mmol) 3-hydroxy-1,2,3-benzotriazine-4-one and 0.506 g (5.0 mmol) TEA in 15 mL dry THF, 1.314 g (5.0 mmol) diphenyl phosphorochloridate was added dropwise with stirring at room temperature, and the mixture was stirred at room temperature for 30 min. After the resulting TEA hydrochloride had been removed by filtration, the solvent was removed *in vacuo* to yield crude BTDP, which was purified by recrystallization from carbon tetrachloride. Yield 1.747 g (88%), mp 97-98°C.

Analysis. Calculated for $C_{19}H_{14}N_3PO_5$: C, 57.58; H, 3.57; N, 10.60%. Found: C, 57.41; H, 3.68; N, 10.42%. IR (KBr): 1710 cm^{-1} (C=O), 1310 cm^{-1} (P=O), 1170, 1160, 1150 cm^{-1} (P–O–C). UV(CH_3CN): 225, 265, 280, 310 nm. NMR ($CDCl_3$): δ (ppm) 8.39 (d, 1H, H-benzotriazine-3-one unit), 8.25 (d, 1H, H-benzotriazine-4-one unit), 8.00 (t, 1H, H-benzotriazine-4-one unit), 7.82 (t, 1H, H-benzotriazine-4-one unit) 7.12-7.50 (m, 10H, C_6H_5–O).

Reaction of Benzoic Acid with Aniline (Model Reaction)

Method A (*One-Step Method*). To a solution of 0.122 g (1.0 mmol) benzoic acid, 0.093 g (1.0 mmol) aniline, and 0.101 g (1.0 mmol) TEA in 2 mL NMP, 0.395 g (1.0 mmol) BTDP was added with stirring. The mixture was stirred at room temperature for 3 h and then poured into 50 mL of 1% aqueous sodium hydrogen carbonate. The resulting precipitate was filtered, washed with water, and dried (mp 161-162.5°C; Ref. 14, 163-164°C).

Method B (*One-Pot Method*). To a solution of 0.122 g (1.0 mmol) benzoic acid and 0.093 g (1.0 mmol) TEA in 2 mL NMP, 0.395 g (1.0 mmol) BTDP was added with stirring. The mixture was stirred for 2 h, then 0.093 g (1.0 mmol) aniline was added dropwise. The mixture was stirred at room temperature for an additional 3 h, then poured into 50 mL of 1% aqueous sodium hydrogen carbonate and worked up by the procedure described above.

Polycondensation

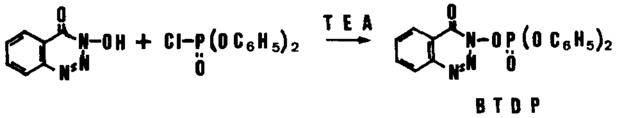
Method A (*One-Step Method*). A solution of 0.948 g (2.4 mmol) BTDP, 0.166 g (1.0 mmol) isophthalic acid, 0.200 g (1.0 mmol) 4,4′-diaminodiphenyl ether, and 0.242 g (2.4 mmol) TEA in 2 mL NMP was stirred at room temperature for 4 days. The reaction mixture was diluted with 8 mL NMP and poured into 200 mL of 1% aqueous sodium hydrogen carbonate. The precipitated polymer was washed with 50 mL hot methanol and dried *in vacuo*. The yield was 0.326 g (99%). The inherent viscosity of the polymer was 1.14 dL/g in concentrated sulfuric acid (95%) (0.5 g/dL at 30 ± 0.1°C).

IR (KBr): 3240 cm^{-1} (–NH–), 1640 cm^{-1} (C=O).

Method B (*One-Pot Method*). A solution of 0.948 g (2.4 mmol) BTDP, 0.166 g (1.0 mmol) isophthalic acid, and 0.242 g (2.4 mmol) TEA in 2 mL NMP was stirred at room temperature for 3 h, and then 0.200 g (1.0 mmol) of 4,4′-diaminodiphenyl ether was added. The mixture was stirred at room temperature for 4 days, poured into 200 mL of 1% aqueous sodium hydrogen carbonate, and worked up described above.

RESULTS AND DISCUSSION

BTDP was prepared from 3-hydroxy-1,2,3-benzotriazine-4-one and diphenyl phosphorochloridate in good yield (88%) and examined as a condensing reagent for the synthesis of polyamides.



As a model reaction for polyamides synthesis, we first studied the synthesis of benzanilide by two methods. Method A consists of simultaneously reacting benzoic acid, aniline, BTDP, and TEA in NMP. Method B involves adding aniline to the reaction mixture of benzoic acid, BTDP, and TEA without isolation of the intermediate.

As shown in Tables 1 and 2, most of these reactions proceed smoothly at room temperature to give benzanilide in excellent yield. The yield is lower when HMPA was used as a solvent, due to the simultaneous reaction of amine with HMPA [19].

Since BTDP has been found to be an excellent activating agent for amide formation, we attempted to prepare a polyamide from isophthalic acid and 4,4′-diaminodiphenyl ether by using a stoichiometric amount of BTDP at room temperature for 4 days. Since the inherent viscosity of the obtained polymer was low, 0.14 dL/g, we investigated the effect of the quantity of BTDP, and the results are shown in Figs. 1 and 2.

The inherent viscosities of the resulting polymers reached a maximum when 20 mol% excess of BTDP was used, probably due to the presence of moisture in the solvent and formation of diphenyl phosphoric anilide from BTDP and the amines.

The rate of polycondensation (see Fig. 3) in the presence of BTDP by Method A was relatively slow, and it required 4 days for completion. In the polycondensation of adipic acid with 4,4′-diaminodiphenyl ether, the result-

TABLE 1. Synthesis of Benzanilide by Method A[a]

Molar ratio (BTDP/reactant)	Solvent (2 mL)	Reaction time, h	Yield, %
1.0	DMF	3.0	97
1.0	DMSO	3.0	97
1.0	HMPA	3.0	82
1.0	NMP	0.5	95
1.0	NMP	1.0	98
1.0	NMP	2.0	98
1.0	NMP	3.0	98
1.1	NMP	3.0	98
1.2	NMP	3.0	98

[a] Reactions carried out with 1.0 mmol each of benzoic acid, aniline, and TEA at room temperature.

TABLE 2. Synthesis of Benzanilide by Method B[a]

Molar ratio (BTDP/reactant)	Solvent (2 mL)	Reaction time,[b] h	Yield, %
1.0	DMF	3.0	94
1.0	DMSO	3.0	95
1.0	HMPA	3.0	90
1.0	NMP	1.0	98
1.0	NMP	2.0	98
1.0	NMP	3.0	98

[a] Reactions carried out with 1.0 mmol each of benzoic acid, aniline, and TEA at room temperature.

[b] After addition of aniline.

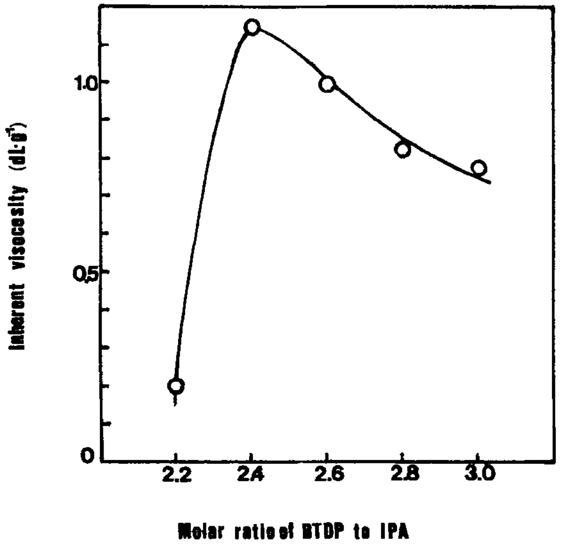


FIG. 1. Effect of the amount of BTDP. Carried out with IPA (1.0 mmol), DDE (1.0 mmol), and TEA (equimolar to BTDP) in NMP (2 mL) at room temperature for 4 days by Method A.

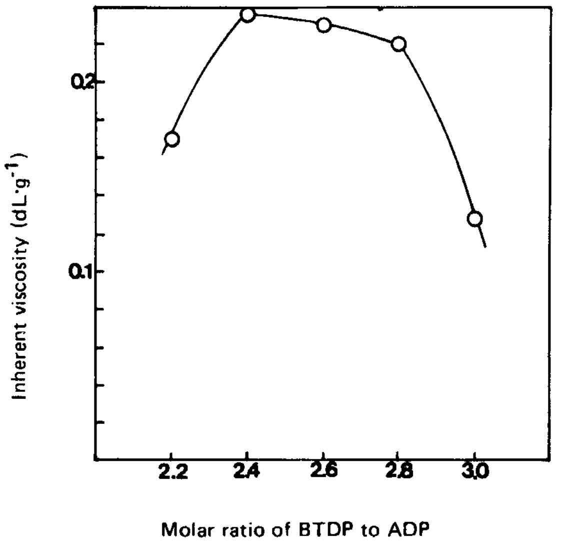


FIG. 2. Effect of the amount of BTDP. Carried out with ADP (1.0 mmol), DDE (1.0 mmol), and TEA (equimolar to BTDP) in NMP (2 mL) at room temperature for 4 days by Method A.

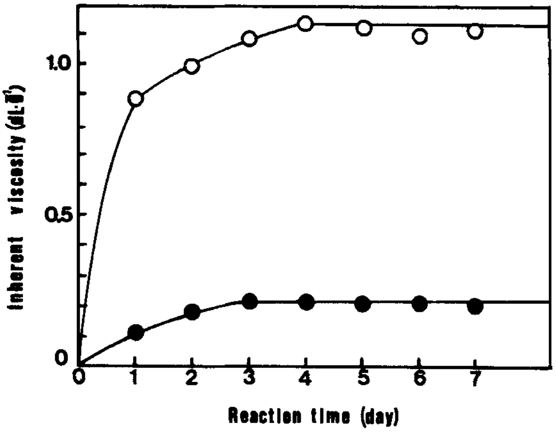


FIG. 3. Effect of the reaction time. Carried out with BTDP (2.4 mmol) and TEA (2.4 mmol) in NMP (2 mL) at room temperature by Method A. Reactant: (○) IPA (1.0 mmol) and DDE (1.0 mmol), (●) ADP (1.0 mmol) and DDE (1.0 mmol).

ing polymer precipitated out, and the polycondensation did not proceed further.

Based on these results, subsequent polycondensations were carried out with 20 mol% excess of the activating agent for 4 days (see Table 3). Higher molecular weight polymers were obtained from diamines with electron-donating substituents, such as ether and methylene groups, while lower molecular weight polymers were obtained from diamines with electron-withdrawing substituents, such as the sulfone group, i.e., the molecular weight of the polymer depends on the nucleophilicity of the amine used.

In the polycondensation of aliphatic dicarboxylic acids with diamines, high molecular weight polymer could not be obtained. The reaction mixture became heterogeneous by separation of the polymer from the solution, and no further polymerization took place. When the reaction mixture was maintained homogeneous by using large amounts of NMP (10 mL), polymer with a higher inherent viscosity, 0.51 dL/g, was obtained.

The polymers obtained by Method B (Table 4) were of lower molecular weight than those by Method A. It is concluded that the lower molecular weight of the polymer from Method B is due to reaction of the amine with BTDP, as mentioned previously.

TABLE 3. Polycondensation of Dicarboxylic Acids and Aromatic Diamines by Method A[a]

Acid	Amine	Solvent, mL	Yield, %	η_{sp}/c, dL/g	Reaction phase[b]
IPA	DDE	2	99	1.14	+
IPA	DDM	2	99	0.83	+
IPA	DDS	2	78	0.05	-
IPA	BEN	2	78	0.30	-
TPA	DDE	2	99	1.01	-
TPA	DDM	2	98	0.80	-
TPA	DDS	2	73	0.11	-
TPA	BEN	2	99	0.22	-
PDA	DDE	2	92	0.68	+
PDA	DDM	2	98	0.73	+
PDA	DDS	2	98	0.35	+
PDA	BEN	2	91	0.18	+
ADP	DDE	2	88	0.21	-
ADP	DDE	10	98	0.51	+
ADP	DDM	2	84	0.06	-
SBA	DDE	2	74	0.12	-
SBA	DDM	2	50	0.10	-

[a] Polycondensations carried out in NMP (2 mL) with reactant (1.0 mmol), BTDP (2.4 mmol), and TEA (2.4 mmol) at room temperature for 4 days.

[b] + Homogeneous; - heterogeneous.

TABLE 4. Polycondensation of Isophthalic Acid and Aromatic Diamines by Method B[a]

Amine	Molar ratio (BTDP/reactant)	η_{sp}/c, dL/g	Reaction phase[b]
DDE	1.2	0.41	+
DDM	1.2	0.41	+
BEN	1.2	0.27	-
DDE	1.0	0.22	+
DDM	1.0	0.16	+
DDS	1.0	0.08	-
BEN	1.0	0.14	-

[a] Polycondensations carried out in NMP (2 mL) with reactant (1.0 mmol) and TEA (equimolar to BTDP) at room temperature for 4 days.

[b] + Homogeneous; - heterogeneous.

The effect of organic bases is shown in Table 5. Among the bases examined, TEA, pyridine, and γ-pycoline, TEA gave polymer with the highest inherent viscosity.

As the reaction temperature was increased, the inherent viscosities of the polymer decreased (see Fig. 4), probably due to acceleration of the reaction between BTDP and the amines.

TABLE 5. Polycondensation of Isophthalic Acid and 4,4′-Diaminodiphenyl Ether in the Presence of Organic Bases by Method A[a]

Organic base	pk_b (25°C)	η_{sp}/c, dL/g
TEA	3.25	1.14
Pyridine	8.63	0.15
γ-Pycoline	8.14	0.14

[a] Polycondensations carried out in NMP (2 mL) with reactant (1.0 mmol), BTDP (2.4 mmol), and organic base (2.4 mmol) at room temperature for 4 days.

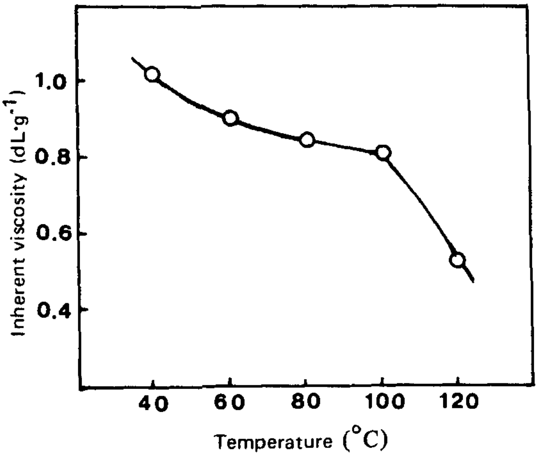
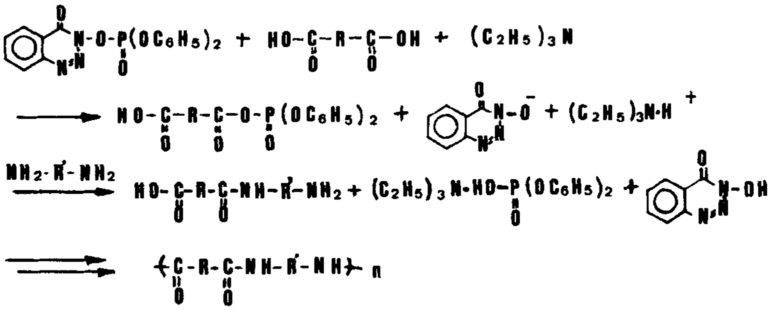


FIG. 4. Effect of the reaction temperature. Carried out with IPA (1.0 mmol), DDE (1.0 mmol), BTDP (2.4 mmol), and TEA (2.4 mmol) in NMP (2 mL) for 8 h by Method A.

It is considered that the polycondensation probably proceeds by the following reaction sequence.



The activating reagent (BTDP) reacts with carboxylic acids to form a carboxylic-phosphoric anhydride, which is a highly activated acylating reagent, and its enhanced reactivity makes it react easily with the amines to give amides.

In conclusion, BTDP was found to be an excellent reagent for amide condensation of carboxylic acids, and amines under mild conditions.

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