# Synthesis of Polyamides by Direct Polycondensation with *N,N'*-Phenylphosphonobis[2(3*H*)-benzothiazolone] as a New Activating Agent

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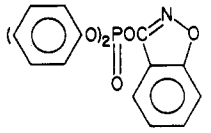
ABSTRACT: A new activating agent for amide condensations, *N,N'*-phenylphosphonobis[2(3*H*)-benzothiazolone] (**4**), was readily prepared by the reaction of 2-benzothiazolone (**2**) with phenylphosphonic dichloride (**3**) in the presence of triethylamine in acetonitrile at room temperature. The new activating agent **4** was found to be very useful for the preparation of amides from carboxylic acids and amines. The direct polycondensation of dicarboxylic acids with aromatic diamines using the activating agent **4** in the presence of triethylamine proceeded rapidly at room temperature to produce polyamides with inherent viscosities up to 1.0 dL·g$^{-1}$. Furthermore, the activating agent **4** was used for the synthesis of polyamides from bis(keto carboxylic acids) or 2,6-pyridinedicarboxylic acid and 4,4'-oxydianiline, which had not been prepared successfully by ordinary methods.

## Introduction

Developing efficient and mild methods for the synthesis of condensation polymers continues to be a significant aspect of polymer chemistry. There has been a considerable research effort to develop new methods. These include the use of the active esters[1] and direct polycondensation by phosphorylation,[2] both of which are replacements for the method employing diacid chlorides.

As part of a program directed toward the synthesis of new activating agents for the preparation of polyamides from dicarboxylic acids and diamines, we have reported on a series of such activating agents. On examining 3-substituted 1,2-benzothiazole 1,1-dioxide,[3] *N,N'*-carbonylbis[1,2-benzisoxazol-3(2*H*)-one],[4] *N,N'*-carbonylbis[2(3*H*)-benzoxazolethione],[5] and 1,3-benzisoxazol-3-yl diphenyl phosphate[6] (**1**), we found that the phosphorus-



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based activating agent **1** is most useful for the formation of high molecular weight polyamides. However, polycondensations using **1** proceeded slowly, and it took 4 days for the completion of polycondensation because of the formation of a small amount of the active ester in place of the desired mixed carboxylic–phosphoric anhydride. To prevent nucleophilic attack on the mixed anhydride by the leaving-group anion, a poorer leaving group, 2-benzothiazolone (**2**), compared with benzisoxazol-3-ol was introduced to the activating agent.

We would like to report that *N,N'*-phenylphosphonobis[2(3*H*)-benzothiazolone] (**4**) is a highly efficient and mild activating agent for the preparation of polyamides by the direct polycondensation of several dicarboxylic acids and diamines.

The methods presently available for the direct phosphorylation of carboxylic acids rely on phosphorus(III) and phosphorus(V) reagents of the general structures **5** and **6**,

$$\underset{5}{>P\text{–}X} \qquad \underset{6}{>P(O)\text{–}X}$$

X = leaving group

where X is a suitable leaving group. The effectiveness of the reagents depends upon the leaving ability of X, which in turn is related to the strength of the acid HX. In this regard, numerous activating agents have been developed in peptide chemistry. Reagents with chlorine as a leaving group remain the most widely used activating agents. Since phosphorus(V) reagents with chlorine as a leaving group are often not suitable for use in a direct amidation because of the formation of phosphoramide by the reaction of activating agents with amines, a number of reactive activating phosphorus(V) agents have been developed. These include diphenyl phosphorazide,[7] diethyl phosphorocyanidate,[8] *N*-succinimido diphenyl phosphate,[9] norborn-5-ene-2,3-dicarboximido diphenyl phosphate,[10] and diphenyl 2-oxo-3-oxazolinyl phosphate.[11] However, there are no reports that these reagents are generally applicable to polyamide synthesis by the direct procedure.

## Experimental Section

**Materials. Solvents, Amines, and Carboxylic Acids.** *N*-Methyl-2-pyrrolidone (NMP) (supplied by Idemitsu Kosan Co., Ltd.) and hexamethylphosphoramide (HMPA) were purified by vacuum distillation and stored over 4-Å molecular sieves. 4,4'-Oxydaniline (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 benzene, respectively. Isophthalic acid, adipic acid, and sebacic acid were purified by recrystallization. 3-Benzoylpropionic acid, *p,p'*-oxybis(3-benzoyl propionic acid), and 7,16-diketodocosanedioic acid acid were prepared by literature procedures.[12–14] Other reagents and solvents were obtained commercially and used as received.

***N,N'*-Phenylphosphonobis[2(3*H*)-benzothiazolone] (4).** 2-Benzothiazolone (**2**) was synthesized according to the method of Hunter[15] in 88% yield by the acid hydrolysis of 2-chlorobenzothiazole, which was prepared readily from 2-mercaptobenzothiazole and sulfuryl chloride,[16] mp 136–137 °C (lit.[15] mp 138 °C). A solution of **2** (4.53 g, 30 mmol) and TEA (8.4 mL, 60 mmol) in acetonitrile (12 mL) was cooled in an ice–water bath. To this solution was added dropwise with stirring a solution of phenylphosphonic dichloride (**3**) (2.98 g, 15 mmol) in acetonitrile (12 mL). The addition was completed in 5 min, and stirring was continued at room temperature for an additional 30 min. The solution was poured into water (100 mL). A precipitate formed, and it was collected by filtration, washed with water, and dried in vacuo: yield 5.40 g (85%). Recrystallization from benzene produced white needles: mp 193 °C; IR (KBr) $\nu$ 1690, 1720 (C=O), 1240 cm$^{-1}$ (P=O); MS (*m/e*) 424.4 (M$^+$). Anal. Calcd for $C_{20}H_{13}N_2O_3S_2P$: C, 56.61; H, 3.07; N, 6.60. Found: C, 56.4; H, 3.2; N, 6.8.

**Model Reaction.** Typical examples of the model reaction follow.

**Benzanilide (7a).** Activating agent **4** (0.466 g, 1.1 mmol) was added to a stirred solution of benzoic acid (0.122 g, 1.0 mmol), aniline (0.09 mL, 1 mmol), and triethylamine (TEA) (0.14 mL, 1.0 mmol) in NMP (2 mL) at room temperature. The solution was stirred for 2 h and poured into 1% aqueous sodium carbonate

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(50 mL). The precipitate was filtered, washed with water, and dried. The yield was 0.185 g (94%), mp 163–164 °C (lit.[17] mp 162 °C).

**Isophthalanilide (8a).** To a solution of isopthalic acid (0.166 g, 1.0 mmol), aniline (0.18 mL, 2.0 mmol), and TEA (0.28 mL, 2.0 mmol) in NMP (2 mL) was added activating agent **4** (0.933 g, 2.2 mmol). The mixture was stirred at room temperature for 2 h. The product was isolated as described above. The yield was 0.303 g (96%), mp 294–295 °C (lit.[18] mp 295–296 °C).

**Polycondensation.** Typical examples of the polycondensation follow.

**Polyamide 10a from Isophthalic Acid and ODA.** To an ice-cooled (−10 °C) solution of isophthalic acid (0.166 g, 1.0 mmol), ODA (0.200 g, 1.0 mmol), and TEA (0.28 mL, 2.0 mmol) in NMP (1 mL) was added activating agent **4** (0.933 g, 2.2 mmol). The mixture was stirred at −10 °C for 10 min and then at room temperature for 2 h. The resulting viscous solution was diluted with NMP (9 mL) and poured into methanol (200 mL). The polymer that precipitated was filtered and was refluxed in methanol for 2 h. The fibrous polymer was collected and dried in vacuo at 100 °C. The yield was essentially quantitative. The inherent viscosity of the polymer in concentrated sulfuric acid was 0.95 $dL \cdot g^{-1}$ at a concentration of 0.5 $g \cdot dL^{-1}$ at 30 °C: IR (film) $\nu$ 3240 (N–H), 1660 $cm^{-1}$ (C=O).

**Polyamide 11a from *p,p'*-Oxybis(3-benzoylpropionic acid) and ODA.** The mixture of activating agent **4** (0.933 g, 2.2 mmol), *p,p'*-oxybis(3-benzoylpropionic acid) (0.3704 g, 1 mmol), ODA (0.200 g, 1.0 mmol), and TEA (0.28 mL, 2.0 mmol) was stirred at −10 °C for 10 min and then at room temperature for 2 h. The polymer solution was worked up as described above. The inherent viscosity of the polymer in NMP was 0.77 $dL \cdot g^{-1}$ at a concentration of 0.5 $g \cdot dCl^{-1}$ at 30 °C: IR (film) $\nu$ 3240 (N–H), 1660 $cm^{-1}$ (C=O). Anal. Calcd for $C_{32}H_{26}N_2O_6 \cdot {}^1/_2H_2O$: C, 70.71; H, 5.00; N, 5.15. Found: C, 70.5; H, 5.00; N, 5.2.

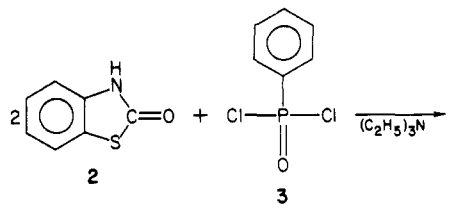
**Polyamide 11b.** Anal. Calcd for $C_{34}H_{46}N_2O_5 \cdot {}^1/_2H_2O$: C, 71.42; H, 8.29; N, 4.90. Found: C, 71.5; H, 7.4; N, 5.0.

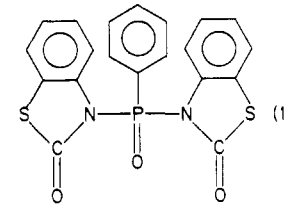
**Polyamide 12 from 2,6-Pyridinedicarboxylic Acid and ODA.** The activating agent **4** (0.933 g, 2.2 mmol) was added at −10 °C with stirring to a solution of 2,6-pyridinedicarboxylic acid (0.167 g, 1.0 mmol), ODA (0.200 g, 1.0 mmol), and TEA (0.42 mL, 3 mmol) in NMP (1 mL). The mixture was stirred at this temperature for 10 min and then at room temperature for 4 h. The polymer was worked up as described above. A 99% yield of the polymer having an inherent viscosity of 1.89 $dL \cdot g^{-1}$ in concentrated sulfuric acid ($c$ = 0.5 $g \cdot dL_{-1}$ at 30 °C) was obtained: IR film $\nu$ 3260 ($C_{19}H_{13}N_3O_3 \cdot {}^1/_2H_2O$: C, 67.05; H, 4.15; N, 12.35. Found: C, 67.3; H, 4.2; N, 12.5.

## Results and Discussion

**Synthesis of *N,N'*-Phenylphosphonobis[2(3*H*)-benzothiazolone] (4).** Recently, we found that *N*- or *O*-acyl products from the acylation of 2-benzothiazolone (**2**) were susceptible to aminolysis under mild conditions.[19,20] The corresponding amides were produced in quantitative yields. This finding led us to try the synthesis of *N,N'*-phenylphosphonobis[2(3*H*)-benzothiazolone] (**4**), which was expected to function as a new activating agent with a wide range of preparative applications in condensations.

The new activating agent **4** was readily prepared from **2** and phenylphosphonodichloridic acid (**3**) in the presence of TEA in acetonitrile at room temperature (eq 1). Recrystallization from benzene gave white needles. However, it is possible to employ the crude product, without further purification, in the preparation of amides and polyamides. Phosphorylation of **2** 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 **4**. The structure of **4** was assigned on the basis of elemental analysis, IR, and mass spectroscopy. The IR spectrum showed carbonyl absorptions at 1690 and 1720 $cm^{-1}$ and the P=O bond absorption at 1240 $cm^{-1}$.

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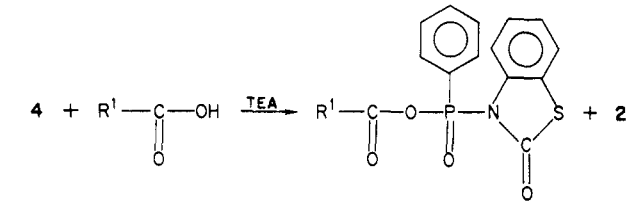
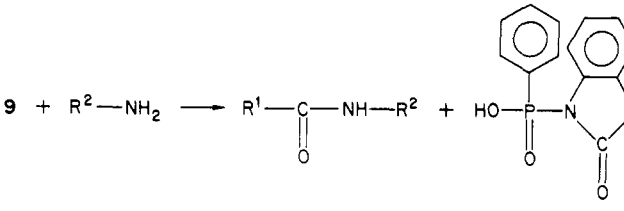
**Model Reaction.** In order to clarify the reactivity of the reagent **4**, we studied the synthesis of amides by a direct procedure. This procedure consists of adding the reagent **4** to a solution of carboxylic acid and amine in NMP that contains TEA as a tertiary organic base to form carboxylate anion (eq 2 and 3). The results are summarized in Table I. The condensations proceeded very rapidly at room temperature, and most of the corresponding amides were obtained in 90% yield. The most probable reaction pathway is as follows:

$$4 + R^1\text{–COOH} + R^2\text{–NH}_2 \xrightarrow{\text{TEA}} \underset{\mathbf{7}}{R^1\text{–CONH–}R^2} \quad (2)$$

$$2\,4 + \text{HOOC–}R^3\text{–COOH} + 2R^2\text{–NH}_2 \xrightarrow{\text{TEA}} \underset{\mathbf{8}}{R^2\text{–NHOC–}R^3\text{–CONH–}R^2} \quad (3)$$

$R^1 = C_6H_5,\ n\text{-}C_5H_{11}$; $R^2 = C_6H_5,\ CH_2C_6H_5,\ C_6H_{11}$; $R^3 = m\text{-}C_6H_4,\ (CH_2)_4$




The activating agent **4** first reacts with carboxylic acids to form the mixed carboxylic–phosphoric anhydride **9**, a highly activated acylating agent. The active intermediate **9** is less stable, and its enhanced reactivity causes it to react rapidly with amines to give amides.

**Polycondensation.**

$$2.2\,4 + \text{HOOC–}R^1\text{–COOH} + \text{H}_2\text{N–}R^2\text{–NH}_2 \xrightarrow{\text{TEA}} \underset{\mathbf{10}}{\text{–(OC–}R^1\text{–CONH–}R^2\text{–NH)}_n\text{–}} \quad (5)$$

$R^1 = m\text{-}C_6H_4,\ (CH_2)_4,\ (CH_2)_8$;

$R^2 = p\text{-}C_6H_4\text{–O–}p\text{-}C_6H_4,\ p\text{-}C_6H_4CH_2\text{–}p\text{-}C_6H_4$

To determine the optimum conditions for the polycondensation we first examined the amount of the activating

**Table I**
**Preparation of Amides 7 and 8 Using Activating Agent 4[a]**

| carboxylic acid | amine | product | % yield |
|---|---|---|---|
| benzoic acid | aniline | benzanilide (**7a**) | 94 |
| benzoic acid | benzylamine | *N*-benzylbenzamide (**7b**) | 82 |
| benzoic acid | cyclohexylamine | *N*-cyclohexylbenzamide (**7c**) | 91 |
| hexanoic acid | aniline | *N*-phenylhexanamide (**7d**) | 92 |
| hexanoic acid | benzylamine | *N*-benzylhexanamide (**7e**) | 83 |
| isophthalic acid | aniline | isophthalanilide (**8a**) | 96 |
| isophthalic acid | benzylamine | *N,N'*-dibenzylisophthalamide (**8b**) | 91 |
| adipic acid | aniline | adipanilide (**8c**) | 95 |

[a] Reaction was carried out with 1 mmol of the reactants in the presence of TEA in NMP (2 mL) for 2 h at room temperature.

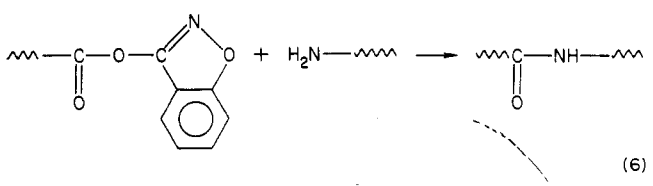
**Table II**
**Polycondensation of Isophthalic Acid with ODA Using Activating Agent 4 under Various Conditions[a]**

| solvent, mL | init temp,[b] °C | molar equiv of 4 rel to monomer | time, h | polymer $\eta_{inh}$,[c] dL·g$^{-1}$ |
|---|---|---|---|---|
| 2.0 | 20 | 2.2 | 48 | 0.52 |
| 1.0 | 20 | 2.2 | 2 | 0.44 |
| 1.0 | 0 | 2.2 | 2 | 0.74 |
| 1.0 | −10 | 2.2 | 2 | 0.95 |
| 1.0 | −20 | 2.2 | 2 | 0.63 |
| 1.5 | −10 | 2.2 | 2 | 0.70 |
| 2.0 | −10 | 2.2 | 24 | 0.67 |
| 1.0 | 20 | 2.4 | 2 | 0.64 |
| 1.0 | 20 | 2.6 | 2 | 0.64 |
| 1.5 | 20 | 3.0 | 2 | 0.47 |

[a] Polycondensation was carried out with 1 mmol of the monomer using the activating agent 4 in NMP. [b] For 10 min. [c] Measured at a concentration of 0.5 g·dl$^{-1}$ in concentrated sulfuric acid at 30 °C.

agent 4, the reaction temperature, and the concentration of the reactants 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 4 based on each monomer was appropriate, and 1 mL of NMP was found to be enough for the reaction on a 1-mmol scale. The initial temperature of the polycondensation greatly influenced the molecular weight of the resulting polyamide. An appropriate initial temperature appeared to be around −10 °C. This finding is in accord with the fact that polycondensation was initiated exothermically.

In a previous paper,[6] we reported the synthesis of polyamides from dicarboxylic acids and aromatic diamines with activating agent **1**, where the polycondensation proceeded slowly because of the formation of active ester to a small extent (eq 6). In contrast, the polycondensation



(6)

in the presence of activating agent **4** was complete in 2 h at room temperature. This result indicates that the polycondensation proceeds only via the formation of the active intermediate **9** without the formation of the active amide, which would be formed by the nucleophilic attack of leaving group **2** to the active intermediate **9**.

On the basis of these studies, the direct polycondensation of various dicarboxylic acids with aromatic diamines

**Table III**
**Polycondensation of Dicarboxylic Acids with Diamines Using Activating Agent 4[a]**

| HOOC–R–COOH | R in $H_2N$-*p*-$C_6H_4$-R-*p*-$C_6H_4NH_2$ | solvent (mL) | polymer[b] type | polymer[b] $\eta_{inh}$,[c] dL·g$^{-1}$ | polymer[b] appearance[d] |
|---|---|---|---|---|---|
| *m*-$C_6H_4$ | O | NMP (1.0) | **10a** | 0.95 | s |
| *mh*$C_6H_4$ | $CH_2$ | HMPA (1.0) | **10b** | 0.66 | p |
| *m*-$C_6H_4$ | $CH_2$ | HMPA (1.5) | **10b** | 0.44 | p |
| *m*-$C_6H_4$ | $CH_2$ | NMP (2.0) | **10b** | 0.47 | p |
| $(CH_2)_4$ | O | HMPA (1.0) | **10c** | 0.62 | p |
| $(CH_2)_4$ | O | HMPA (2.0) | **10c** | 0.45 | s |
| $(CH_2)_4$ | O | NMP (1.0) | **10c** | 0.39 | p |
| $(CH_2)_4$ | O | NMP (1.5) | **10c** | 0.70 | p |
| $(CH_2)_4$ | O | NMP (2.0) | **10c** | 0.62 | s |
| $(CH_2)_4$ | $CH_2$ | HMPA (1.5) | **10d** | 0.48 | p |
| $(CH_2)_4$ | $CH_2$ | NMP (1.5) | **10d** | 0.56 | p |
| $(CH_2)_8$ | O | HMPA (1.5) | **10e** | 0.98 | s |
| $(CH_2)_8$ | O | HMPA (2.0) | **10e** | 1.00 | s |
| $(CH_2)_8$ | O | NMP (1.5) | **10e** | 0.73 | s |
| $(CH_2)_8$ | $CH_2$ | HMPA (2.0) | **10f** | 0.74 | s |

[a] Polycondensation was carried out with 1 mmol of the monomers using activating agent (2.2 mmol) in solvent at −10 °C for 10 min and then at room temperature for 2 h. [b] Yields were quantitative. [c] Measured at a concentration of 0.5 g·dL$^{-1}$ in concentrated sulfuric aid at 30 °C. [d] Appearance of polymerization mixture: s, homogeneous solution; p, polymer precipitation.

was carried out with activating agent **4** in the presence of TEA in polar aprotic solvents (eq 5). Table III indicates that polyamides were easily produced in quantitative yields with inherent viscosities of 1.0 dL·g$^{-1}$.

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

In order to further demonstrate the preparative utility of our method, it was applied to the synthesis of polyamides that have not been prepared successfully by ordinary methods. First, the synthesis of poly(keto amides) (**11**) was tried with our method. We previously reported that linear poly(keto amides) having inherent viscosities up to 0.8 dL·g$^{-1}$ were prepared by the ring-opening polyaddition of 4,4'-oxydi-*p*-phenylenebis(3-buten-4-olide) with aliphatic diamines at room temperature by using *m*-cresol as the polymerization medium.[21] However, the polymerization proceeded fairly slowly and required more than 30 days to reach appreciable solution viscosity of the polymer. Furthermore, polyamides from aromatic diamines were not obtained because of low reactivity of the monomer, bis(butenolide), toward aromatic diamines. Subsequently, model compounds were prepared primarily to determine if their yields were adequate to warrant reaction attempts at the polyamide. The reaction of 3-benzoylpropionic acid with aniline or benzylamine, employing activating agent **4**, progressed rapidly, and almost quantitative conversion to amides could be achieved in 2 h (Table I). The direct polycondensation of bis(keto carboxylic acids) *p,p'*-oxybis(3-benzoylpropionic acid) and 7,16-diketodocosanedioic acid with ODA was carried out with activating agent **4** in the presence of TEA in HMPA (eq 7). Polymerization

$$2.2\,4 + \mathrm{HOOC\text{–}R^1\text{–}COOH} + \mathrm{H_2N\text{–}}p\text{-}\mathrm{C_6H_4\text{–}O\text{–}}p\text{-}\mathrm{C_6H_4\text{–}NH_2} \xrightarrow{\mathrm{TEA}} -[\mathrm{OC\text{–}R^1\text{–}CONH\text{–}}p\text{-}\mathrm{C_6H_4\text{–}O\text{–}}p\text{-}\mathrm{C_6H_4NH}]_n- \quad (7)$$

**11**

$R^1$ = $(CH_2)_2CO$–*p*-$C_6H_4$–O–*p*-$C_6H_4CO(CH_2)_2$, $(CH_2)_5$–CO–$(CH_2)_8$–CO–$(CH_2)_5$

**Table IV**
**Polycondensation of Bis(keto carboxylic acids) with ODA Using Activating Agent 4[a]**

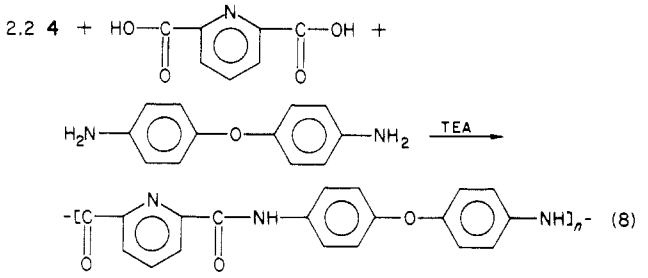
| bis(keto carboxylic acid) HOOC-R-COOH | polymer type | polymer $\eta_{inh}$, dL·g$^{-1}$ |
|---|---|---|
| $-(CH_2)_2-CO-p-C_6H_4O-p-C_6H_4-CO-(CH_2)_2-$ | 11a | 0.77[b] |
| $-(CH_2)_5-CO-(CH_2)_8-CO-(CH_2)_5-$ | 11b | 0.75[c] |

[a] Polycondensation was carried out with 1 mmol of the monomers using activating agent 4 (2.2 mmol) in HMPA (2.0 mL) at −10 °C for 10 min and then at room temperature for 2 h. [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.

proceeded rapidly and gave poly(keto amides) 11 having inherent viscosities of 0.8 dL·g$^{-1}$ in 2 h. The formation of a Schiff base as a side reaction was not observed. These results are shown in Table IV.

The next target was to prepare the aromatic polyamide 12 from 2,6-pyridinedicarboxylic acid and ODA. Hasegawa et al.[22] have studied the synthesis of polyamides from 2,6-pyridinedicarboxylic acid derivatives and aliphatic diamines by using various methods that include melt (nylon salt, phenyl ester) and interfacial polycondensations. Aliphatic polyamides having high molecular weights were obtained by the phenyl ester method. Later, Banihashemi et al.[23] reported that aromatic polyamides with moderate molecular weights could be formed by the melt polycondensation of diphenyl pyridine-2,6-dicarboxylate and aromatic diamines.

Synthesis of polamide 12 from 2,6-pyridinedicarboxylic acid and ODA was performed under conditions similar to those described for the preparation of polyamides (eq 8).

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Although the polymer was isolated in quantitative yield, the molecular weight remained moderate. Then the influence of the amount of TEA was considered because TEA is almost consumed at an early stage of polymerization. Accordingly, the pyridine lone pair in place of TEA may interact with the carboxylic acid. When pyridine was used as the base in the model reaction, the rate of amide formation was greatly reduced. Table V lists the effect of the amount of TEA on the polycondensation. As can be seen from Table V, very high molecular weight polyamide was obtained where 3 molar equiv of TEA relative to dicarboxylic acid was employed.

Transparent films cast from the solution of polyamides 11 and 12 in aprotic solvents showed a high degree of toughness and flexibility. IR spectroscopy and elemental analyses of these polymers indicated materials corresponding to the expected polyamides.

In summary, our studies indicate that the new activating agent 4 is very useful for the preparation of amides and high molecular weight polyamides under mild conditions. This new reagent 4 is a crystalline solid having excellent hydrolytic stability, and therefore it is handled more easily than conventional activating agents. It will be used to synthesize polyamides that contain various functional groups without any protection.

**Table V**
**Polycondensation of 2,6-Pyridinedicarboxylic Acid with ODA Using Activating Agent 4[a]**

| reaction conditions: solvent, mL | molar equiv of TEA rel to monomer | time, h | polymer[b] $\eta_{inh}$,[c] dL·g$^{-1}$ |
|---|---|---|---|
| 1.0 | 2 | 2 | 0.40 |
| 1.5 | 3 | 4 | 1.40 |
| 1.0 | 3 | 4 | 1.89 |
| 1.0 | 4 | 4 | 0.96 |

[a] Polycondensation was carried out with 1 mmol of the monomers using activating agent (2.2 mmol) in NMR at −10 °C for 10 min and then at room temperature. [b] Yields were quantitative. [c] Measured at a concentration of 0.5 g·dL$^{-1}$ in concentrated sulfuric acid at 30 °C.

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