Macromolecules **2000,** *33,* 6211−6213

Novel Polymerization Method for Polyamides by the Reaction of 2-Methyl-2-oxazoline with Aromatic Diisocyanates

Hiroyuki Fukuda,[*,†] Mitsuo Oda, and Takuya Taketa

Nagoya Municipal Industrial Research Institute,
Rokuban 3-chome, Atsuta-ku, Nagoya 456−0058, Japan

Takeshi Endo[‡,§]

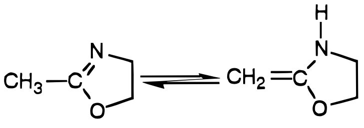
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Nagatsuta, Midori-ku,
Yokohama 226, Japan

Received April 5, 2000
Revised Manuscript Received July 5, 2000

Introduction. Preparation methods for polyamides have been well established and various polyamides are commercially produced mainly either by polycondensation reaction of diacids and diamines, or by ring-opening polymerization of lactames. Further, several efforts focusing on developing new preparation methods for polyamides have been made for applying reaction injection molding by employing isocyanates and enamines.[1−4]

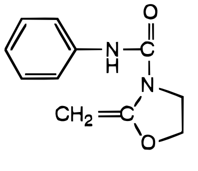
We have been studing ketene cyclic acetal chemistry and have designed ketene cyclic *N*,*O*-acetals by taking into consideration the fact that the β-carbon atoms of carbon−carbon double bond in ketene *N*,*O*-acetals are more polarized and have far higher neucleophilicity than those of ketene *O*,*O*-acetals due to the stronger electron-donating property of the nitrogen atom compared to the oxygen atom. It has already been reported that ketene cyclic *N*,*O*-acetals spontaneously copolymerize with carbon disulfide[5] and with phenylisothiocyanate[6] to give 1:1 alternating copolymers through a macrozwitterionic mechanism. Further, we have found that cyclotrimerization and/or homopolymerization of phenylisocyanate takes place by using ketene cyclic *N*,*O*-acetals as a catalyst.[7]

In the course of our investigation on the chemistry of ketene cyclic *N*,*O*-acetals, we considered that 2-methyl-2-oxazoline (**1**) might have 2-methylene-1,3-oxazolidine (**2**), which is the simplest ketene cyclic *N*,*O*-acetal and a kind of enamine, as a tautomer. If this assumption is correct, **2** should react with phenylisocyanate (**PhNCO**) to afford amide compounds similar to the reaction of 2-methylene-3-methyl-1,3-oxazolidine with **PhNCO**.[7] Taking into account this concept, we studied the reaction of **1** with **PhNCO** in detail to find that **1** behaves as a bifunctinal monomer toward **PhNCO**.


1 **2**

In this paper, we describe the novel polymerization method for polyamide, preparation of polyamide by the reactions of 2-methyl-2-oxazoline with polyisocyanate on the basis of the model reaction.

Results and Discussion. It is reasonable to anticipate that the reaction of 2-methyl-2-oxazoline (**1**) with phenylisocyanate (**PhNCO**) may afford a mixture consisting of five products such as, 2-methylene-3-phenylcarbamoyl-1,3-oxazolidine (**3**), 2-(phenylcarbamoyl)methylene-1,3-oxazolidine (**4**), 3-phenylcarbamoyl-2-(phenylcarbamoyl)methylene-1,3-oxazolidine (**5**), 2-(bisphenylcarbamoyl)methylene-1,3-oxazolidine (**6**), and 2-(bisphenylcarbamoyl)methylene-3-phenylcarbamoyl-1,3-oxazolidine (**7**), because **1** is assumed to be a trifunctional monomer. About 30 years ago, two groups reported the reaction of **1** and **PhNCO**. However, their results were somewhat different from each other; R. Nehring and W. Seeliger[8] reported the isolation of **4**, **5**, and **6**, whereas R. Richer and H. Ulrich[9] obtained **4** and **5**. Their isolation yields were not always satisfactorily. Then we decided to investigate the same reaction carefully in order to clarify the reaction products.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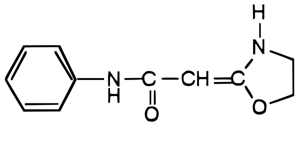
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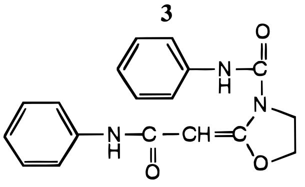
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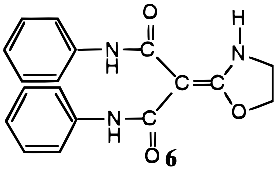
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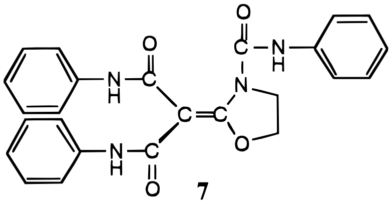
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The reaction of **1** and **PhNCO** with a feed molar ratio of 1:3 was carried out in THF, since **1** could be regarded as a trifunctional monomer, as described above. When both components were mixed, a mild exothermic reaction immediately took place. After the mixture was allowed to react at the ambient temperature for 5 h, a small amount of white precipitate separated out, and yellow crystals were isolated from the filtrate by removing the solvent. The IR spectrum of the precipitates clearly shows two characteristic amide carbonyl bands at 1645 and 1690 cm^{-1} together with that for carbon−carbon double bond at 1600 cm^{-1} while that of yellow crystals shows only one amide band at 1650 cm^{-1} and another for the carbon−carbon double bond at 1600 cm^{-1}. The ^{1}H NMR spectrum of the precipitates shows signals at 4.05 ppm (t, 2H, $NC\mathbf{H}_2CH_2O$), 4.45 ppm (t, 2H, $NCH_2C\mathbf{H}_2O$), and 5.92 ppm (s, 1H, $C{=}C\mathbf{H}$), which are assignable to the methylene-1,3-oxazolidine struc-

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[*] To whom correspondence shloud be addressed.

[†] Telephone: +81-52-654-9898. Fax: +81-52-652-6776.

[‡] Telephone: +81−45−924−5244. Fax +81−45−924−5276.

[§] Present address: Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, Jonan 4-3-16, Yonezawa, Yamagata 992-8501, Japan.

10.1021/ma0006068 CCC: $19.00

Table 1. Reaction of 2-Methyl-2-oxazoline(1) with Phenylisocyanate[a]

no.	reaction conditions [PhNCO]/[**1**]	 temp (°C)	products; yield (%)	
1	3	25	**5**; 4	**6**; 95
2	2	25	**5**; 5	**6**; 92
3	2	80		**6**; 98
4	2	0	**5**; 18	
5	1	25	**5**; 2	**6**; 47

[a] Reaction was carried out in THF for 5 h.

Table 2. Reaction of 2-Methyl-2-oxazoline(1) with 2,4-Tolylenediisocyanate[a]

		polymers			
no.	solvent	yield (%)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	remarks[d]
1	benzene	81	700	1.3	P
2	chloroform	72	930	1.3	P
3	THF	92	1300	1.3	P
4	acetonitrile	96	1100	1.4	P
5	DMF	99	6200	4.8	S
6	DMAc	96	5000	4.4	S
7	HMPA	99	3900	4.2	S
8	NMP	88	5200	4.7	S

[a] Polymerization was carried out with 3.0 mmol of each monomer in 2 mL of solvent at room temperature for 48 h. [b] Insoluble in methanol. [c] Determined by GPC (eluent DMF, 50 °C, polyethylene glycol standards). [d] Appearance of the polymerization mixture: S, homogeneous solution throughout the reaction; P, precipitation during the reaction.

ture, and a multiple signal at around 6.95−7.72 ppm, which can be ascribed to the 10 aromatic protons, respectively. These spectra strongly suggests that the structure of the isolated precipitates is **5**.[10] The ^{13}C NMR spectrum also supports this structure. On the other hand, ^{1}H NMR spectrum of the yellow crystals from the filtrate shows two signals due to methylene protons of the oxazolidine stucture at 3.85 ppm (t, 2H, NC**H**$_2$CH$_2$O) and 4.60 ppm (t, 2H, NCH$_2$C**H**$_2$O), and a multiple signal at the range of 6.86−7.74 ppm attributable to the 10 aromatic protons. Further ^{13}C NMR spectrum shows two signals asignable to amide carbonyl carbon at 166.5 and 167.9 ppm, and two signals due to unsaturated carbon−carbon double bond of methylene-1,3-oxazolidine at 169.1 ppm (C=**C**(NH)(O)) and 78.8 ppm (**C**=C(NH)(O)). These spectral data demonstrate that this compound is a diamide **6**.[11] The isolation yields were 4% for **5** and 95% for **6** on the basis of the amount of **1** employed. Unexpectedly, trisubstituted methylene-1,3-oxazolidine, **7**, was not detected but **6** was quantitatively obtained after the reaction was carried out at 80 °C for 5 h. Interestingly, it was found that isolation yields of the products in the feed ratio of 1:2 are almost same as those obtained in the feed ratio of 1:3. On the other hand, monosubstiuted methylene-1,3-oxazolidines, **3** and/or **4**, were not detected but **5** and **6** were obtained in 2% and 47% yield, respectively, when the reaction was performed with a feed ratio of 1:1 for **1**/**PhNCO**. Moreover, it was revealed that the reaction **1** and **PhNCO** at 0 °C preferentially produced **5** (Table 1, run No. 4).

On the basis of the model reactions we propose the most plausible reaction mechanism as follows; (a) the reaction of **1** and **PhNCO** forms a betaine (**8**) by nucleophilic attack of nitrogen atom of **1** on heterocummulen carbon atom of **PhNCO**, (b) subsequently a proton extraction reaction of carbamic anion from methyl group takes place to give **3**, (c) **3** instantaneously reacts with **PhNCO** to give a betain (**9**) followed by a proton transfer from the methylene adjacent to the carbamoyl anion to produce **5** because β-carbon atom of ketene-*N*,*O*-acetal has a strong anionic character mentioned before, and (d) a thermal rearrangement reaction occurs to give rise to **6**.

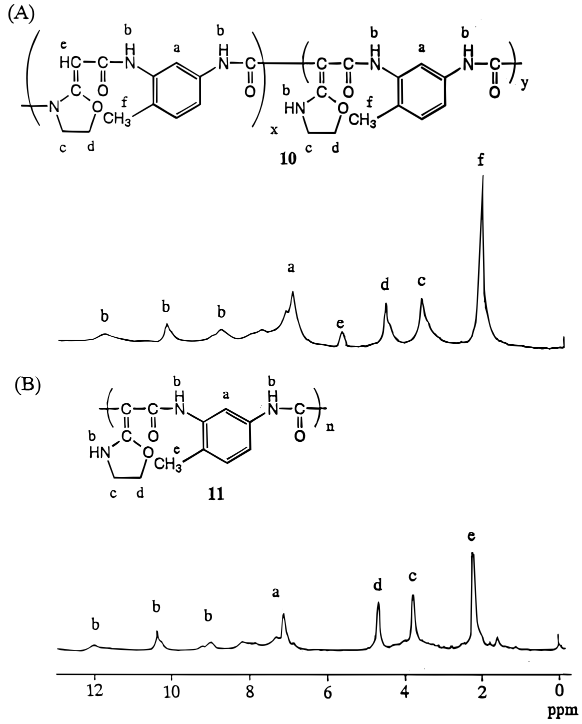
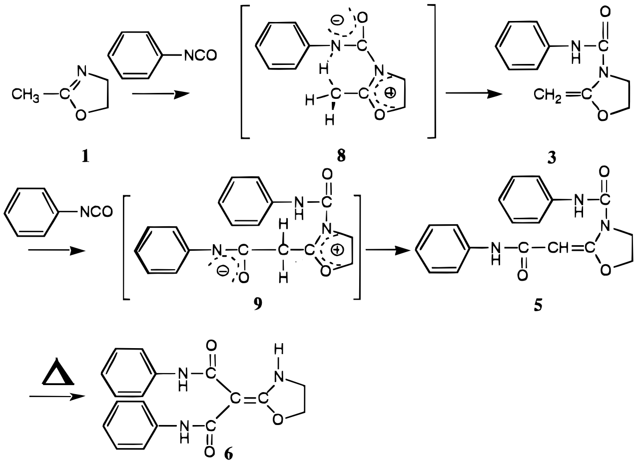


Figure 1. ^{1}H NMR spectra of the reaction mixture of **1** and TDI: (A) after 24 h at 25 °C; (B) after 24 h at 25 °C followed by thermal treatment at 80 °C for 10 min.

Consequently, it can be demonstrated that 2-methyl-2-oxazoline is a bifunctional monomer when the reaction is carried out with a stoichiometric feed ratio contrary to our asumption.

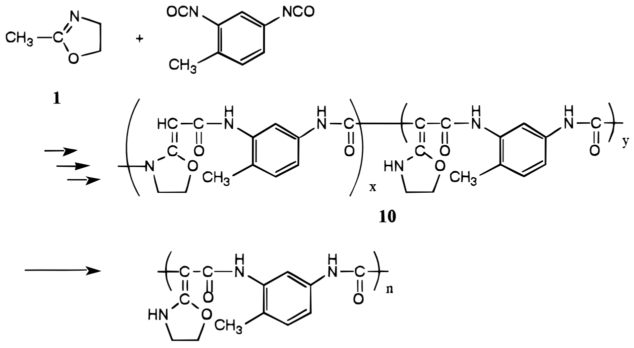


It can be anticipated that polyamide should be obtained by the reaction of 2-methyl-2-oxazoline with aromatic diisocyanate on the basis of the model reaction. Therefore, the polyaddition reaction of **1** with 2,4-tolylenediisocyanate (**TDI**) was investigated by using various solvents at room temperature.[12] The results were summarized in Table 2. As can be seen from Table 2, polymers with molecular weights of 4000−6000 were obtained in fairly good yield when the dipolar aprotic solvents such as DMF, DMAc, HMPA, and NMP were employed. On the other hand, only polymers with low molecular weights were isolated in cases when poor solvents for polyamide, such as chloroform, THF, benzene, and acetonitrile, were used, because precipitation of polymers took place during the polymerization.

IR, ^{1}H NMR, and ^{13}C NMR spectroscopic studies were carried out in order to determine the polymer structure. The IR spectrum of the polymer showed strong characteristic absorptions at 1650 and 1600 cm^{-1}, which were assignable to amide carbonyl and carbon−carbon double bond, respectively. ^{1}H NMR spectum showed signals at 2.27 (3H, C**H**$_3$), 3.76 (2H, NC**H**$_2$CH$_2$O), 4.68 (2H, NCH$_2$C**H**$_2$O), 6.58−8.40 (3H, aromatic **H**), 9.0 (1H, N**H**), 10.5 (1H, N**H**), and 12.0 ppm (1H, N**H**). The ^{13}C NMR spectrum showed the characteristic signals due to the amide carbonyl at 166.3 ppm and the unsaturated carbons at 168.2 (C═**C**(NH)(O)) and 78.0 (**C**═C(NH)(O)) ppm. These spectral data clearly suggest that the obtained polymer is not the copolymer **10** but consists of only one unit structure **11**, whose result is not in accordance with that of the model reaction.

Then, the reaction of **1** with **TDI** was carried out at 25 °C by monitoring ^{1}H NMR spectrum in order to confirm whether the polymerization process was actually different from the model reaction. Consequently, it was found that an olefinic methylene proton (C**H**═C) at 6.0 ppm was clearly observed by admixing both the components. This signal gradually increased with the reaction time until about 24 h. When the reaction temperature was raised to 80 °C, the signal immediately disappeared, as shown in Figure 1. This fact means that polymerization of **1** with **TDI** produced copolymer **10**, similar to the model reaction, and then the units of the ketene-*N*,*O*-acetal monoamide structure thermally rearranged to those of the ketene-*N*,*O*-acetal diamide structure (**11**). This rearrengement, in fact, was acertained by the ^{1}H NMR spectroscopic study of the thermal treatment of **5**.

In conclusion, novel preparation method for polyamide has been demonstrated on the basis of the detailed model reactions. The reaction of 2-methyl-2-oxazoline with diisocyanate gave polyamide having the ketene-*N*,*O*-acetal monoamide structure, which completely rearranged to the ketene-*N*,*O*-acetal diamide structure with thermal treatment, as shown in **11**. Further study aimed at an industrial application of this convienient method for the preparation of polyamide is now in progress.



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(10) Mp: 122−123 °C. IR (neat): ν 3410, 3270, 1690, 1645, 1600 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 4.05 (t, J = 6.8 Hz, 2H), 4.45 (t, J = 6.8 Hz, 2H), 5.92 (s, 1H), 6.95−7.72 (m, 10H), 9.03 (s, 1H), 9.42 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 44.6, 66.5, 79.3, 118.6, 118.7, 120.8, 121.8, 123.5, 128.5, 138.7, 140.5, 150.5, 157.0, 164.5.

(11) Mp: 157−158 °C (recrystalization from chloroform). IR (neat): ν 3410, 1650, 1600 cm^{1}. ^{1}H NMR (CDCl$_3$) δ 3.85 (dd, J = 12.5 Hz, 2H), 4.60 (dd, J = 12.5 Hz, 2H), 6.85−7.74 (m, 10H), 8.75 (s, 1H), 10.94 (s, 1H), 12.44 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 42.2, 68.9, 78.8, 120.4, 121.2, 122.8, 123.7, 128.6, 138.2, 139.1, 166.5, 167.9, 169.1.

(12) Typically, 2-methyl-2-oxazoline (**1**) (0.26 g, 3.0 mmol), 2,4-tolylenediisocyanate (0.52 g, 3.0 mmol), and 2 mL of DMF were placed in a polymerization tube equipped with a No-Air stopper. Ten minutes of purging with a stream of argon at room temperature were performed, and the reaction mixture was maintained at the same temperature for 48 h. The reaction mixture was dissolved in 5 mL of DMF, and the resulting solution was poured into methanol to precipitate the polymer. The precipitated white powder was collected and dried under reduced pressure, yielding (**11**) 0.75 g (96%).

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