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**Registry No.** Curdlan sulfate, 115743-28-7.

# Synthesis and Properties of Polyamides Having Anti Head-to-Head Umbelliferone Dimer as a Component

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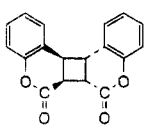
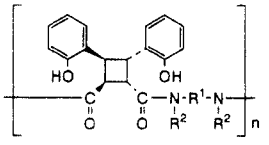
ABSTRACT: Anti head-to-head umbelliferone dimer (**6**) was synthesized from anti head-to-head 7-acetoxycoumarin dimer (**5**). The ring-opening polyaddition reaction of **6** with diamines in an aprotic polar solvent was carried out, and the properties of the resulting polyamides were investigated. Dimer **6** reacted successfully with aliphatic and aromatic diamines to give the corresponding high-molecular-weight polyamides (**8**). Upon photoirradiation, the cyclobutanes in the main chain of **8** were preferentially cleaved in an asymmetric manner to give fumaramide (or maleamide) units. In contrast, in an alkaline solution, the cyclobutanes in **8** were cleaved only in a symmetric manner to give low-molecular-weight products, accompanying the isomerization of the configuration of the substituents on the cyclobutanes. These reactions in alkaline medium are considered to occur through an intermediate of a quinoid enolate structure.

## Introduction

In previous papers, we have reported on the reactions and properties of anti head-to-head coumarin dimer (**1**), its lactone-opened derivatives,[1-5] and polyamides **2** derived from **1**.[6-14] Dimer **1** is susceptible to lactone ring-



**1**



**2**

opening reactions with various nucleophiles, because **1** has highly reactive lactone rings fused to a strained cyclobutane ring.[2] Moreover, **1** reacts easily with diamines to give the corresponding high-molecular-weight polyamides **2**.[8] Polyamides **2** show characteristic photobehavior and thermal behavior. The cyclobutanes in **2** are cleaved in an asymmetric manner by photoirradiation with UV light to give poly(fumaramide) and 2,2′-dihydroxystilbene.[6-8] In contrast, upon heating, the amide linkages of **2** are severed to regenerate lactone rings, followed by a successive cyclobutane cleavage.[5] Furthermore, optically active polyamides, prepared from optically active **1**, form an ordered conformation and show a high chiral recognition ability.[9-14] The phenolic hydroxyl groups in the side chain play an important role in revealing these characteristic properties.

In the present paper, we report the synthesis and behavior of a new type of polyamide consisting of anti head-to-head umbelliferone (7-hydroxycoumarin) dimer, which has more phenolic hydroxyl groups than those of the coumarin dimer **1**.

## Results and Discussion

**Synthesis of Anti Head-to-Head Umbelliferone Dimer (Scheme I).** Anti head-to-head 7-acetoxycoumarin dimer (**5**) can be easily prepared from umbelliferone (7-hydroxycoumarin) (**3**) via 7-acetoxycoumarin (**4**) according to a procedure reported by Leenders et al.[15] The deacetylation of **5** was tried in order to synthesize anti head-to-head umbelliferone dimer (**6**), but the hydrolysis of **5** in an aqueous NaOH solution resulted in a cyclobutane cleavage in a symmetric manner to give 2,4-dihydroxycinnamic acid (umbellic acid) (see below). In contrast, the hydrolysis of **5** in an aqueous HCl solution, followed by relactonization in acetic acid, gave **6** in high yield. Dimer **6**, deposited from an acetic acid solution, contained a small amount of acetic acid. Dimer **6** is barely soluble in most organic solvents but is soluble in aprotic polar solvents such as *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO). Recrystallization from DMF/$CHCl_3$ gave **6** free from acetic acid, though it contained DMF.

**Ring-Opening Polyaddition Reaction of Anti Head-to-Head Umbelliferone Dimer with Diamines.** The ring-opening polyaddition reaction of anti head-to-head umbelliferone dimer (**6**), recrystallized from DMF/$CHCl_3$, with 1,6-hexanediamine (**7a**) proceeded smoothly at room temperature in DMAc (Scheme II). However, the resulting polyamide (**8a**) did not possess a very high molecular weight ($\eta_{inh}$ = 0.32 dL·g$^{-1}$, 0.3 g of polymer/dL in DMAc at 30 °C). Next, the ring-opening polyaddition reaction of **6**, crystallized from acetic acid, with diamines was carried out in the presence of triethylamine equimolar with acetic acid contaminated.

At first, the conditions for polymerization were optimized by using 1,4-phenylenediamine (**7b**) as a diamine

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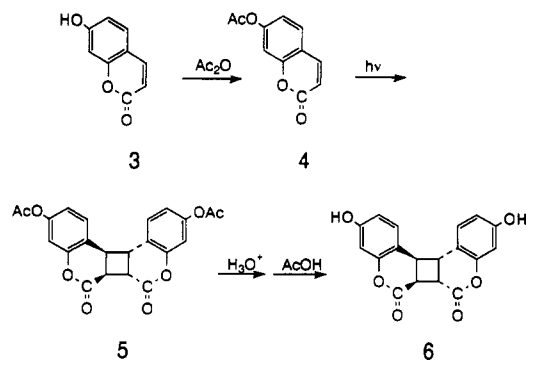
**Scheme I**



**Scheme II**

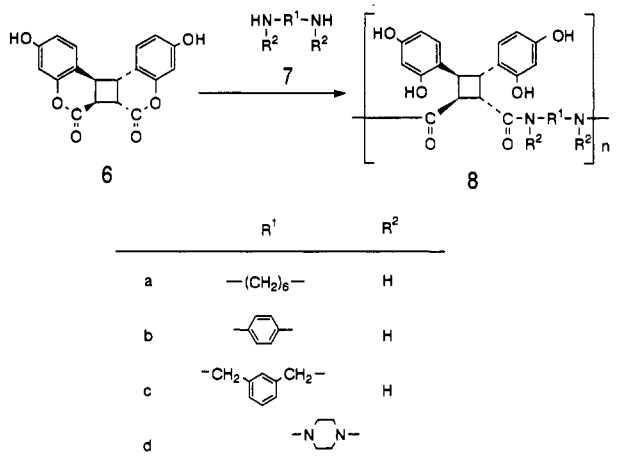


**Table I**
**Ring-Opening Polyaddition Reaction of 6 with 7b[a]**

| run | concn, mol·L$^{-1}$ | temp, °C | solvent | reprecip solvent | $\eta_{inh}$,[b] dL·g$^{-1}$ | yield, % |
|---|---|---|---|---|---|---|
| 1 | 1 | rt | DMAc | acetone | 0.22 | 65 |
| 2 | 1 | 50 | DMAc | acetone | 0.53 | 69 |
| 3 | 1 | 80 | DMAc | acetone | 0.33 | 62 |
| 4 | 0.5 | 50 | DMAc | acetone | 0.34 | 82 |
| 5 | 1 | 50 | DMAc | ethyl acetate | 0.41 | 96 |
| 6 | 1 | 50 | DMF | ethyl acetate | 0.38 | 92 |
| 7 | 1 | 50 | DMSO | ethyl acetate | 0.38 | 93 |
| 8 | 1 | 50 | NMP | ethyl acetate | 0.45 | 80 |

[a] Reaction time: 24 h. [b] 0.3 g·dL$^{-1}$ in DMAc at 30 °C.

component (Table I). Concerning the temperature, the best result was achieved at 50 °C among the temperatures examined (runs 1–3). Regarding the concentration of the solution, 1 mol·L$^{-1}$ was better than 0.5 mol·L$^{-1}$ (runs 2 and 4). The kind of solvent used had little influence on the reaction (runs 5–8). Furthermore, the time versus inherent viscosity curve of the reaction (Figure 1) showed that polymerization was substantially completed within 30 h under these conditions.

Referring to these optimized conditions, the polymerization of **6** with diamines **7** was carried out under suitable conditions. The results are summarized in Table II. Dimer **6** reacted very smoothly with all of the diamines to give high-molecular-weight polyamides (**8**). All of the polyamides could form a transparent and flexible film by casting their DMAc solutions on a glass plate.

In comparison with the ring-opening polyaddition reaction of anti head-to-head coumarin dimer (**1**),[8] the reaction temperature should be low in all cases in order to obtain high-molecular-weight polyamides (**8**) by the ring-opening polyaddition reaction of **6** with **7**. Especially, milder reaction conditions (concentration of the solution and reaction temperature) were required for the reaction

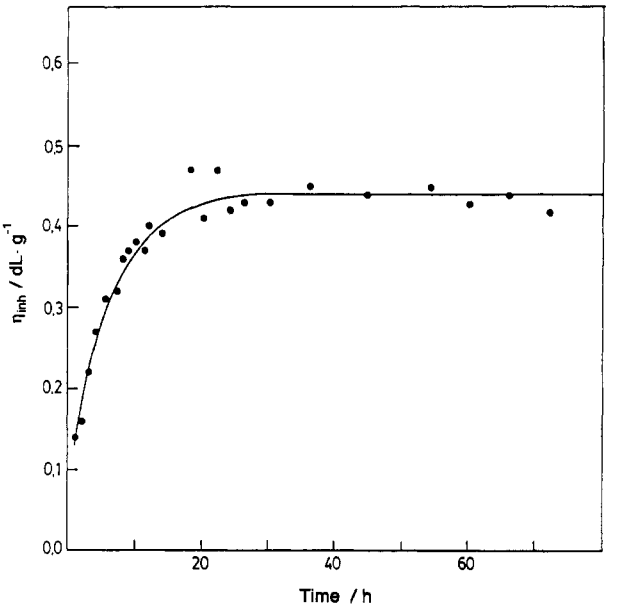



**Figure 1.** Time vs inherent viscosity curve for the ring-opening polyaddition of **6** with **7b** under the conditions of run 5 in Table I.

**Table II**
**Ring-Opening Polyaddition Reaction of 6 with 7[a]**

| polyamide | concn, mol·L$^{-1}$ | temp, °C | time, h | yield,[b] % | $\eta_{inh}$,[c] dL·g$^{-1}$ |
|---|---|---|---|---|---|
| **8a** | 0.5 | rt | 24 | quant[d] | 0.81 |
| **8b** | 1 | 50 | 36 | 95 | 0.41 |
| **8c** | 1 | 50 | 36 | 90 | 0.52 |
| **8d** | 0.5 | 50 | 36 | 91 | 0.96[e] |

[a] In DMAc. [b] Ethyl acetate insoluble part. [c] 0.3 g·dL$^{-1}$ in DMAc at 30 °C. [d] Water-insoluble part. [e] 0.3 g·dL$^{-1}$ in DMF at 30 °C.

with the aliphatic diamine **7a**. Two reasons are possible for this phenomenon: (1) The thermal relactonization of the ring-opened amide linkage takes place at higher temperature in competition with the lactone-opening reaction. (2) The thermal symmetric scission of the cyclobutanes in the polymer main chain occurs under the basic environment of the diamine at higher temperature, resulting in the termination reaction (see below). For the synthesis of **8d**, the concentration of the solution was determined to be 0.5 mol·L$^{-1}$ because of its low solubility in DMAc. Nevertheless, the solution became heterogeneous at the later stage of polymerization.

In order to investigate the properties of polyamides **8**, the corresponding model diamides **10** were synthesized by the ring-opening addition reaction of **6** with amines **9** by almost the same procedure as the polymerization (Scheme III, Table III).

There have been reports concerning the lactone-opening reaction of a six-membered lactone with a nucleophile.[16,17] Contrary to these results, **6** was found to be extremely reactive with such nucleophiles as amines and diamines, doubtlessly because of a high strain in the six–four–six membered ring system, which had accumulated in the course of photodimerization of umbelliferone.

**Photochemical Behavior of the Polyamide.** The photolysis of **8a** or **8b** in a DMAc solution was carried out with 277 ± 10 nm light. A new UV absorption appeared at 340 nm ($\lambda_{max}$) and gradually increased upon the photoirradiation of **8b**, indicative of the formation of product(s) with an elongated conjugated system (Figure 2). However, the UV spectral curve deviated from the isosbestic point during the early stage of the reaction. The photolysis in the film state resulted in a UV spectral change similar to that in

**Scheme III**

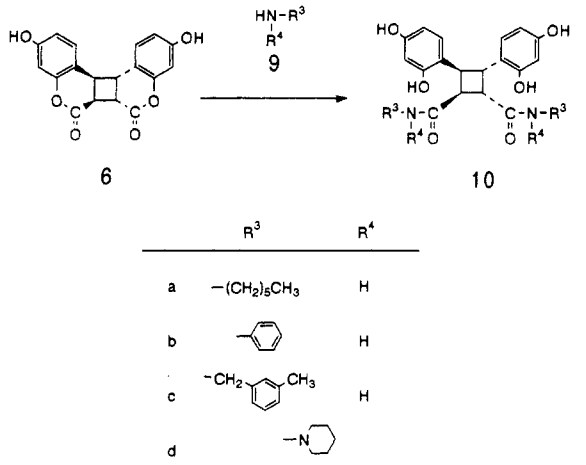



**Table III**
**Synthesis of Model Diamides 10**

| diamide | recryst solvent | yield, % | dec point,[a] °C |
|---|---|---|---|
| **10a** | EtOH/water | 77 | 182 |
| **10b** | EtOH/water | 68 | 228 |
| **10c** | EtOH/water | 49 | 249 |
| **10d** | DMAc/$CH_2Cl_2$ | 67 | 191 |

[a] Determined by DSC.

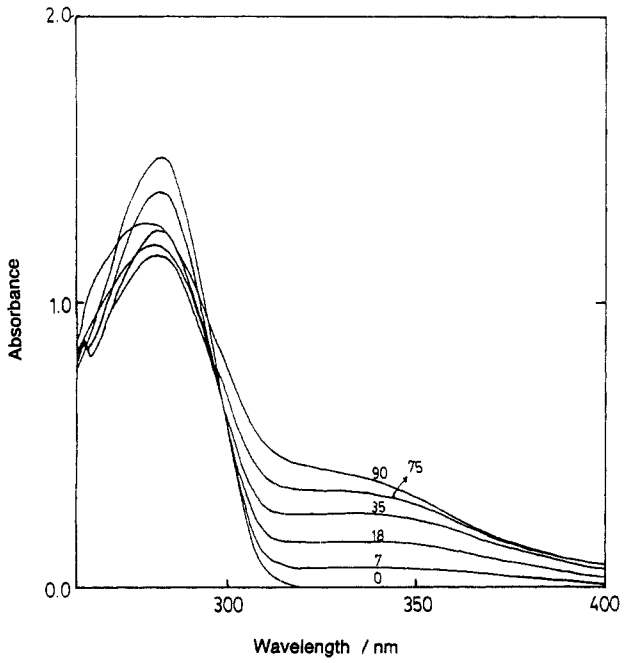



**Figure 2.** UV spectral change of **8b** in DMAc ($5.2 \times 10^{-5}$ repeating unit mol/L) on photoirradiation with light of 277 ± 10 nm wavelength.

a DMAc solution. Polyamide **8a** also showed a photochemical behavior similar to that of **8b**. The $^1H$ NMR spectra of the photoproducts from **8a**, irradiated with a superhigh-pressure mercury lamp in a DMAc solution and in the film state on a large scale, showed the characteristic signals of fumaramide and maleamide units at 6.81 and 6.05 ppm as singlets, in addition to the signals of the repeating unit of **8b**. These results indicate that the cyclobutanes in the main chain of **8** are cleaved in an asymmetric manner upon photoirradiation. Further irradiation of **8** in the film state produced DMSO-insoluble products, and the structural determination by $^1H$ NMR could not be adopted.

In order to clarify these phenomena, photolysis of the model diamides **10a** and **10b** in a methanol solution was

**Scheme IV**

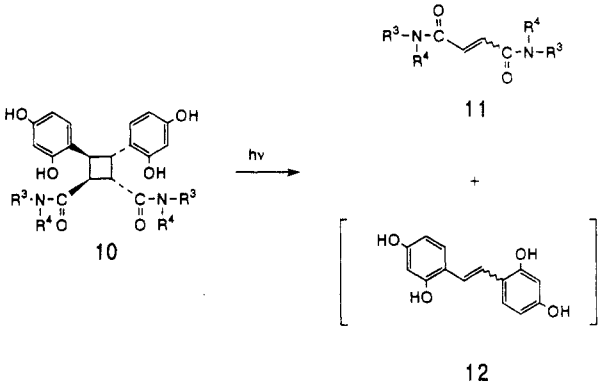
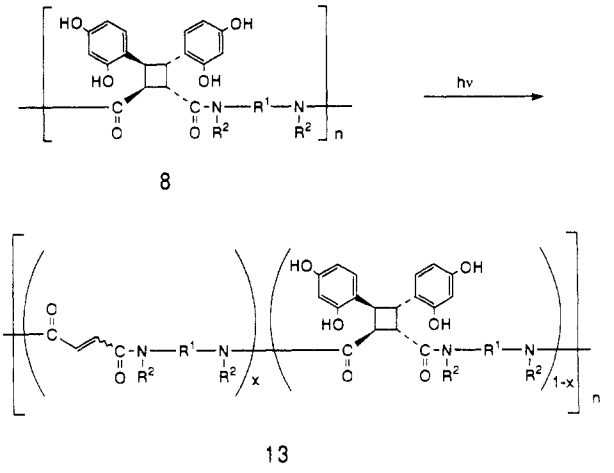



**Table IV**
**Photolysis of 10**

| diamide | product | yield, % | $E/Z$[a] |
|---|---|---|---|
| **10a** | **11a** | 86 | 64/36 |
| **10b** | **11b** | 64 | 70/30 |

[a] Determined by $^1H$ NMR.

**Scheme V**




carried out with 277 ± 10 nm light. The photolysis gave a mixture of fumaramide and maleamide derivatives (**11a** and **11b**, respectively), the products of the asymmetric cleavage of the cyclobutane, in a high yield (Scheme IV, Table IV). However, 2,2′,4,4′-tetrahydroxystilbene (**12**), another product of the asymmetric cleavage, could not be detected, because **12** underwent further reactions to give a mixture of very complicated compounds. The products of a symmetric cyclobutane cleavage, however, could not be detected. These results indicate that the cyclobutane cleavage of **10** upon photoirradiation occurs preferentially in an asymmetric manner.

On the basis of the results on the photocleavage of model diamides **10**, it is concluded that the photoirradiation of polyamides **8** results in the preferentially asymmetric cleavage of the cyclobutanes in the main chain, as shown in Scheme V. Upon prolonging the photoirradiation, the polymer (**13**) having fumaramide (or maleamide) units deposited and eliminated 2,2′,4,4′-tetrahydroxystilbene underwent further complicated reactions, resulting in a deviation of the UV spectral curve from the isosbestic point.

**Behavior of the Polyamide in Alkaline Solution.** The time versus inherent viscosity curves of **8a** and **8b** in an aqueous NaOH solution are shown in Figure 3. The inherent viscosities of the polyamides decreased immediately upon treatment with an alkaline solution. This means that both **8a** and **8b** are degradable in an alkaline

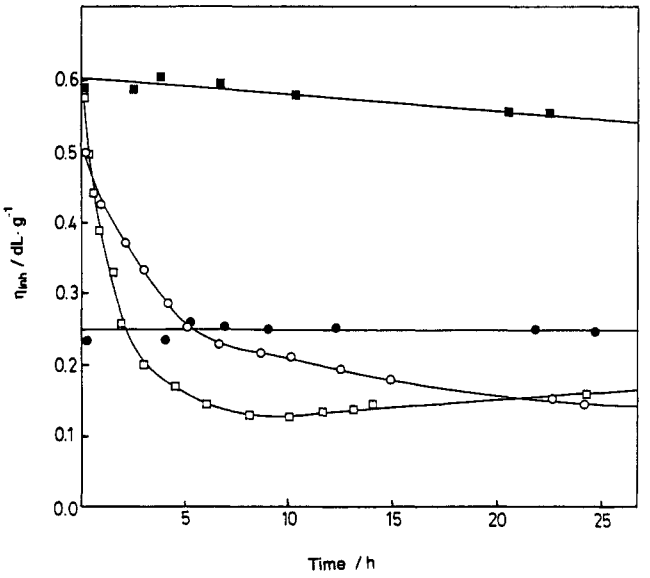
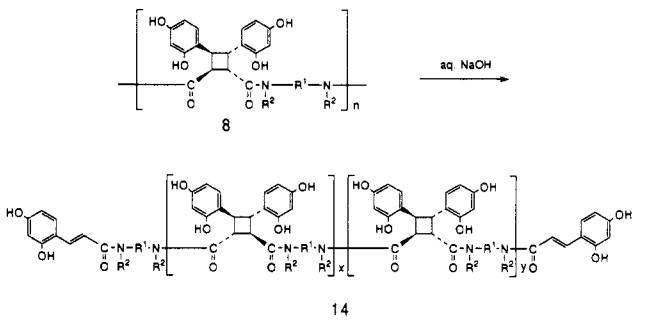



**Figure 3.** Time vs inherent viscosity curves of polyamides in 0.5 M NaOH solution at 30 °C: (□) polyamide **8a**; (○) polyamide **8b**; (■) the polyamide derived from anti head-to-head coumarin dimer and 1,6-hexanediamine; (●) the polyamide derived from the dimer and 1,4-phenylenediamine.

**Scheme VI**




solution; i.e., the scission of the main chain occurs easily to produce lower molecular weight products. In contrast, the inherent viscosities of polyamides **2**, derived from anti head-to-head coumarin dimer (**1**), scarcely decreased under the same conditions (Figure 3). Therefore, the degradation of the main chain of **8** is considered not to be caused by the scission of the amide linkage of either hydrolysis or relactonizaton. Moreover, the $^1H$ NMR spectrum of the degraded products of **8a** showed the signals of the terminal 2,4-dihydroxycinnamamide unit and of the isomerized cyclobutane unit other than the original signals. This result indicates that the symmetric scission of the cyclobutanes is the origin of the decrease of the inherent viscosity, as shown in Scheme VI.

The alkaline degradation behavior was investigated in detail by using model diamides **10** (Scheme VII, Table V). During the early stage of the reaction, the main products were isomer **15**, which has an all-trans configuration for the substituents on the cyclobutane, 2,4-dihydroxycinnamamide (**16**), and umbelliferone (**3**) (runs 1, 2, and 4). Among them, **16** and **3** would be produced by the symmetric cleavage of the cyclobutane; **3** can be produced from (*Z*)-**16** by lactonization with the elimination of the amine. Finally, **16** and **3** became the main products of this degradation (runs 3 and 5). Especially, in the case of **10a** the total yield of **16** and **3** reached over 70%. Several kinds of products other than **15**, **16**, and **3** were detected. All of them were very complicated and could not be identified, though the major product among them may be a benzofuran derivative, produced by a nucleophilic attack of

**Scheme VII**

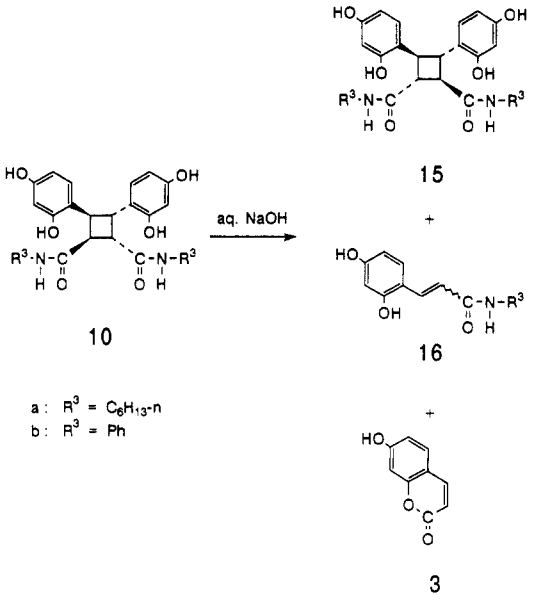



**Table V**
**Reaction of 10 in 0.5 M NaOH Solution at Room Temperature**

| | | | yield, % | | | |
|---|---|---|---|---|---|---|
| run | diamide | time, h | **15** | **16** (*E*/*Z*) | **3** | **10** |
| 1 | **10a** | 3.5 | 23 | 33 (73/27) | | 16 |
| 2 | **10a** | 14.5 | 1 | 35 (89/11) | 6 | |
| 3 | **10a** | 75 | | 68 (92/8) | 3 | |
| 4 | **10b** | 3.5 | 10 | 13 (100/0) | 3 | 11 |
| 5 | **10b** | 35 | | 23 (100/0) | 7 | |

the phenoxide anion to the cyclobutane carbon in **10**. However, the fumaramide and maleamide derivatives, asymmetrically cleaved products, were not detected.

The same reaction of **10a** was carried out in a NaOD/$D_2O$ solution. The cyclobutane protons of the resulting isomer (**15**) as well as the olefin protons of **16** and **3** contained no deuterium. This result indicates that the isomerization of **10** is not caused by the abstraction of the cyclobutane protons by hydroxide anion.

In order to elucidate the participation of the phenolic hydroxyl groups for this reaction, the behavior of four diamides (**10a**, **17a**, **18a**, and **19a**) was compared. The results are summarized in Table VI. Diamide **10a** easily degraded with the symmetric cleavage of the cyclobutane at room temperature to give type III and type IV compounds as products (Scheme VIII). In contrast, **17a** did not degrade at all at room temperature. At 50 °C **17a**, however, gave type II and type III compounds, although the yields were very low (6% and 7%, respectively) and the starting material was recovered in >60% yield. Moreover, **18a** and **19a** did not degrade even at 50 °C, and the starting materials were almost quantitatively recovered. From these results, it is concluded that the reactivity of **10a**, **17a**, **18a**, and **19a** in alkaline solution decreases in this order and that the phenolic hydroxyl groups at the 2- and 4-positions contribute cooperatively to the progress of degradation. Thus, **10a**, which has phenolic hydroxyl groups in both the 2- and 4-positions, degraded more easily than **17a**, **18a**, and **19a**, which have only one hydroxyl group at either the 2- or 4-position; the rate of degradation of **10a** is ca. $10^2$ times as fast as that of **17a**.

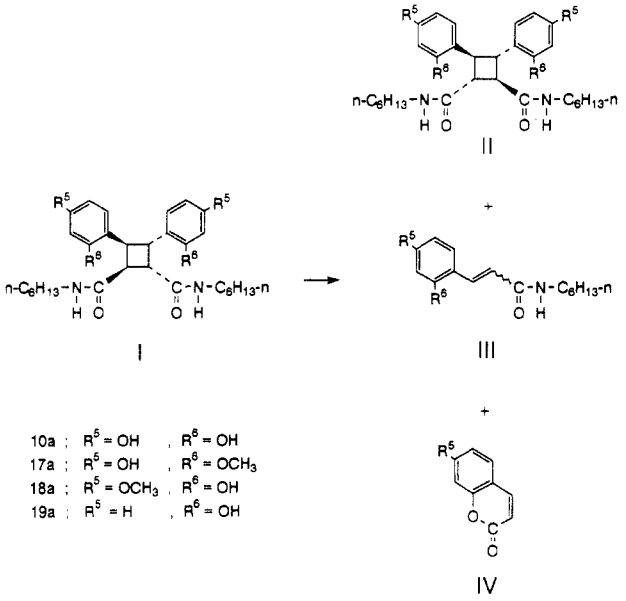
Such behavior of **10** in an alkaline solution can be consistently explained by the mechanism shown in Scheme IX. The diamide has a strained cyclobutane, to which 2,4-dihydroxyphenyl groups and carbamoyl groups are bonded.

**Table VI**
**Degradation of Diamides in Alkaline Solution**

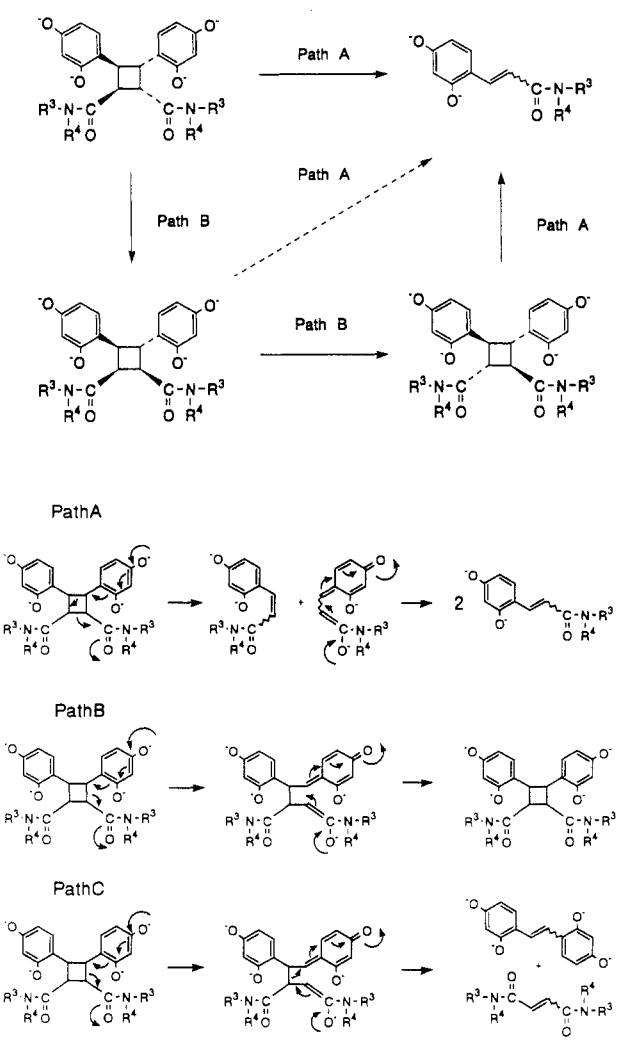
| diamide I | aq NaOH[a]/MeOH, mL/mL | temp, °C | time, h | yield, % I | II | III | IV |
|---|---|---|---|---|---|---|---|
| **10a** | 5/1 | rt | 75 | | | 66 | 1 |
| **17a** | 5/3 | rt | 120 | no reaction | | | |
| **17a** | 5/3 | 50 | 120 | 61 | 6 | 7 | |
| **18a** | 5/1 | 50 | 120 | no reaction | | | |
| **19a** | 5/1 | 50 | 120 | no reaction | | | |

[a] 0.5 M NaOH solution.

**Scheme VIII**



**Scheme IX**



The 2,4-dihydroxyphenyl group can be an electron donor in an alkaline solution, while the carbamoyl group can be an electron acceptor. The phenolate species of **10** can be converted to a quinoid enolate species with the scission of the cyclobutane to release ring strain. There are two possible routes for the formation of the quinoid enolate species: paths A and B. Path A results in a symmetric cleavage of the cyclobutane (the scission of two C–C bonds of the cyclobutane) and leads **10** to 2,4-dihydroxycinnamamide (**16**). Path B results in isomerization of **10** to form another type of quinoid enolate species by the cleavage of one C–C bond in the cyclobutane, and the quinoid enolate species reacts intramolecularly to re-form a cyclobutane ring. In this stage, the substituents at the newly formed C–C bond of the cyclobutane should be in the trans configuration in order to avoid steric repulsion. Consequently, only the most stable isomer (**15**), which has an all-trans configuration on the cyclobutane, can be isolated finally. The isomer may also degrade to **16** through path A. Holm and Zienty reported[18] a similar cyclobutane cleavage of the head-to-tail type dimer of $\alpha,\alpha'$-bis(4-acetoxy-3-methoxybenzylidene)-*p*-benzenediacetonitrile in an alkaline solution. They proposed a mechanism similar to path C. However, in our case, no asymmetrically cleaved product could be detected, indicating that cleavage through path C might be negligible. Moreover, the remarkably high reactivity of **10** in an alkaline solution can be explained as follows: **10** has phenolic hydroxyl groups at the 2- and 4-positions. The quinoid part of the intermediate can be stabilized by resonance between the *o*-quinoid and *p*-quinoid structures.

These reactions would also occur for polyamides **8** and result in a rapid decrease of the inherent viscosities of the polyamides.

## Conclusions

Anti head-to-head umbelliferone dimer is susceptible to a nucleophilic attack of amines and diamines. The ring-opening polyaddition reaction with diamines gives a new type of functional polyamide. The high reactivity of the dimer is attributed to the large strain energy in the six-four-six membered fused-ring system, which is accumulated during the photodimerization of umbelliferone. The photochemical behavior of the polyamides is explained in a similar manner to that of the corresponding diamides prepared from the dimer; the photocleavage of the cyclobutanes of the main chain in the polyamides occurs preferentially in an asymmetric manner, resulting in the structural transformation of the main chain. The polyamides show a unique behavior in solution. The polyamides degrade very easily in an alkaline solution, resulting in a rapid decrease of their inherent viscosities. The model reaction using the lactone-opened diamide demonstrates that the cyclobutanes in the polyamides are cleaved in a symmetric manner via a quinoid enolate species and that the phenolic hydroxyl groups at the 2- and 4-positions play an important role in the transformation.

## Experimental Section

**Material.** Anti head-to-head 7-acetoxycoumarin dimer (**5**) was synthesized from umbelliferone (**3**) via 7-acetoxycoumarin (**4**) by a method reported by Leenders et al.[15] The crude product was purified by recrystallization from acetic acid.

Acetic acid and methyl iodide were purified by distillation at atmospheric pressure. Triethylamine and piperidine were pre-

dried with NaOH pellets and purified by distillation at atmospheric pressure. 1,6-Hexanediamine was distilled into a reaction flask under reduced pressure. 1,3-Xylylenediamine, hexylamine, and 3-methylbenzylamine were predried with NaOH pellets and then purified by distillation under reduced pressure. 1,4-Phenylenediamine and piperazine were purified by recrystallization from benzene, followed by drying at room temperature in vacuo for a few hours. Other reagents were of commercial origin.

Aprotic polar solvents were predried with 4-Å molecular sieves and then distilled under reduced pressure before use. Methanol was of spectral grade.

**Instrumentation.** Decomposition points (dp) were determined on the basis of differential scanning calorimetric (DSC) curves recorded on a Shimadzu DSC-50 instrument under a nitrogen stream at a heating rate of 10 °C/min. Inherent viscosities were measured at 30 °C with an Ostwald viscometer. The concentrations were 0.30 g/dL in DMAc. $^1$H NMR spectra were measured at 22–25 °C by using a JEOL GX-400 (400 MHz) spectrometer. Infrared spectra (KBr pellets) were measured with a Jasco IR-810 infrared spectrophotometer.

**Preparation of Anti Head-to-Head Umbelliferone Dimer (6).** Anti head-to-head 7-acetoxycoumarin dimer (**5**) (24.50 g, 60 mmol) was dissolved in a mixture of 4 M HCl (450 mL) and ethanol (450 mL), through which nitrogen was bubbled for 2 h just before use in order to purge dissolved oxygen. The solution was heated under reflux for 4 h with bubbling nitrogen and then cooled to room temperature. After the addition of water (250 mL), the solution was extracted with ethyl acetate (3 × 300 mL). The extracts were combined, washed with a saturated NaCl solution (2 × 200 mL), and dried with anhydrous $Na_2SO_4$. After the solvent was removed, the remaining residue was dissolved in acetic acid (100 mL), and the mixture was refluxed for 11 h under an argon atmosphere. The precipitate, deposited from the acetic acid solution upon standing at room temperature overnight, was collected by filtration and dried at 60 °C for 24 h under reduced pressure to give **6** (17.59 g, 90%). Thus-obtained **6** contained a trace amount of acetic acid. On the basis of its $^1$H NMR spectrum, the amount of acetic acid contained was estimated to be 7 mol %, which was in good agreement with the result of the elemental analysis. Dp 290 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 3.63 (pseudo dd, 2 H), 3.83 (pseudo dd, 2 H), 6.46 (d, 2 H, $J$ = 2.1 Hz), 6.63 (dd, 2 H, $J$ = 8.2 Hz, $J'$ = 2.1 Hz), 7.14 (d, 2 H, $J$ = 8.2 Hz), 9.83 (s, 2 H); IR (KBr) 3330, 1745, 1635, 1605, 1515, 1460, 1300, 1280, 1160, 1120, 875, 835, 820, 800 cm$^{-1}$. Anal. Calcd for $C_{18}H_{12}O_6 \cdot 0.07CH_3CO_2H$: C, 66.33; H, 3.77. Found: C, 66.18; H, 3.91.

**Synthesis of Polyamides 8.** A typical procedure for the preparation of **8b** is as follows: 1,4-Phenylenediamine (**7b**) (324 mg, 3 mmol) and anti head-to-head umbelliferone dimer (**6**) (986 mg, 3 mmol) were placed in a reaction flask, and DMAc (3 mL) was added to give a clear solution. The solution was warmed at 50 °C for 36 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was diluted with DMAc (ca. 5 mL), and the solution was added drop by drop into ethyl acetate (500 mL). The precipitate that appeared was collected by filtration and dried over $P_2O_5$ at room temperature in vacuo. The yields and inherent viscosities of **8** are listed in Table II.

**8a**: $^1$H NMR (DMSO-$d_6$) $\delta$ 0.8–0.9 (m, 4 H), 0.9–1.0 (m, 4 H), 2.6–2.7 (m, 2 H), 2.8–2.9 (m, 2 H), 3.42 (pseudo d, 2 H), 4.44 (pseudo d, 2 H), 6.03 (dd, 2 H, $J$ = 8.1 Hz, $J'$ = 2.2 Hz), 6.20 (d, 2 H, $J$ = 2.2 Hz), 6.74 (d, 2 H, $J$ = 8.1 Hz), 7.08 (s, 2 H), 8.87 (s, 2 H), 9.28 (s, 2 H); IR (KBr) 3260, 2930, 1620, 1520, 1460, 975, 840 cm$^{-1}$. Anal. Calcd for $(C_{24}H_{28}N_2O_6 \cdot DMAc \cdot 1.5H_2O)_n$: C, 60.64; H, 7.27; N, 7.58. Found: C, 60.69; H, 6.93; N, 7.45.

**8b**: $^1$H NMR (DMSO-$d_6$) $\delta$ 3.72 (pseudo d, 2 H), 4.58 (pseudo d, 2 H), 6.03 (dd, 2 H, $J$ = 8.3 Hz, $J'$ = 2.0 Hz), 6.19 (d, 2 H, $J$ = 2.0 Hz), 6.82 (d, 2 H, $J$ = 8.3 Hz), 7.16 (s, 4 H), 8.87 (s, 2 H), 9.28 (br s, 4 H); IR (KBr) 3275, 1620, 1510, 1455, 1400, 970, 840 cm$^{-1}$. Anal. Calcd for $(C_{24}H_{20}N_2O_6 \cdot DMAc \cdot 1.5H_2O)_n$: C, 61.53; H, 5.90; N, 7.69. Found: C, 61.37; H, 5.78; N, 7.85.

**8c**: $^1$H NMR (DMSO-$d_6$) $\delta$ 3.55 (pseudo d, 2 H), 3.7–3.9 (m, 2 H), 4.1–4.3 (m, 2 H), 4.60 (pseudo d, 2 H), 6.08 (dd, 2 H, $J$ = 8.0 Hz, $J'$ = 2.2 Hz), 6.25 (d, 2 H, $J$ = 2.2 Hz), 6.42 (pseudo d, 2 H), 6.5–6.7 (m, 1 H), 6.81 (d, 2 H, $J$ = 8.0 Hz), 6.9–7.0 (m, 1 H), 7.69 (s, 2 H), 8.96 (s, 2 H), 9.20 (s, 2 H); IR (KBr) 3400, 1620, 1520, 1455, 1395, 970, 840 cm$^{-1}$. Anal. Calcd for $(C_{26}H_{24}N_2O_6 \cdot 2DMAc \cdot 1.5H_2O)_n$: C, 61.71; H, 6.85; N, 8.47. Found: C, 61.89; H, 6.40; N, 8.13.

**8d**: $^1$H NMR (DMF-$d_7$) $\delta$ 1.7–1.9 (m, 2 H), 2.5–2.6 (m, 2 H), 3.1–3.3 (m, 2 H), 3.73 (pseudo d, 2 H), 3.9–4.0 (m, 2 H), 4.75 (pseudo d, 2 H), 6.25 (dd, 2 H, $J$ = 8.0 Hz, $J'$ = 2.1 Hz), 6.44 (d, 2 H, $J$ = 2.1 Hz), 7.02 (d, 2 H, $J$ = 8.0 Hz), 9.24 (s, 2 H), 9.71 (s, 2 H); IR (KBr) 3425, 1610, 1520, 1460, 1435, 975, 840 cm$^{-1}$. Anal. Calcd for $(C_{22}H_{22}N_2O_6 \cdot DMAc \cdot 1.5H_2O)_n$: C, 59.53; H, 6.53; N, 8.01. Found: C, 59.22; H, 6.26; N, 7.47.

**Synthesis of Model Diamides 10.** A typical procedure for the preparation of **10a** is as follows: Hexylamine (**9a**) (2.03 g, 20 mmol) and anti head-to-head umbelliferone dimer (3.24 g, 10 mmol) were dissolved in DMAc (58 mL), and the solution was stirred for 24 h at room temperature under an argon atmosphere. The solution was poured into ether (500 mL), and the precipitate that appeared was collected by filtration. Recrystallization of the crude product from a mixture of ethanol (55 mL) and water (50 mL) gave pure **10a**. The yields, decomposition points, and solvents for recrystallization are listed in Table III.

**10a**: $^1$H NMR (DMSO-$d_6$) $\delta$ 0.83 (t, 6 H, $J$ = 7.3 Hz), 0.9–1.3 (m, 16 H), 2.6–2.7 (m, 2 H), 2.9–3.0 (m, 2 H), 3.41 (pseudo dd, 2 H), 4.42 (pseudo dd, 2 H), 6.02 (dd, 2 H, $J$ = 8.5 Hz, $J'$ = 2.1 Hz), 6.21 (d, 2 H, $J$ = 2.1 Hz), 6.74 (d, 2 H, $J$ = 8.5 Hz), 7.07 (pseudo t, 2 H), 8.86 (s, 2 H), 9.18 (s, 2 H); IR (KBr) 3380, 2960, 2930, 2860, 1620, 1605, 1540, 1520, 1460, 840 cm$^{-1}$. Anal. Calcd for $C_{30}H_{42}N_2O_6$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.09; H, 7.98; N, 5.22.

**10b**: $^1$H NMR (DMSO-$d_6$) $\delta$ 3.79 (pseudo d, 2 H), 4.62 (pseudo d, 2 H), 6.03 (dd, 2 H, $J$ = 8.5 Hz, $J'$ = 2.4 Hz), 6.20 (d, 2 H, $J$ = 2.4 Hz), 6.84 (d, 2 H, $J$ = 8.5 Hz), 6.95 (pseudo t, 2 H), 7.19 (pseudo t, 4 H), 7.36 (pseudo d, 4 H), 8.90 (br s, 2 H), 9.36 (s, 2 H), 9.45 (s, 2 H); IR (KBr) 3430, 1620, 1600, 1540, 1520, 1500, 1440, 840, 750, 690 cm$^{-1}$. Anal. Calcd for $C_{30}H_{26}N_2O_6 \cdot 0.5H_2O$: C, 69.35; H, 5.23; N, 5.39. Found: C, 69.28; H, 5.53; N, 5.61.

**10c**: $^1$H NMR (DMSO-$d_6$) $\delta$ 2.21 (s, 6 H), 3.55 (pseudo d, 2 H), 3.87 (pseudo dd, 2 H), 4.23 (pseudo dd, 2 H), 4.60 (pseudo d, 2 H), 6.08 (dd, 2 H, $J$ = 8.2 Hz, $J'$ = 2.1 Hz), 6.26 (d, 2 H, $J$ = 2.1 Hz), 6.49 (d, 2 H, $J$ = 7.3 Hz), 6.73 (s, 2 H), 6.83 (d, 2 H, $J$ = 8.2 Hz), 6.94 (d, 2 H, $J$ = 7.3 Hz), 7.03 (t, 2 H, $J$ = 7.3 Hz), 7.73 (pseudo t, 2 H), 8.96 (br s, 2 H), 9.20 (s, 2 H); IR (KBr) 3290, 1615, 1540, 1520, 1455, 840, 780, 695 cm$^{-1}$. Anal. Calcd for $C_{34}H_{34}N_2O_6 \cdot 0.5H_2O$: C, 70.94; H, 6.13; N, 4.87. Found: C, 70.83; H, 6.29; N, 4.76.

**10d**: $^1$H NMR (DMSO-$d_6$) $\delta$ 0.7–0.9 (m, 2 H), 1.0–1.4 (m, 10 H), 2.7–2.9 (m, 2 H), 3.0–3.2 (m, 4 H), 3.95 (pseudo d, 2 H), 4.43 (pseudo d, 2 H), 6.12 (dd, 2 H, $J$ = 8.7 Hz, $J'$ = 2.3 Hz), 6.19 (d, 2 H, $J$ = 2.3 Hz), 6.87 (d, 2 H, $J$ = 8.7 Hz), 8.99 (s, 2 H), 9.22 (s, 2 H) (the peak(s) corresponding to two protons could not be found, presumably because of the overlap with the peaks of the solvent); IR (KBr) 3300, 2940, 2860, 1600, 1580, 1515, 1460, 1445, 840 cm$^{-1}$. Anal. Calcd for $C_{28}H_{34}N_2O_6 \cdot 0.5H_2O$: C, 65.07; H, 7.51; N, 7.11. Found: C, 65.27; H, 7.43; N, 7.02.

**Photolysis of Polyamides 8a and 8b.** A solution of polyamide **8** (0.25 repeating unit mmol) in DMAc (4 mL), through which nitrogen was bubbled for 2 h in order to purge dissolved oxygen, was placed in a quartz cell for a UV measurement and irradiated for 30 h with a superhigh-pressure mercury lamp (Ushio UHS-500D) placed outside; the light was passed through a filter (Kenko U-340; cut-off light shorter than 260 nm and longer than 390 nm). The reaction mixture was poured into chloroform (150 mL), and the precipitate that appeared was collected by filtration and dried over $P_2O_5$ at 40 °C overnight in vacuo. The $^1$H NMR and IR spectra of the product indicated the presence of fumaramide and maleamide units.

**Photolysis of Model Diamides 10a and 10b.** A solution of **10a** (250 mg, 0.47 mmol) in methanol (85 mL), through which nitrogen was bubbled for 1.5 h in order to purge dissolved oxygen, was placed in a quartz flask and irradiated with 277 ± 10 nm light (Jasco CRM-FA) for 8 days under an argon atmosphere. After evaporation of the solvent, ethyl acetate (50 mL) was added to the remaining residue to give a precipitate, which was identified as *N*,*N*′-dihexylfumaramide ((*E*)-**11a**) (73 mg, 55%) by comparing its $^1$H NMR and IR spectra with those of an authentic sample prepared from fumaroyl dichloride and hexylamine: $^1$H NMR (DMSO-$d_6$) $\delta$ 0.86 (t, 6 H, $J$ = 6.8 Hz), 1.2–1.3 (m, 12 H), 1.3–

1.5 (m, 4 H), 3.12 (pseudo q, 4 H), 6.79 (s, 2 H), 8.34 (pseudo t, 2 H); IR (KBr) 3450, 3395, 1620, 1545, 1460, 1320, 1190, 995, 670, 660 $cm^{-1}$.

Preparative TLC (Wako Gel B-5F; eluent, $CH_2Cl_2$/EtOAc (2/1 (v/v)) separation of the residue obtained on concentration of the filtrate gave (*Z*)-**11a** (41 mg, 31%) as an oil: $^1H$ NMR (DMSO-$d_6$) $\delta$ 0.86 (t, 6 H, $J$ = 6.8 Hz), 1.2–1.3 (m, 12 H), 1.3–1.5 (m, 4 H), 3.10 (pseudo q, 4 H), 6.09 (s, 2 H), 9.24 (br s, 2 H).

In a similar manner, the photolysis of **10b** (128 mg, 0.25 mmol) in methanol (40 mL) gave (*E*)-**11b** and (*Z*)-**11b** in 45 and 19% yields as a precipitate and an oil, respectively. (*E*)-**11b**: $^1H$ NMR (DMSO-$d_6$) $\delta$ 7.11 (pseudo t, 2 H), 7.20 (s, 2 H), 7.35 (pseudo t, 4 H), 7.70 (pseudo d, 4 H), 10.52 (s, 2 H). (*Z*)-**11b**: $^1H$ NMR (DMSO-$d_6$) $\delta$ 6.44 (s, 2 H), 7.07 (pseudo t, 2 H), 7.32 (pseudo t, 4 H), 7.62 (pseudo d, 4 H), 10.52 (s, 2 H).

**Treatment of Polyamides 8a and 8b in Alkaline Solution.** Polyamide **8a** (30 mg) was dissolved in a 0.5 M NaOH solution (10 mL); its inherent viscosity was measured at 30 °C after a definite standing time to give the time vs inherent viscosity curve in Figure 3. The curves for **8b** and for the polyamides derived from anti head-to-head coumarin dimer were also prepared in a similar manner.

Polyamide **8a** (139 mg) was dissolved in a 0.5 M NaOH solution (10 mL), and the solution was stirred for 4 h at room temperature. After the addition of a 2 M HCl solution (10 mL) to the reaction mixture, the white solid mass that appeared was collected by filtration and dried over $P_2O_5$ at room temperature in vacuo overnight. In a similar manner, polyamide **8b** was treated with an alkaline solution. The $^1H$ NMR spectra of the DMSO-$d_6$-soluble parts of the products both from **8a** and from **8b** showed the characteristic signals of 2,4-dihydroxycinnamamide units.

**Treatment of Model Diamides 10a and 10b in Alkaline Solution.** Model diamide **10** (0.25 mmol) was dissolved in a 0.5 M NaOH solution (10 mL), and the solution was stirred at room temperature for the definite time shown in Table V. After the addition of a 2 M HCl solution (10 mL), the reaction mixture was extracted with ethyl acetate (3 × 20 mL). The extracts were combined, washed with a saturated NaCl solution (3 × 20 mL), and dried with anhydrous $Na_2SO_4$. Separation by preparative TLC (Wako Gel B-5F; eluent, $C_6H_6$/EtOAc (1/1 (v/v)) and $CH_2Cl_2$/EtOAc (8/1 (v/v)) for the products of **10a** and **10b**, respectively) gave **15**, **16**, **3**, and **10**, of which the yields are listed in Table V.

**15a**: $^1H$ NMR (DMSO-$d_6$) $\delta$ 0.85 (t, 6 H, $J$ = 7.0 Hz), 1.1–1.3 (m, 12 H), 1.3–1.4 (m, 4 H), 2.88 (pseudo dd, 2 H), 2.9–3.0 (m, 2 H), 3.0–3.1 (m, 2 H), 3.77 (pseudo dd, 2 H), 6.1–6.2 (m, 4 H), 7.03 (pseudo d, 2 H), 7.80 (pseudo t, 2 H), 9.03 (s, 2 H), 9.38 (s, 2 H); IR (KBr) 3400, 2950, 2925, 2850, 1620, 1605, 1560, 1460, 840 $cm^{-1}$.

(*E*)-**16a**: $^1H$ NMR (DMSO-$d_6$) $\delta$ 0.86 (t, 3 H, $J$ = 7.1 Hz), 1.1–1.3 (m, 6 H), 1.3–1.4 (m, 2 H), 3.1–3.6 (m, 2 H), 6.25 (dd, 1 H, $J$ = 8.3 Hz, $J'$ = 2.2 Hz), 6.33 (d, 1 H, $J$ = 2.2 Hz), 6.43 (d, 1 H, $J$ = 15.9 Hz), 7.21 (d, 1 H, $J$ = 8.3 Hz), 7.50 (d, 1 H, $J$ = 15.9 Hz), 7.86 (pseudo t, 1 H), 9.64 (s, 1 H), 9.87 (s, 1 H).

(*Z*)-**16a**: $^1H$ NMR (DMSO-$d_6$) $\delta$ 0.85 (t, 3 H, $J$ = 7.4 Hz), 1.1–1.3 (m, 6 H), 1.3–1.4 (m, 2 H), 3.1–3.6 (m, 2 H), 5.71 (d, 1 H, $J$ = 13.1 Hz), 6.15 (dd, 1 H, $J$ = 8.2 Hz, $J'$ = 2.1 Hz), 6.22 (d, 1 H, $J$ = 2.1 Hz), 6.72 (d, 1 H, $J$ = 13.1 Hz), 7.59 (d, 1 H, $J$ = 8.2 Hz), 8.04 (pseudo t, 1 H), 9.50 (s, 1 H), 9.99 (s, 1 H).

**15b**: $^1H$ NMR (DMSO-$d_6$) $\delta$ 3.24 (pseudo dd, 2 H), 3.97 (pseudo dd, 2 H), 6.21 (dd, 2 H, $J$ = 8.1 Hz, $J'$ = 2.0 Hz), 6.22 (d, 2 H, $J$ = 2.0 Hz), 7.00 (pseudo t, 2 H), 7.13 (d, 2 H, $J$ = 8.1 Hz), 7.26 (pseudo t, 4 H), 7.64 (pseudo d, 4 H), 9.05 (s, 2 H), 9.21 (s, 2 H), 9.90 (s, 2 H); IR (KBr) 3430, 2920, 2850, 1620, 1595, 1560, 1440, 840, 750, 690 $cm^{-1}$.

(*E*)-**16b**: $^1H$ NMR (DMSO-$d_6$) $\delta$ 6.29 (dd, 1 H, $J$ = 8.7 Hz, $J'$ = 2.3 Hz), 6.37 (d, 1 H, $J$ = 2.3 Hz), 6.68 (d, 1 H, $J$ = 15.6 Hz), 7.02 (pseudo t, 1 H), 7.28 (d, 1 H, $J$ = 8.7 Hz), 7.32 (pseudo t, 2 H), 7.67 (d, 1 H, $J$ = 15.6 Hz), 7.69 (pseudo d, 2 H), 9.76 (s, 1 H), 9.99 (s, 1 H), 10.04 (s, 1 H).

**Synthesis of *rel*-(1*R*,2*R*,3*R*,4*R*)-*N*,*N'*-Dihexyl-3,4-bis(4-hydroxy-2-methoxyphenyl)cyclobutane-1,2-dicarboxamide (17).** Finely powdered anti head-to-head 7-acetoxycoumarin dimer (**5**) (4.00 g, 9.8 mmol) was dissolved in dioxane (70 mL); to the solution was added a solution of hexylamine (1.98 g, 19.6 mmol) in dioxane (40 mL) under an argon atmosphere. After 26 h of stirring, the solvent was evaporated. Recrystallization of the crude product from dioxane gave pure O,O'-diacetylated diamide (5.57 g, 93%): $^1H$ NMR (DMSO-$d_6$) $\delta$ 0.83 (t, 6 H, $J$ = 7.3 Hz), 0.9–1.3 (m, 16 H), 2.19 (s, 6 H), 2.6–2.7 (m, 2 H), 2.8–3.0 (m, 2 H), 3.49 (pseudo dd, 2 H), 4.59 (pseudo dd, 2 H), 6.38 (dd, 2 H, $J$ = 8.7 Hz, $J'$ = 2.3 Hz), 6.50 (d, 2 H, $J$ = 2.3 Hz), 6.94 (d, 2 H, $J$ = 8.7 Hz), 7.30 (pseudo t, 2 H), 9.74 (s, 2 H); IR (KBr) 3390, 3300, 2955, 2940, 2855, 1765, 1630, 1600, 1540, 1425, 850 $cm^{-1}$.

Sodium hydride (ca. 55% in oil, 576 mg) was washed with petroleum ether (5 × 15 mL) and dried in vacuo. To the dried sodium hydride were successively added the O,O'-diacetylated diamide (3.66 g, 6 mmol) and DMF (150 mL). A solution of methyl iodide (0.75 mL) in DMF (30 mL) was added to the mixture at 0 °C over a period of 30 min with stirring. After an additional 8 h of stirring at 0 °C followed by 13.5 h of stirring at room temperature, the reaction mixture was poured into water (2 L), and a 2 M HCl solution (8 mL) was added to the mixture. The precipitate that appeared was collected by filtration and recrystallized from chloroform and then from dioxane to give pure **17** (490 mg, 15%): $^1H$ NMR (DMSO-$d_6$) $\delta$ 0.83 (t, 6 H, $J$ = 7.3 Hz), 0.8–1.3 (m, 16 H), 2.5–2.7 (m, 2 H), 2.8–3.0 (m, 2 H), 3.37 (pseudo dd, 2 H), 3.73 (s, 6 H), 4.46 (pseudo dd, 2 H), 6.14 (dd, 2 H, $J$ = 8.6 Hz, $J'$ = 2.1 Hz), 6.27 (d, 2 H, $J$ = 2.1 Hz), 6.69 (d, 2 H, $J$ = 8.6 Hz), 7.24 (pseudo t, 2 H), 9.09 (s, 2 H); IR (KBr) 3360, 3300, 2960, 2940, 2860, 1640, 1615, 1535, 1510, 1460, 1430, 830 $cm^{-1}$.

**Synthesis of *rel*-(1*R*,2*R*,3*R*,4*R*)-*N*,*N'*-Dihexyl-3,4-bis(2-hydroxy-4-methoxyphenyl)cyclobutane-1,2-dicarboxamide (18).** Sodium hydride (ca. 55% in oil, 0.96 g) was washed with petroleum ether (5 × 20 mL) and then dried in vacuo. To the dried sodium hydride were added anti head-to-head umbelliferone dimer (**6**) (3.24 g, 10 mmol) and DMF (80 mL). After the mixture was cooled in an ice bath, methyl iodide (1.8 mL) was added drop by drop over a period of 20 min with stirring. After stirring for an additional 4 h at 0 °C and then 11 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (300 mL), and the solution was successively washed with a 3 M HCl solution (2 × 200 mL) and a saturated NaCl solution (2 × 200 mL) and then dried with anhydrous $Na_2SO_4$. The product obtained upon evaporation of the solvent, followed by drying at 50 °C for a few hours in vacuo, was dissolved in acetic acid (50 mL); the solution was refluxed for 29 h under an argon atmosphere. Evaporation of the solvent, followed by drying at 60 °C for 12 h in vacuo, gave crude anti head-to-head 7-methoxycoumarin dimer (2.93 g, 83%).

To a solution of the crude dimer (1.41 g) in dioxane (50 mL) was added a solution of hexylamine (0.81 g) in dioxane (30 mL); the solution was stirred for 24 h at room temperature. After removal of the solvent under reduced pressure, the crude product was crystallized from dioxane to give pure **18** (1.49 g, 56% from **6**): $^1H$ NMR (DMSO-$d_6$) $\delta$ 0.82 (t, 6 H, $J$ = 7.3 Hz), 0.8–1.2 (m, 16 H), 2.5–2.7 (m, 2 H), 2.8–3.0 (m, 2 H), 3.44 (pseudo dd, 2 H), 3.61 (s, 6 H), 4.50 (pseudo dd, 2 H), 6.21 (dd, 2 H, $J$ = 8.6 Hz, $J'$ = 2.7 Hz), 6.32 (d, 2 H, $J$ = 2.7 Hz), 6.86 (d, 2 H, $J$ = 8.6 Hz), 7.17 (pseudo t, 2 H), 9.41 (s, 2 H); IR (KBr) 3300, 2960, 2940, 2860, 1635, 1620, 1545, 1520, 1470, 1430, 835 $cm^{-1}$.

**Degradation of Diamides 10a, 17a, 18a, and 19a in Alkaline Solution.** The diamide (0.125 mmol) was dissolved in a mixture of a 0.5 M NaOH solution (5 mL) and methanol (the quantity is shown in Table VI). After the mixture was stirred for a definite time (Table VI), a 2 M HCl solution (2 mL) was added to the solution. The mixture was extracted with ethyl acetate (3 × 20 mL), and the extracts were combined, washed with a saturated NaCl solution (20 mL), and dried with anhydrous $Na_2SO_4$. After evaporation of the solvent, the product(s) was monitored by using a precoated TLC plate (Merck). When any product(s) other than the starting material was detected, separation by preparative TLC (Wako Gel B-5F) was performed.

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# Modeling and Experimental Investigation of Melamine–Formaldehyde Polymerization


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ABSTRACT: Polymerization of melamine with formaldehyde has been studied at high temperatures and molar ratios of monomers similar to those used in industry. Melamine dissolves in formaldehyde slowly and ionizes in the reaction mass to some extent. The polymer formation is a complex process of polymerization of the un-ionized molecules of melamine. Using the functional group approach, we have modeled the batch polymerization and determined the rate constants through curve-fitting. We find that the rate constants are a function of temperature only, and the kinetic model proposed in our work describes the polymerization in the entire region.

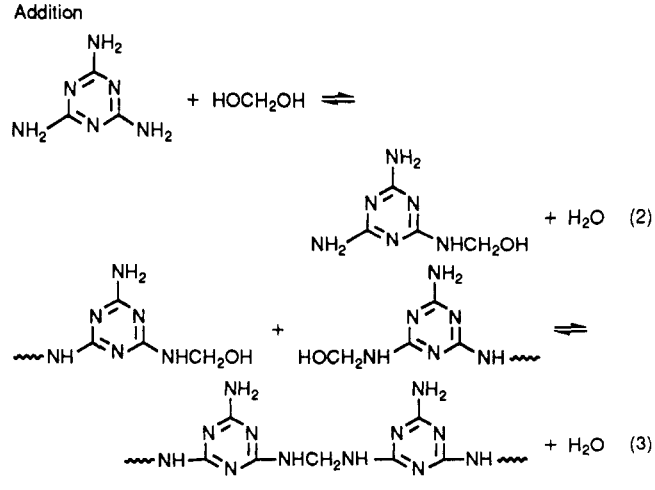

## Introduction

Polymers of melamine (2,4,6-triamino-*s*-triazine) and formaldehyde form an important class of amino resins and have a large industrial application. Melamine molding compound is the hardest commercial plastic and is used mainly for molded dinnerware because of its outstanding hardness and water stain resistance.[1–4] It is also used as protective coating because of its high chemical resistance and is preferred for applications involving outdoor exposures. In recent applications it has also been used as automobile top coats and in textile finishes. In the latter it provides wash and wear properties to cellulosic fibers, enhances wash durability, and gives flame-retardant finishes. The resin has also been applied as an adhesive in plywood industries in place of urea–formaldehyde polymer due to its higher strength, durability, and chemical resistance. In the polymerization of melamine with formaldehyde, formalin (37% by weight of formaldehyde in water) is mixed with melamine. In the aqueous state formaldehyde combines with water to give methylene glycol[5] as

$$HCHO + H_2O \rightarrow HOCH_2OH \qquad (1)$$

The reaction of methylene glycol with melamine has been described by Okano and Ogata[6] in the following two steps.

In the first one melamine adds on a molecule of $HOCH_2OH$. This is an addition reaction, and it takes place for all pHs. The second step is a condensation reaction, which involves the linking of melamine with the product of reaction 2 to form either a dimer or a polymer chain (multiring compound). The product of eq 2 can also self-condense to provide a dimer and a polymer chain. This is referred to as methylene bridge formation and can schematically be represented as

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