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## Photocrosslinking of Polyamides Containing $\alpha$ -Diketone Linkage in the Main Chain

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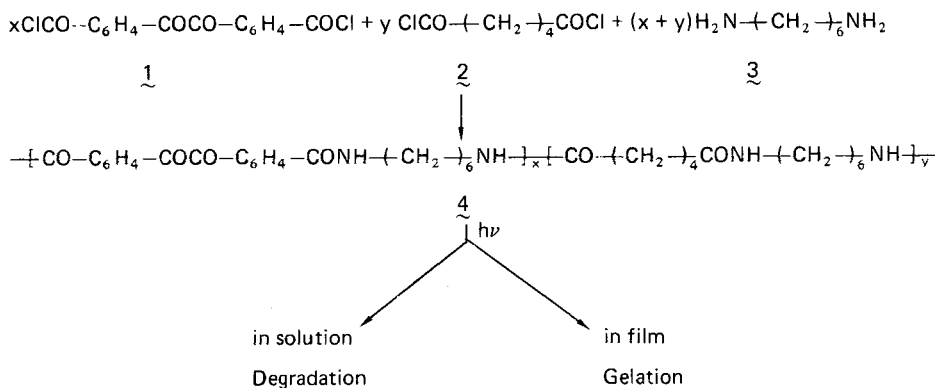
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### ABSTRACT

Copolyamides containing  $\alpha$ -diketone linkages were prepared from adipoyl chloride, 4,4'-dichloroformylbenzil, and hexamethylenediamine. Three polycondensation methods (unstirred interfacial, stirred interfacial, and solution method) were examined. The unstirred interfacial method gave soluble high molecular weight polymers. The copolymer composition was generally equal to that of the monomer feed. The content of the  $\alpha$ -diketone linkage was varied from 5 to 20 mol%. The UV-induced gel formation was studied on films of copolyamides containing more than 10 mol% of the  $\alpha$ -diketone linkage. The gel fraction, degree of gel swelling, changes in the IR spectrum, and Charlesby-Pinner's plots were examined. The photochemical reactions in the film are discussed.

## INTRODUCTION

UV irradiation of copolyamides having  $\alpha$ -diketone linkages in the main chain has led to polymer degradation in solution and to gel formation in film [1]. However, we noted some gel formation prior to UV irradiation when the copolyamides were subjected to a purification procedure, i.e., reprecipitation. This preirradiation gel formation was found to disturb the subsequent analysis of gelation by UV irradiation. In the present work we have reevaluated the preparation methods of the copolyamides, characterized the copolyamides obtained in detail, and reexamined their gelation by UV irradiation.



## EXPERIMENTAL

Materials

4,4'-Dichloroformylbenzil (1) was prepared by a method reported previously [1] and recrystallized from benzene (mp 188.5-189°C). Adipoyl dichloride (2) and hexamethylenediamine (3) were distilled under reduced pressure just before use. Solvents were purified by conventional methods, and other commercially available reagents (JIS GR grade) were used as received. The copolyamide (4) was obtained by three preparation methods. (A) Stirred interfacial method, as reported previously [1]. (B) Unstirred interfacial method: 1 and 2 in 100 mL of  $\text{CHCl}_3$  were placed in a 300-mL beaker. A solution of hexamethylenediamine (3) and sodium hydroxide in 100 mL of water was slowly poured over the acid chloride solution. The polymer formed at the interface of the two solution was taken from the beaker as a continuously forming thread. In most cases, sodium hydroxide and the amount of 3 used were equimolar with respect to total acid chloride. If

excess diamine was used, additional aqueous solution of **3** was added when the rate of polymer formation at the interface decreased. The polymer was washed with methanol and dried in vacuo. The polymer was reprecipitated in methanol from formic acid solution. The results are shown in Table 1. (C) Solution method: The copolyamide was prepared from **1** or 4,4'-bis(benzotriazolyloxycarbonyl)benzil and **3** in N-methylpyrrolidone as described previously [1].

### Film Preparation

The polymer was dissolved in formic acid (~7 wt%). The polymer solution was cast on a glass plate, and the solvent was allowed to evaporate slowly at room temperature. The film was released from the plate by immersing it in water and drying in vacuo. The thickness of the film obtained was ~30  $\mu\text{m}$ .

### Irradiation of Film by UV Light

The irradiation was carried out by using a 400-W mercury lamp (Toshiba H-400P) at room temperature with a 1-cm thick water filter.

Measurement of gel content: A sample (~50 mg) was placed in a glass filter and extracted with formic acid for 48 h in a modified Soxhlet apparatus in which the formic acid entering the extraction chamber was at room temperature; this procedure prevented the formolysis reaction between polyamide and formic acid which would have occurred had hot formic acid been in contact with polyamide for an extended period of time. The glass filter together with the gel was dried in vacuo at 60°C for 24 h, and the gel content was calculated from the increase of the weight of the glass filter.

### Irradiation of Low-Molecular-Weight Model Compound Containing Benzil

A mixture of N-butylbutanamide and benzil (14 mol% with respect to N-butylbutanamide) was placed on a hot plate thermostated at 58°C. UV irradiation was carried out for 200 h under condition similar to those employed for film irradiation. The reaction products were separated by column chromatography on silica gel (Wakogel C-200) and found to consist of ~25 components. The isolated products were characterized by mp measurement and IR, <sup>1</sup>H-NMR, and mass spectrometry. The identified products were benzoic acid and benzoin benzoate.

TABLE 1. Results of the Three Polycondensation Methods

Polymer code <sup>a</sup>	Reaction temperature, °C	Yield, %	$\eta_{inh}^b$ , dL/g	Drying temperature, °C	Color	Gel formation
PS(5)	-20	62.7	0.33	60	Yellow	-
PSI(5)1	Room temperature	92.5	1.13	60	Brown	++
PSI(5)2	"	-	1.03	RT <sup>c</sup>	Yellow	+
				RT <sup>d</sup>	Brown	+
				60 <sup>e</sup>	Brown	+
PSI(5)3B	"	-	-	RT	Brown	+
PUI(5)A	"	51.5	2.42	RT	Yellow	-
PUI(5)B	"	46.6	1.80	RT	Yellow	-

<sup>a</sup>Polymer code; PS = polymer obtained by solution method, PSI = polymer obtained by stirred interfacial method, PUI = polymer obtained by unstirred interfacial method. A = Excess diamine was used. B = Polymer was treated with acetyl chloride after polymerization.

<sup>b</sup>0.5% in m-cresol at 30°C.

<sup>c</sup>One-third of the polymer was reprecipitated from formic acid solution to methanol.

<sup>d</sup>The second portion of the polymer was dried in vacuo at room temperature.

<sup>e</sup>The third portion of the polymer was dried in vacuo at 60°C.

### Measurements

IR spectra were recorded on a JASCO A-202 spectrophotometer, and UV spectra on a Shimadzu UV-200A spectrophotometer.  $^1\text{H-NMR}$  was performed with a Hitachi R-600 FT-NMR spectrometer. Mass spectra were obtained by a Hitachi RMU-7M spectrometer.  $T_g$ 's were obtained by differential scanning calorimetry (DSC) with a Rigakudenki Thermal Analyser (8085D1).

## RESULTS AND DISCUSSION

### Preparation of Copolyamides Containing $\alpha$ -Diketone Linkage in the Main Chain

The polymers prepared by the solution method did not form a gel, but the viscosity measurements suggest that they are of rather low molecular weight. As mentioned in the Introduction, the copolyamide prepared by the stirred interfacial method contains small gel particles. The sol portion of the polymer obtained by the stirred interfacial method showed high viscosities. To clarify the gel-forming step, the effects of drying temperature and the treatment of acetyl chloride before polymer separation to protect the end amine groups were examined. As shown in Table 1, the gel formation decreased on drying at room temperature and on treatment with acetyl chloride, but these procedures could not totally prevent gel formation. It is suggested that gel formation occurs during the polymerization step in the stirred interfacial method. On the other hand, the polymer PUI(5) prepared by the unstirred interfacial method with or without treatment with acetyl chloride does not form gel and has a high viscosity. Therefore, copolyamides containing various amounts of  $\alpha$ -diketone linkages were prepared by the unstirred interfacial method. The results of polymerization are summarized in Table 2. The content of  $\alpha$ -diketone varied from 5 to 20%. Polymer with a high content of  $\alpha$ -diketone linkages could not be obtained by the unstirred interfacial method due to the low solubility of 1 in  $\text{CHCl}_3$ . All the polymers (PUI(5-20)) have high molecular weights and show no gel formation upon heating. The use of excess 3 increased the polymer yield and the viscosity to some extent. A polymer with 100%  $\alpha$ -diketone linkage (PS-100) was prepared by the solution method from 1 or 4,4'-bis(benzotriazolylloxycarbonyl)-benzil and 3. The use of an active ester increased the polymer yield and the viscosity to some extent.

### Determination of the Polymer Composition

The UV spectra of PUI(5-20) in sulfuric acid showed absorption maxima near 280 nm, but the absorption band shifted to shorter wave-

TABLE 2. Results of Polycondensation

Polymer code <sup>a</sup>	Content of $\lambda$ in feed, %	Yield, %	$\eta_{inh}^b$ , dL/g	mp, °C	T <sub>g</sub> , °C	Content <sup>c</sup> of benzil unit in copolymer, %
PUI(5)A	5	52	2.42	244	-	4.7
PUI(5)B	5	47	1.80	-	36	-
PUI(10)A	10	59	2.31	240	-	10.0
PUI(10)B	10	52	1.86	-	25	-
PUI(15)A	15	60	2.11	231	-	14.0
PUI(15)B	15	38	1.58	-	19	-
PUI(20)A	20	56	1.29	227	17	21.0
PS(100)	100 <sup>e</sup>	99	0.50 <sup>d</sup>	-	-	-
PS(100)	100 <sup>f</sup>	83	0.41 <sup>d</sup>	251	-	-

<sup>a</sup> Code: PUI = polymer obtained by unstirred method, PS = polymer obtained by solution method. A = excess diamine was used, B = treated with acetyl chloride.

<sup>b</sup> 0.5% in m-cresol at 30°C.

<sup>c</sup> Measured by UV spectroscopy (see text).

<sup>d</sup> 0.5% in concentrated H<sub>2</sub>SO<sub>4</sub> at 30°C.

<sup>e</sup> 4,4'-Di(benzotriazoloxycarbonyl)benzil was used.

<sup>f</sup> 4,4'-Bischloroformylbenzil was used.

lengths and the intensity changed with time. This phenomenon is known to be caused by the protonation of carbonyl groups [2, 3]. Therefore, it is difficult to determine the content of the  $\alpha$ -diketone directly by UV spectroscopy. The polymers were then trifluoroacetylated since this reportedly makes aliphatic polyamides soluble in common organic solvents, such as tetrahydrofuran, chloroform, and methylene chloride [4-6]. N-Trifluoroacetylation of PS(100) proceeded smoothly, and the UV spectrum now became stable ( $\lambda_{\max} = 268$  nm,  $\log \epsilon = 4.422$ ). The contents of  $\alpha$ -diketone linkages of PUI(5-20) were determined by comparing the absorbance at 268 nm of trifluoroacetylated PUI(5-20) with the calibration curve obtained from trifluoroacetylated nylon 66 and trifluoroacetylated PS(100). The results, shown in Table 2, indicate that the composition of the polymer is roughly the same as in the monomer feed.

#### Gelation of the Film by UV Irradiation

The results of irradiation of polyamide 1 and nylon 66 are shown in Table 3. Gelation did not occur with nylon 66 and PUI(5). With PUI(10, 15, 20), gel formation is noted, but in the case of PUI(10) the reproducibility of the gel formation was poor. The gelation of the copolyamide was found to depend upon its  $T_g$ . The polymers with  $T_g$  higher than room temperature did not form gel, apparently because the polymer radicals formed do not react with each other. On the other hand, the polymers with  $T_g$  lower than room temperature easily form gel by polymer radical coupling. The  $T_g$  dependency of gel formation thus explains the poor reproducibility found with PUI(10).

Plots of gel fraction and degree of swelling vs irradiation time for PUI(15) and PUI(20) are shown in Figs. 1 and 2. In both cases the gel fraction rapidly increased initially and decreased slowly after 5 h.

TABLE 3. Results of Irradiation

Polyamide	Time, h	Results
Nylon 66	0-44	Soluble
PUI(5)	0-90	Soluble
PUI(10)	0-6	Gelation <sup>a</sup>
PUI(15)	0-6	Gelation
PUI(20)	0-6	Gelation

<sup>a</sup>Poor reproducibility



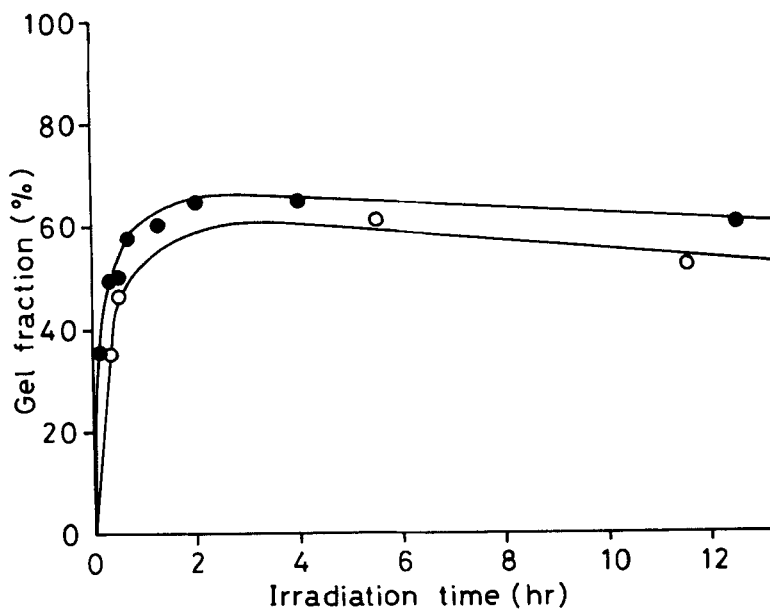


FIG. 1. Gelation of PUI(15) (○) and PUI(20) (●) by UV irradiation.

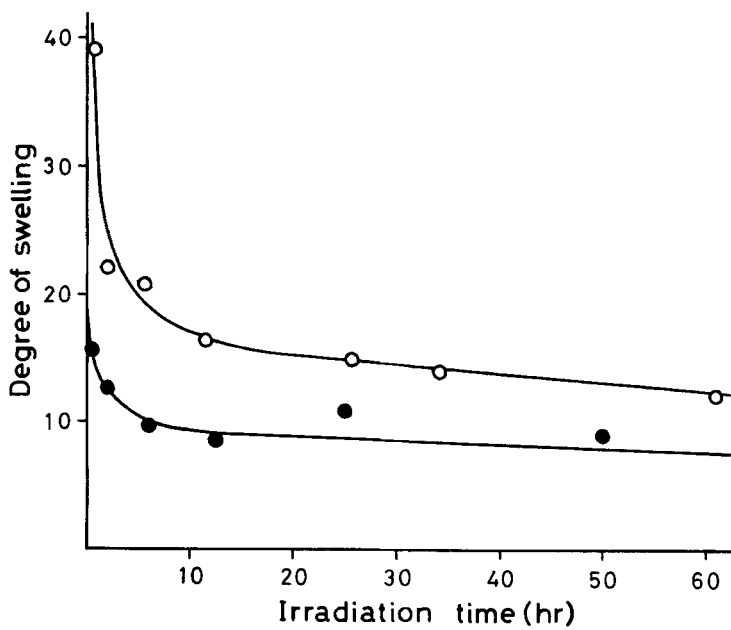


FIG. 2. Degree of swelling of the gel formed in PUI(15) (○) and PUI(20) (●).

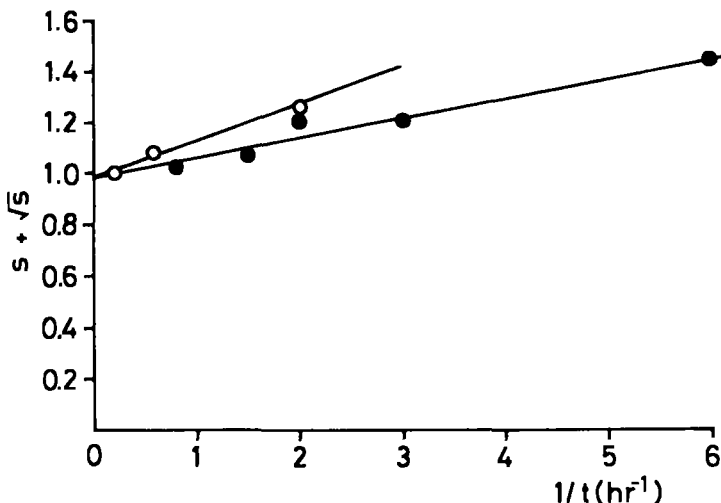


FIG. 3. Charlesby-Pinner plots for PUI(15) (○) and PUI(20) (●).

This decrease was apparently caused by scission of the main chain. The gel fraction of PUI(20) was consistently higher than that of PUI(15). The gel formed from PUI(20) gave a smaller degree of swelling than that of PUI(15). This shows that the density of crosslinking in PUI(20) is higher than that in PUI(15), indicating that the crosslinking was closely related to the concentration of the  $\alpha$ -diketone linkages.

The theory of Charlesby and Pinner proposed for the crosslinking of polymers by high-energy radiation [7] can be applied to the UV-induced gelation of the copolyamides. Assuming that the extent of crosslinking and that of scission are both proportional to irradiation time and that crosslinking and scission occur at random, the Charlesby-Pinner treatment leads to the following relationship:

$$s + s^{1/2} = p_0/q_0 + (1/(q_0 ut)),$$

where  $s$  is the sol fraction in the irradiated polymer,  $p_0$  and  $q_0$  are the probabilities of any given monomer unit being crosslinked and severed, respectively, per unit irradiation time,  $t$  is the irradiation time, and  $u$  is the number-average degree of polymerization. As shown in Fig. 3, the Charlesby-Pinner plots for PUI(15) and PUI(20) for the early stage of the irradiation gave straight lines. The intercepts of the straight lines were virtually the same and approximately equal to unity, indicating that the number of crosslinks is almost equal to that of scission regardless of the concentration of benzil units. It is thus suggested that

one pair of free radicals formed by scission of a benzil unit produces one crosslink. That the slope for PUI(15) ( $\eta_{inh} = 1.58$ ) was larger than that for PUI(20) ( $\eta_{inh} = 1.29$ ) indicates that PUI(20) with a higher benzil content showed higher  $q_0$  than PUI(15), and this is consistent with the fact mentioned above that density of crosslinking in PUI(20) is higher than that in PUI(15).

### IR Spectral Changes of Polyamides 4

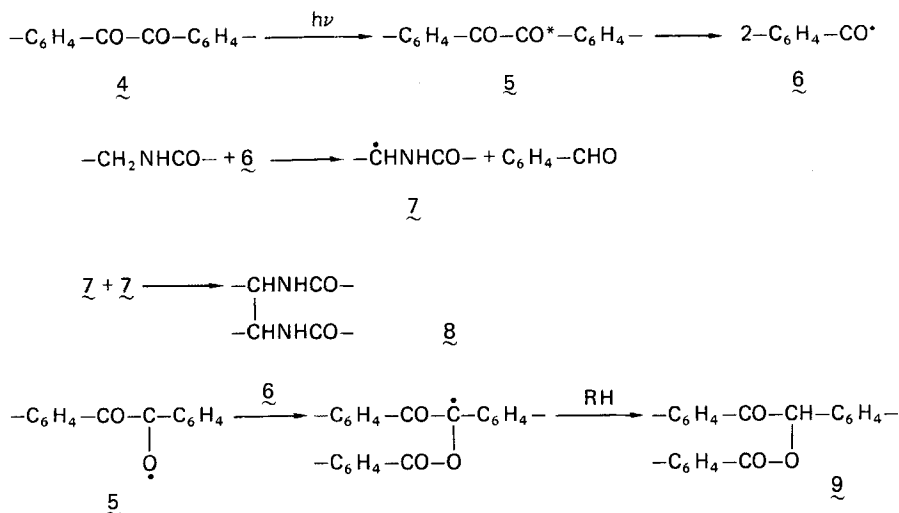
The absorption bands at  $1680$  and  $1210\text{ cm}^{-1}$ , which are characteristic of the benzil unit, was decreased by irradiation, and the shoulder absorption in the range of  $1750$  to  $1700\text{ cm}^{-1}$  increased with irradiation time. This indicates the degradation of benzil units and the formation of carboxyl groups and imide linkages  $-\text{CONHCO}-$  [8]. Since evidence for crosslinking was not obtained from the IR spectral change of the irradiated film, the photochemical reaction of low-molecular-weight model compounds was examined.

### Photochemical Reactions of Low-Molecular-Weight Model Compounds

Photochemical reactions of low-molecular-weight benzil derivatives in solution have been widely studied. However, there are few reports on their reactions in the absence of solvent. The low melting point of N-butylbutanamide allows the model photoreaction to proceed without solvent. The mixture of N-butylbutanamide and benzil was thus irradiated for 200 h at  $58^\circ\text{C}$  in the molten state. The reaction products isolated by column chromatography on silica gel consist of  $\sim 25$  components. The identified components were the unreacted model compound, benzoic acid, and benzoin benzoate. Others have not been identified yet. These results indicated that benzil degraded to benzoyl radical and abstracted hydrogen atoms from other molecules.

### Photochemical Reaction in the Film of Polyamide 4

The results obtained above suggest that the photochemical reactions occurred in a film as follows. The benzil unit is excited by absorption of UV light to give benzoyl radicals. The radical  $\mathfrak{6}$  reacts with the polymer chain to form the polymer radical  $\mathfrak{7}$ . The coupling of polymer radical  $\mathfrak{7}$  forms a crosslink  $\mathfrak{8}$ .



The unity of the intercept ( $p_0/q_0$ ) and linear plot of the Charlesby-Pinner equation suggest the formation of crosslink  $\underline{8}$ . The formation of crosslink  $\underline{9}$  as suggested by the model reaction was assumed to be small because the concentration of the benzil unit was low and the probability of collision between excited benzil and polymeric benzoyl radical may be low in the film.

## CONCLUSIONS

Unstirred interfacial polycondensation of adipoyl chloride and 4,4'-dichloroformylbenzil with hexamethylenediamine gave soluble high-molecular-weight copolyamides containing  $\alpha$ -diketone linkages, while stirred interfacial polycondensation resulted in gel formation. Solution polycondensation gave low-molecular-weight copolyamides. UV irradiation of the film prepared from these copolyamides led to gel formation. The amount of gel fraction depended upon the concentration of the  $\alpha$ -diketone linkage. The number of crosslinks formed was found from Charlesby-Pinner plots to be equal to that of bond scissions. UV irradiation of model compound benzil in *N*-butylbutanamide gave benzoic acid and benzoin benzoate. From these results the following mechanism for UV-induced crosslinking was proposed: Benzoyl radicals formed by the scission of the  $\alpha$ -diketone linkage abstract hydrogen atoms from the polyamide. The coupling of the resulting polymer radicals results in gelation.

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