Synthesis and photodegradation of copolyamides containing α-diketone linkage in the main chain

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Copolyamides were prepared from 4,4'-dichloroformylbenzil, adipyldichloride and hexamethylenediamine. The melting points and solubilities of the copolyamides varied with benzil content. The copolyamides were irradiated by u.v. light in solution and in a film. The copolyamide irradiated in solution was still soluble but the copolyamide irradiated in a film was crosslinked. The mechanisms of the photochemical reactions are discussed.

Keywords Synthesis; degradation; 4,4'-dichloroformylbenzil; benzil; copolyamide; photolysis; crosslink

The photodegradation of aliphatic polyamides has been extensively studied[1-8]. However, photolysis of copolyamides containing photodegradable groups in the main chain has not. It is known that benzil and its derivatives are split into benzoyl radicals by u.v. irradiation[9-11]. Therefore, it should be expected that the introduction of a benzil unit into the main chain of the polyamide enhances its photodegradable properties. In this communication we wish to report on the preparation of copolyamides containing benzil units in the main chain and a study of the photodegradation of the copolyamides.

Experimental

Materials. 4,4'-Dichloroformylbenzil (DCFB) was prepared by an already reported method and recrystallized twice from dry benzene, mp: 190°–191°C[12]. 4,4'-Bis(butylcarbamoyl)benzil. Butylamine (excess) (70 ml) was placed in a 100 ml four necked round flask equipped with a stirrer, a reflux condenser, and a thermometer. DCFB (3.35 g) was added to the flask immediately under stirring. The stirring was continued for 4 h at room temperature. The reaction mixture was then poured into 1000 ml dilute hydrochloric acid solution, and the precipitate formed was collected on a glass filter and washed with distilled water and after drying a 64.6% product was obtained. M.p.: 210°C (toluene), i.r.: 1640 cm^{-1} (amide 1), 1550 cm^{-1} (amide 2), u.v.: $\lambda_{max} = 275$ nm ($\varepsilon = 34100$). Elemental analysis, found: C, 70.71%; H, 6.97%; N, 6.87%. Calculated for $C_{24}H_{28}N_2O_4$: C, 70.56%; H, 6.91%; N, 6.86%.

Polycondensation. Typical examples are as follows; Solution polycondensation method. In a 100 ml four necked round flask equipped with a stirrer, a condenser and a dropping funnel, 1.231 g (10.59 mmol) of HMDA, 0.5 g of lithium chloride and 10 ml of NMP were placed. DCFB (0.432 g:1.02 mmol) was added to the solution and then a solution of ADDC 1.754 (9.54 mmol) in 10 ml of NMP was added over a few minutes. A stoichiometrical amount of triethylamine was then added to the reaction mixture. The reaction continued under stirring over the prescribed time. The solution was poured into methanol to precipitate the copolyamide. The polymer was collected and washed with methanol and dried *in vacuo* at 60°C. The inherent viscosity of the 0.5% *m*-cresol solution was 0.21 dl/g.

Interfacial polycondensation. A solution of HMDA (1.246 g (10.8 mmol)), and sodium hydroxide (0.928 g (23.2 mmol)) in distilled water (50 ml) was placed in a blender. A solution of DCFB (0.168 g (0.5 mmol)) and ADDC (1.85 g (10.1 mmol)) in chloroform (50 ml) was added over a 10 s period under a moderate stirring speed. After the mixture had been stirred for 15 min, the polymer was collected and washed with an acetone–water mixture. The polymer was dried *in vacuo* at 60°C. The yield was 2.29 g (92.5%). The inherent viscosity was 1.13 dl/g (0.5%, *m*-cresol, 30°C).

U.v. irradiation. The u.v. irradiation was carried out by using a high pressure mercury lamp (H-400P, Toshiba) at room temperature. A solution of 0.5% *m*-cresol or a polyamide film was irradiated at a distance of 15 cm. The viscosity changes are shown in *Figure 3.*

Results and Discussion

Preparation of copolyamides. The copolyamides were prepared from 4,4'-dichloroformylbenzil (DCFB)[12], adipyldichloride (ADDC), and hexamethylenediamine (HMDA) by the solution or the interfacial polycondensation method. Results of the polycondensation are summarized in *Table 1.* Copoly-

Table 1 Results of polycondensation

Polyamide and copolyamide no.	Benzil content (%)	Yield (%)	η_{inh} (dl/g)	$T_m{}^c$ (°C)
1	0	64.9	1.33[a]	248
2	5	92.5	1.13[a]	215
3	10	56.6	1.03[a]	205
4	20	56.0	–	170
5	30	62.0	–	165
6	40	58.5	–	145
7	0	66.6	0.54[a]	243
8	10	61.2	0.21[a]	202
9	60	62.0	0.11[b]	150
10	80	59.7	0.14[b]	210
11	100	82.7	0.41[b]	252

Benzil content: (DCFB(mol)/total acid chloride(mol) x 100)
[a] 0.5% *m*-cresol, 30°C
[b] 0.5% H_2SO_4, 30°C
[c] T_g—d.s.c. in N_2, ΔT = 10°C min^{-1}
Polyamides 1–6 were prepared by the interfacial method and numbers 7~11 were prepared by solution method, reaction times were 10, 13, 7, 7, and 12 h respectively

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amides 2 and 3 obtained by interfacial polycondensation gave relatively higher inherent viscosities than copolyamides 8, 9, and 10 obtained by solution polycondensation. The structure of the copolyamides were identified by comparing their spectroscopic data with those of 4,4'-bis(butylcarbamoyl)benzil (model compound) and poly(hexamethyleneadipamide) (polyamide 1). I.r. spectra of copolyamides and polyamide 1 are shown in *Figure 1*. The intensity of the absorption at 1210 cm^{-1}, which was assigned to the vibration band of the α-diketone[13] of benzil, decreased as the content of the benzil unit in the copolyamides decreased. The ultraviolet spectrum of copolyamide 2 (benzil content; 5%) showed almost the same absorption band as that for the model compound (copolyamide 2, $\lambda_{max} = 273$ nm, model, $\lambda_{max} = 275$ nm).

Melting points and solubilities of copolyamides. The melting points and solubilities of the copolyamides varied with the content of benzil units (*Table 2* and *Figure 2*). The melting point was initially depressed by increasing the content of benzil units, and gave a minimum at a 50% benzil content, and then increased to reach 100% benzil content. Copolyamides 2, 3, 9, 10, and 11 were soluble in polar solvents, but copolyamides 4, 5, and 6 had poor solubility in polar solvents. In the cases of copolyamides, 4, 5, and 6, the polycondensations were carried out at low concentrations of reactants because of the low solubility of DCFB at the reaction temperature. Under these reaction conditions, it was considered that the partial hydrolysis of DCFB might be occurring and the resultant excess amino groups were reacting with the ketone groups in the polymerchain causing branching or crosslinking. Consequently, the resultant copolyamides showed poor solubility in various solvents.

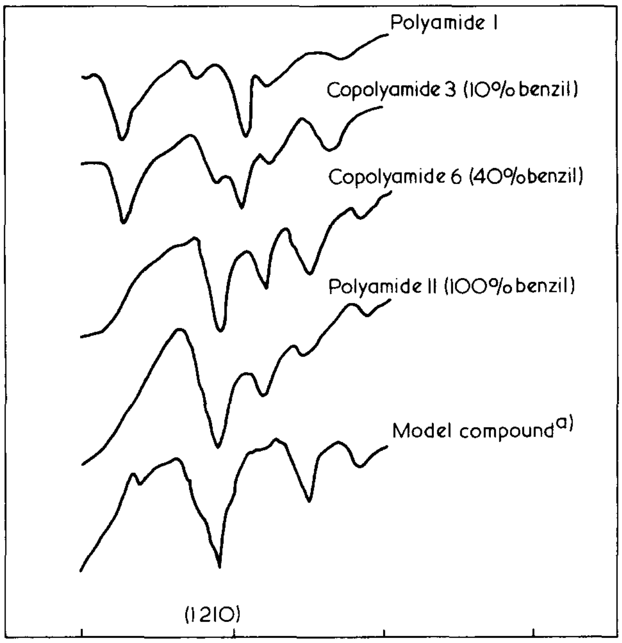


Figure 1 Comparison of i.r. spectrum for polyamide 1, copolyamides and model compound. [a] 4, 4'-Bis(butylcarbamoly)benzil

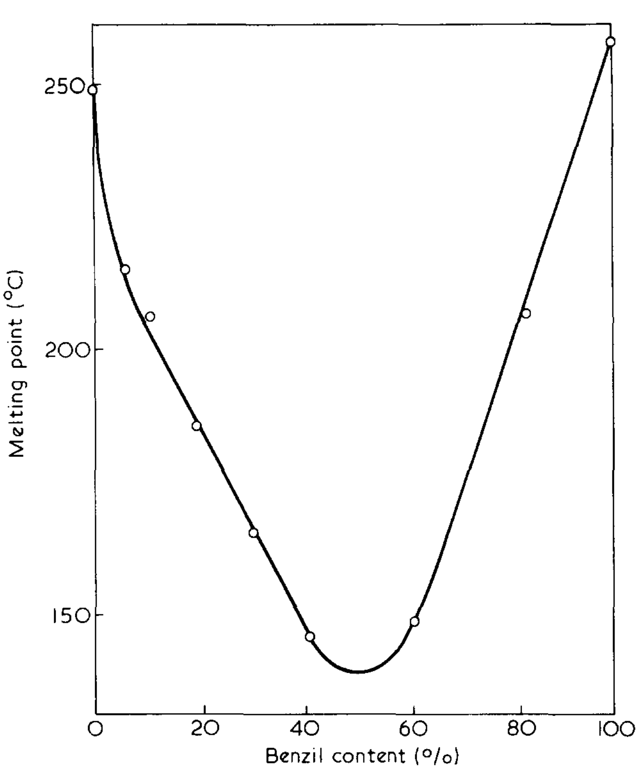


Figure 2 Melting point–benzil content relationship for copolyamides

U.v. irradiation of polyamide. U.v. irradiation was carried out on an *m*-cresol solution and on a polyamide film. In the *m*-cresol solution the degradation of the polyamide was followed by viscometry. The relationship between the viscosity change of the polymer solution and

Table 2 Solubility of copolyamide

Copolyamide No. (benzil content %)	2 (5)	3 (10)	4 (20)	5 (30)	6 (40)	9 (60)	10 (80)	11 (100)
NMP	–	–	–	–	–	±	+	+
NMP(LiCl)	∓	∓	±	∓	∓	±	+	++
DMF	–	–	–	–	–	±	+	–
DMF(LiCl)	–	–	–	–	–	+	+	∓
DMSO	–	–	–	–	–	±	±	±
DMSO(LiCl)	+	–	–	–	–	±	±	±
HMPA	–	–	–	–	∓	±	+	++
HMPA(LiCl)	+	+	–	–	–	±	±	++
m-Cresol	++	++	±	∓	∓	+	+	++
Formic acid	++	++	±	±	∓	±	±	+
H_2SO_4	++	++	±	∓	∓	++	++	++

NMP: *N*-methylpyrrolidone, DMF: dimethylformamide, DMSO: dimethylsulphoxide, HMPA: hexamethylphosphramide, (LiCl): LiCl (5%) was added to the solvent: ++, soluble: +, soluble by heating; ±, poorly soluble; ∓, swelling; –, insoluble

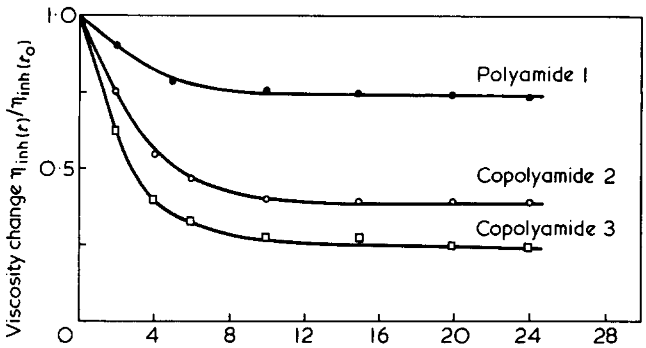
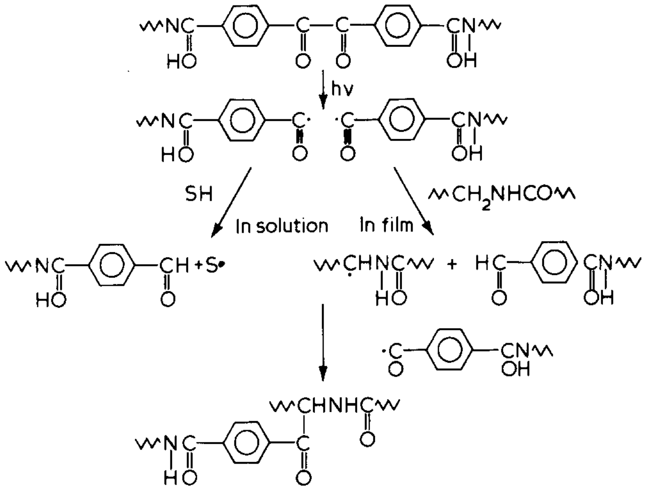


Figure 3 Viscosity change vs. irradiation time polyamide 1 and copolyamides 2 and 3

the irradiation time is shown in *Figure 3*. The copolyamides containing the benzil group were more rapidly degraded than polyamide 1 and the decrease of the viscosity became greater with increased content of benzil groups. When the irradiation was carried out on polyamide films, a different phenomenon was observed. The copolyamide films became insoluble in several polar solvents after irradiation, while the irradiated film of polyamide 1 was soluble and its solution-viscosity curve *versus* irradiation time was similar to that of irradiated polyamide 1 in solution. Therefore the irradiation has caused the copolyamide to crosslink.

To confirm how the crosslinking occurred, a film of polyamide 1 containing 10% of the model compound was prepared and irradiated for 10 h, and then reprecipitated from formic acid solution into methanol. The i.r. spectrum of the resulting polymer showed almost the same absorption as that of the irradiated polymer 1. However, its u.v. spectrum was markedly different from that of the irradiated polyamide 1. The resulting polymer showed a new absorption band at 251 nm. This absorption at 251 nm could be assigned to $-CO-C_6H_4-CO-NH-$ group, as it agreed with the absorption of 4-acetylbenzoic acid ($\lambda_{max}=250$ nm)[14]. These results indicate that the model compound in the polymer film decomposed due to irradiation giving benzoyl radicals, which were then bound to the polymer chain.

The photochemical reaction in the solution and in the film occurred in different ways. The irradiation in solution, caused the benzil unit in the copolyamide to split into two benzoyl radicals, which then reacted with solvent. Therefore, the resultant polymer still remained soluble and the viscosity of the copolyamide decreased more rapidly than for polyamide 1. However, the irradiation of the copolyamide film caused the benzil unit in the copolyamide to split into two benzoyl radicals (as for the solution irradiation), but in this case the benzoyl radicals reacted with another copolyamide chain causing crosslinking, and rendering the copolyamide insoluble.



SH denotes the solvent molecule.

References

1 Achhammer, B. G., Reinhart, F. W. and Kline, G. M. *J. Appl. Chem.* 1951, **1**, 301
2 Sharky, W. H. and Mochel, W. E. *J. Am. Chem. Soc.* 1959, **81**, 3000
3 Schwemmer, M. *Textil-Rundschau* 1956, **11**, 1
4 Hashimoto, T. *Bull. Chem. Soc. Jpn.* 1957, **30**, 950
5 Stephenson, C. V., Moses, B. C. and Wilcox, W. S. *J. Polym. Sci.* 1961, **55**, 451
6 Stephenson, C. V., Moses, B. C., Burks, Jr., R. E., Coburn, Jr., W. C. and Wilcox, W. S. *ibid.* 1961, **55**, 465
7 Moor, R. F. *Polymer* 1963, **4**, 493
8 Anton, A. *J. Appl. Polym. Sci.* 1965, **9**, 1631
9 Bunbury, D. L. and Wang, C. T. *Can. J. Chem.* 1968, **46**, 1473
10 Bunbury, D. L. and Chuang, T. T. *ibid.* 1969, **47**, 2045
11 Maruyama, K., Ono, K. and Osugi, J. *Bull. Chem. Soc. Jpn.* 1972, **45**, 847
12 Nagakubo, K., Akutsu, F., Kawamura, N. and Miura, M. *Nippon Kagaku Kaishi* 1977, 556
13 Shimanouchi, T. 'Analysis of Infrared Spectra', Nankodo, Tokyo, 1969, p. 112
14 Lang, L. 'Absorption Spectra in the Ultraviolet and Visible Region', Academic Press, New York, 1961