Synthesis of New Photoresponsive Polyamides Containing Norbornadiene Residues in the Main Chain

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ABSTRACT: New photoresponsive polyamides containing norbornadiene (NBD) residues in the main chain were synthesized in high yields by interfacial polycondensation between 2,5-norbornadiene-2,3-dicarboxylic acid dichloride (NBDC) and various primary or secondary diamines. The same polyamides were also obtained in high yields by direct polycondensation between 2,5-norbornadiene-2,3-dicarboxylic acid and various diamines using diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate and triethylamine as activating reagents. The degree of viscosity of the copolymers prepared by the reaction of NBDC and adipoyl chloride (ADC) with diamines increased with increasing ADC concentration, although the viscosities of homopolymers prepared by the reaction of NBDC with diamines were low. The photochemical properties of the resulting polyamides were examined in dichloromethane solution and in the film state. Polyamide **5** prepared with aromatic diamines showed higher photochemical reactivity than polyamides **1**-**4** prepared with aliphatic diamines both in dichloromethane solution and in the film state. Furthermore, it was also found that the rates of photochemical reaction of polyamide **1** sensitized with 5 mol % of Michler's ketone or 4-(*N*,*N*-dimethylamino)benzophenone were mostly the same as those of polyamide **5**.

Introduction

Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) has been of interest[1-3] from the viewpoint of solar energy conversion and storage, because this reaction can typically convert solar energy into 97 kJ/mol of thermal energy through the strain energy in the molecule of QC. However, this solar energy conversion system has many problems for practical use. As one example, NBD does not absorb visible sunlight ordinarily. To resolve this problem, photochemical reactions of various NBD compounds with suitable chromophores to absorb sunlight effectively have been reported.[4-7] However, in these reaction systems, low molecular weight NBD compounds in solution had to be used in all cases.

Recently, we reported[8,9] photochemical valence isomerization and catalytic reversion of the polymers containing pendant NBD moieties in the film state. These polymers were prepared by the substitution reaction[10,11] of poly[*p*-(chloromethyl)styrene] with potassium 2,5-norbornadiene-2-carboxylates using a phase transfer catalyst or by the addition reaction[12,13] of poly(glycidyl methacrylate)s with some 2,5-norbornadiene-2-carboxylic acid derivatives. The polymers with pendant NBD moieties were also successfully synthesized by selective cationic polymerization[14] of a vinyl ether containing a 3-phenyl-2,5-norbornadiene-2-carboxylate residue or by the radical polymerization[15-17] of some vinyl monomers containing NBD moieties under specified conditions. However, there is no report on the synthesis of any polymer containing NBD residues in the main chain excepting our recent short communication[18] and Kamogawa's note.[19]

This article describes in detail the synthesis of various new photoresponsive polyamides containing a NBD residue in the main chain by interfacial polycondensation between 2,5-norbornadiene-2,3-dicarboxylic acid chloride (NBDC) and certain diamines or by direct polycondensation between 2,5-norbornadiene-2,3-dicarboxylic acid and the same diamines using certain activating agents. The photochemical properties and catalytic reversion of the resulting polyamides were also examined.

Experimental Section

Materials. The solvents were dried using P_2O_5, CaH_2, or Na metal wire and purified in the usual way before use. Commercial *m*-xylylenediamine (*m*-XDA), hexamethylenediamine (HMDA), triethylamine, pyridine, and adipoyl chloride (ADC) were purified by distillation before use. 1,3-Bis(4-piperidyl)propane (DPP) (donated by Koei Kagaku Co.), 4,4′-methylenedianiline (MDA), 4,4′-oxydianilene (ODA), piperazine, isophthaloyl chloride (IPC), and tetrabutylammonium bromide (TBAB) were purified by recrystallization from suitable solvents. Reagent grade tetraethylammonium bromide (TEAB), tetraethylammonium chloride (TEAC), cetyltrimethylammonium bromide (CTMAB), benzyltriethylammonium chloride (BTEAC), triphenyl phosphate, (5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato)cobalt(II) (Co-TPP) (Wako Pure Chemicals Co.), Michler's ketone (MK), and 4-(*N*,*N*-dimethylamino)benzophenone (DABP) were used without further purification. Activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DTBOP) was prepared according to the reported method.[20] 2,5-Norbornadiene-2,3-dicarboxylic acid (mp 165-166 °C) was obtained in 56% yield by the Diels-Alder reaction of acetylenedicarboxylic acid with freshly distilled cyclopentadiene according to the reported method.[21] NBDC was synthesized with 71% yield as follows: The solution of 18.02 g (0.1 mol) of 2,5-norbornadiene-2,3-dicarboxylic acid in THF (25 mL) was dripped very slowly into 85.3 mL of the cooled oxalyl chloride at 0-5 °C. The reaction mixture was stirred at the same temperature for 2 h and then at room temperature for 1 h. The reaction solvent and unreacted oxalyl chloride were evaporated off, and the obtained crude, oily product was purified by two distillations under reduced pressure (bp 85-87 °C/0.45 mmHg). IR (neat): 1793 (C=O), 1620 cm^{-1} (C=C). ^1H NMR ($CDCl_3$, TMS): δ 1.1-3.0 (m, 2H, CH_2), 4.0-4.2 (m, 2H, CH), 6.2-6.6 (m, 2H, CH=CH).

Apparatus. Infrared (IR) spectra were measured on a JASCO Model IR-700 spectrometer. UV spectra were recorded on Shimadzu Models UV-240 and UV-2100S UV-vis spectrophotometers. The ^1H NMR spectra were recorded on JEOL Models JNM EX-90 (90-MHz) and JNM FX-200 (200-MHz) instruments in $CDCl_3$ or DMSO-d_6 with Me_4Si as an internal standard.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

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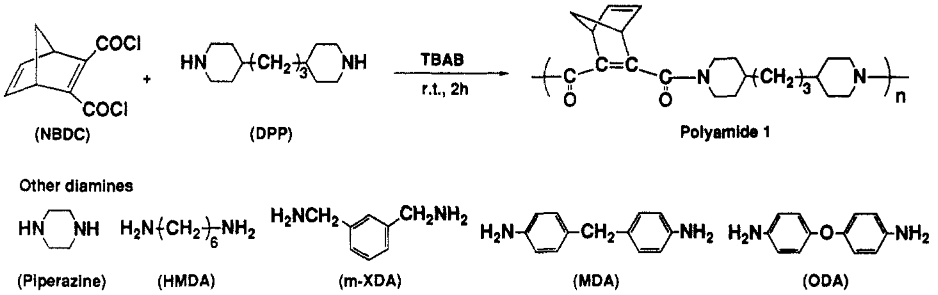
Scheme 1



Synthesis of the Polyamide with the Norbornadiene Residue by Polycondensation of NBDC with Diamine. A typical procedure for polycondensation of NBDC with diamine was as follows: 0.631 g (3 mmol) of DPP and 9.67 mg (0.3 mmol) of TBAB were dissolved in 6 mL of 4 wt % aqueous sodium hydroxide solution. To the solution was added 0.651 g (3 mmol) of NBDC dissolved in 6 mL of chloroform with vigorous stirring, continuing at room temperature for 2 h. Thereafter, the organic layer was concentrated and poured into diethyl ether. The resulting polymer was reprecipitated from methanol into water and then from chloroform into diethyl ether and dried *in vacuo* at 50 °C. The yield of polyamide 1 was 0.98 g (92%). The reduced viscosity was 0.09 dL/g, measured at 0.5 g/dL in DMF at 30 °C. IR (film): 1621 cm^{-1} (C=O and C=C). UV (film): λ_{max} 250 nm. ^{1}H NMR ($CDCl_3$, TMS): δ 0.50–3.75 (m, 28H, CH_2 and CH), 6.50–6.80 (m, 2H, CH=CH).

Synthesis of the Polyamide with the Norbornadiene Residue by Direct Polycondensation of 2,5-Norbornadiene-2,3-dicarboxylic Acid with DPP Using Triphenyl Phosphite–Pyridine as an Activating Agent. 2,5-Norbornadiene-2,3-dicarboxylic acid (0.900 g; 5 mmol) was made to react with 1.052 g (5 mmol) of DPP in the presence 2.5 mL (31 mmol) of pyridine and 3.103 g (10 mmol) of triphenyl phosphite in 10 mL of NMP at 60 °C for 4 h. The mixture was poured into diethyl ether to precipitate the polymer. The polymer was purified by reprecipitating from methanol into 5 wt % sodium bicarbonate aqueous solution and from methanol into water and dried *in vacuo* at 50 °C. The yield of polyamide 1 was 1.65 g (88%). Reduced viscosity was 0.19 dL/g, measured at 0.5 g/dL in DMF at 30 °C.

Synthesis of the Polyamide with the Norbornadiene Residue by Direct Polycondensation of 2,5-Norbornadiene-2,3-dicarboxylic Acid with Diamine Using DTBOP–Triethylamine as an Activating Agent. A typical procedure for direct polycondensation of 2,5-Norbornadiene-2,3-dicarboxylic acid with ODA was as follows: 0.806 g (2.1 mmol) of DTBOP was added to the solution of 0.180 g (1 mmol) of 2,5-norbornadiene-2,3-dicarboxylic acid, 0.200 g (1 mmol) of ODA, and 0.202 g (2 mmol) of triethylamine in 0.5 mL of NMP with stirring at 5 °C, and then the mixture was stirred for 5 min under the same conditions and at room temperature for 24 h. The solution was poured into 50 mL of methanol to precipitate the polymer. The polymer was reprecipitated twice from DMF into methanol, filtered, and dried *in vacuo* at 50 °C. The yield of polyamide 6 was 0.34 g (98%). The reduced viscosity was 0.13 dL/g, measured at 0.5 g/dL in DMF at 30 °C. IR (film): 1645 (C=O), 1606 cm^{-1} (C=C). UV (film): λ_{max} 247 and 335 nm. ^{1}H NMR ($CDCl_3$, TMS): δ 1.85–4.55 (CH_2, CH and NH), 6.05–7.95 (CH=CH and aromatic protons).

Synthesis of the Copolyamide with the Norbornadiene Residue by Polycondensation of NBDC and ADC with DPP. A typical procedure for polycondensation of NBDC and acyl dichloride with DPP was as follows: The reaction of 0.065 g (0.3 mmol) of NBDC and 0.494 g (2.7 mmol) of ADC dissolved in 6 mL of chloroform was carried out with 0.631 g (3 mmol) in 6 mL of 4 wt % aqueous sodium hydroxide solution in the presence of 9.67 mg (0.3 mmol) of TBAB as a phase transfer catalyst at room temperature for 2 h. The reaction mixture was treated by the same method applied to the above reaction of NBDC with DPP. The yield of polymer 11 was 0.88 g (90%). The reduced viscosity was 0.39 dL/g, measured at 0.5 g/dL in DMF at 30 °C. The content of the NBD unit in the copolymer was 9 mol %, which was determined by the ^{1}H NMR spectrum. IR (film): 1621 cm^{-1} (C=O and C=C). ^{1}H NMR ($CDCl_3$, TMS): δ 0.40–4.05 (CH_2 and CH), and 6.80–7.00 (CH=CH).

Table 1. Effect of a Catalyst on the Polycondensation of NBDC with DPP[a]

run no.	catalyst	yield, %	η_{red},[b] dL/g
1	none	29.0	0.02
2	TEAC	90.8	0.07
3	TEAB	91.3	0.08
4	TBAB	92.0	0.09
5	BTEAC	90.3	0.08
6	CTMAB	92.9	0.06

[a] The reaction was performed between 3 mmol of NBDC dissolved in 6 mL of chloroform and 3 mmol of DPP using 10 mol % of TBAB as a phase transfer catalyst in 4 wt % aqueous NaOH solution (6 mL) at room temperature for 2 h. [b] Measured at 0.5 g/dL in DMF at 30 °C.

Typical Procedure for Photochemical Valence Isomerization between the Norbornadiene (NBD) Residue and the Quadricyclane (QC) Group in the Polymer Film. A solution of polymer (0.01 g) in THF (3 mL) was applied on the inside wall of a quartz cell and dried *in vacuo* at room temperature for 24 h. The polymer film on the quartz was irradiated by a 500-W xenon lamp (Ushio Electric Co., UXL-500D-0) both without a filter and through a monochromator (JASCO Model CT-10) under air, with the energy of the incident light being monitored by an electric photon counter (ORC Model UV-M30). Rates of disappearance or appearance of the absorption peak due to the NBD residue were measured using a UV spectrophotometer.

Typical Procedure for Photochemical Reaction of the NBD Residue in the Polyamide in Solution. A solution of polymer (1.0 × 10^{-4} mol/L) in dichloromethane was charged into a quartz cell, and then the solution in the cell was exposed by a xenon lamp under the same irradiation conditions under nitrogen. Rates of disappearance of the absorption peak due to the NBD residue were monitored using a UV spectrophotometer.

Typical Procedure for Catalytic Reversion of the Resulting QC Group in the Polyamide in Solution. The dichloromethane solution of the NBD polymer (1.0 × 10^{-4} mol/L) was irradiated by the same xenon lamp. To the photoirradiated polymer solution was added Co-TPP (3.0 × 10^{-5} mol/L) dissolved in dichloromethane, and then the rate of appearance of the absorption peak due to the NBD residue was monitored using a UV spectrophotometer.

Results and Discussion

Synthesis of Polyamides with NBD Residues in the Main Chain. Interfacial polycondensation between NBDC dissolved in chloroform and DPP in NaOH aqueous solution was performed at room temperature in the presence of some phase transfer catalysts (PTC)s or without any catalyst (Scheme 1). As summarized in Table 1, the yield and the degree of reduced viscosity of the resulting polyamide were very low when the reaction was carried out without PTC. On the other hand, polymers with relatively high reduced viscosities were obtained in very good yields using PTCs such as TEAC, TEAB, TBAB, BTEAC, or CTMAB. This result means that polyamide 1 containing a NBD residue in the main chain was

Table 2. Polycondensation of NBDC with Various Diamines[a]

run no.	polym no.	diamine	yield, %	η_{red},[b] dL/g	λ_{max},[c] nm
7	1	DPP	92	0.09	250
8	2	piperazine	81	0.13[d]	260
9	3	HMDA	79	0.10	250
10	4	*m*-XDA	77	0.09	252
11	5	MDA	53	0.11	242, 326
12	6	ODA	65	0.11	247, 335

[a] The reaction was performed between 3 mmol of NBDC in 6 mL of chloroform and 3 mmol of a diamine using 10 mol % of TBAB in 4 wt % aqueous NaOH solution (6 mL) at room temperature for 2 h. [b] Measured at 0.5 g/dL in DMF at 30 °C. [c] Measured at the film state. [d] Measured at 0.5 g/dL in *m*-cresol at 30 °C.

Table 3. IR and ^{1}H NMR Spectra of Polyamides with NBD Moieties

polym no.	IR, cm^{-1} (film on KRS)	^{1}H NMR, ppm (in CDCl$_3$)
1	1621 (C=O and C=C)	0.50–3.75 (CH$_2$ and CH), 6.50–6.80 (CH=CH)
2	1624 (C=O and C=C)	1.75–4.05 (CH$_2$ and CH), 6.50–7.00 (CH=CH)
3	1640 (C=O)	0.65–4.20 (CH$_2$, CH, and NH), 6.50–6.90 (CH=CH)
4	1642 (C=O) 1610 (C=C)	1.60–5.10 (CH$_2$, CH, and NH), 6.80–7.60 (CH=CH and aromatic protons)
5	1652 (C=O) 1613 (C=C)	1.75–2.65 (CH$_2$), 3.55–4.55 (CH and NH), 6.75–7.85 (CH=CH and aromatic protons)
6	1645 (C=O) 1606 (C=C)	1.85–4.55 (CH$_2$, CH, and NH), 6.05–7.95 (CH=CH and aromatic protons)

synthesized in high yield due to the condensation reaction of NBDC with DPP in the presence of PTCs. However, the molecular weight of the resulting polyamide 1 was rather disappointingly low.

The reactions of NBDC with other secondary and primary diamines such as piperazine, HMDA, *m*-XDA, MDA, and ODA were also carried out to give the corresponding polyamides 2–6, respectively. The results are summarized in Table 2, and IR and ^{1}H NMR spectra of these polyamides are summarized in Table 3. These data show that various polyamides with different NBD residues in the main chain were obtained in good yields under the same reaction conditions, although the molecular weights of the resulting polymers were also not as high as with polyamide 1 even in the presence of TBAB as a PTC. It seems that the bulky substituent group on the NBDC causes steric hindrance and is thus an unsuitable dicarboxylic acid chloride for obtaining high molecular weight polyamides.

Direct polycondensation between 2,5-norbornadiene-2,3-dicarboxylic acid and DPP was performed using a combination of triphenyl phosphite and pyridine as the activating reagent at 60 °C, as previously reported,[22] to obtain the polymer with the high molecular weight (see run no. 13 in Table 4). A polymer with the same structure as polyamide 1 was synthesized in 88% yield. However, the viscosity of the resulting polymer is not as high, and it contained some amount of the byproduct diphenyl phosphate, which was confirmed by the ^{1}H NMR spectrum, although several reprecipitations of the polymer were performed.

Table 4. Direct Polycondensation of 2,5-Norbornadiene-2,3-dicarboxylic Acid with Various Diamines Using DTBOP as Activating Agent[a]

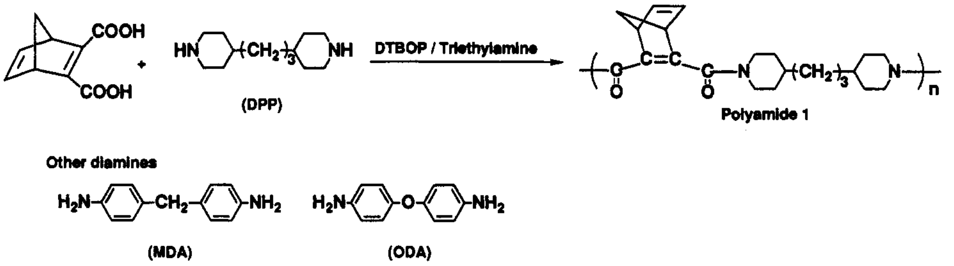
run no.	polym no.	diamine	solvent (amt, mL)	yield, %	η_{red},[b] dL/g
13	1	DPP	NMP (10)[c]	88	0.19
14	1	DPP	NMP (0.5)	92	0.04
15	1	DPP	DMAc (0.5)	76	0.04
16	1	DPP	HMPA (1.0)	96	0.06
17	5	MDA	NMP (1.0)	87	0.11
18	6	ODA	NMP (1.0)	98	0.13

[a] The reaction was performed with 1 mmol of monomers using the DTBOP (2.1 mmol)–triethylamine (2 mmol) system as an activating agent at room temperature for 24 h. [b] Measured at 0.5 g/dL in DMF at 30 °C. [c] The reaction was performed using the triphenyl phosphite–pyridine system as an activating agent (see Experimental Section).

Since separation of the byproduct diphenyl phosphate from the polyamide produced by the above polycondensation using the triphenyl phosphite and pyridine system may be thought to be very difficult, the other method for the direct polycondensation of 2,5-norbornadiene-2,3-dicarboxylic acid and DPP using a DTBOP and triethylamine combination as the activating reagent, as reported by Ueda et al.,[20] was attempted (Scheme 2). As summarized in Table 4, the reaction with DPP proceeded very smoothly to give the corresponding polyamide 1 with high yields (76–96%) in NMP, DMAc, and HMPA. The reaction with aromatic diamines MDA and ODA also gave the corresponding polyamides 5 and 6 with 87 and 98% yields, respectively. However, the viscosities of the thus-obtained polyamides were rather disappointingly low. It may be that some part of the 2,5-norbornadiene-2,3-dicarboxylic acid produced the corresponding 2,5-norbornadiene-2,3-dicarboxylic anhydride as a byproduct during the polycondensation with diamines and thus polyamides of high viscosity were not obtained by both the above direct polycondensation methods.

Since polyamides containing NBD residues in the main chain produced by the reaction of NBDC with some diamines or by the reaction of 2,5-norbornadiene-2,3-dicarboxylic acid with the same diamines did not have high viscosity, the interfacial polycondensation of NBDC and other acyl dichlorides with DPP was also tried using TBAB as a PTC to give the corresponding copolymers with high viscosities (Scheme 3). As summarized in Table 5, the viscosity of the resulting copolyamides (7–11) increased with increasing ADC concentration. Copolyamide 12 prepared by the reaction of NBDC(50) and IPC(50) with DPP also showed a higher viscosity than polyamide 1 prepared with only NBDC.

Scheme 2



Scheme 3

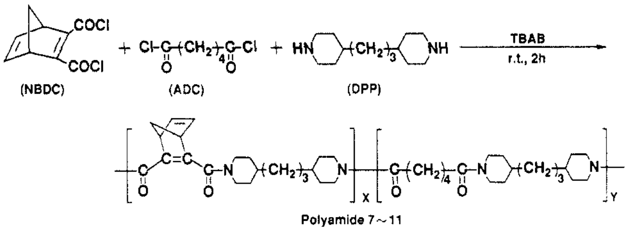


Table 5. Synthesis of Copolyamides with NBD Residues by Polycondensation of NBDC (I) and Acyl Dichloride (II) with DPP[a]

run no.	polym no.	acyl dichloride (II)	feed ratio I:II	yield, %	composition[b] I:II	η_{red},[c] dL/g
19	**7**	ADC	90:10	92.6	88:12	0.07
20	**8**	ADC	70:30	84.5	65:35	0.10
21	**9**	ADC	50:50	95.1	42:58	0.17
22	**10**	ADC	30:70	95.1	24:76	0.23
23	**11**	ADC	10:90	90.0	9:91	0.39
24	**12**	IPC	50:50	96.4	50:50	0.15

[a] The reaction was performed between 3 mmol of acyl dichlorides dissolved in 6 mL of chloroform and 3 mmol of DPP using 10 mol % of TBAB in 4 wt % aqueous NaOH solution (6 mL) at room temperature for 2 h. [b] Estimated by the ^{1}H NMR spectrum. [c] Measured at 0.5 g/dL in DMF at 30 °C.

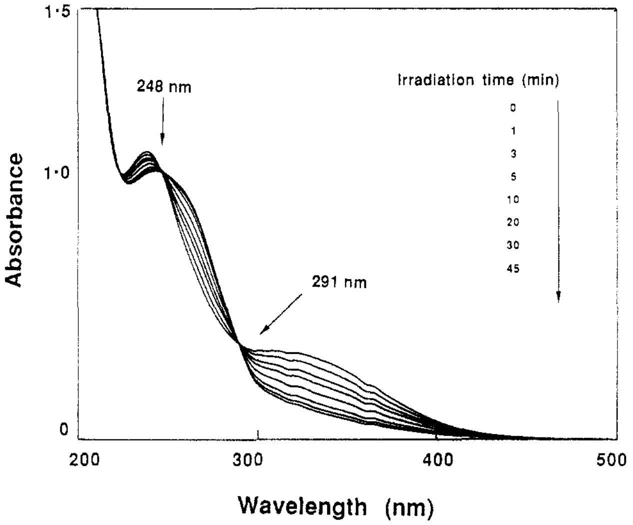


Figure 1. Change in the UV spectrum of polyamide **5** in the film state upon photoirradiation.

Photochemical Valence Isomerization of the NBD Residue in the Polyamide. The UV data for the polyamide films are summarized in Table 2. Although polyamides **1–4** prepared by the reaction with alphatic diamines showed absorption maxima near 250 nm, polyamides **5** and **6** prepared by the reaction with aromatic diamines showed absorption maxima at 326 and 335 nm, respectively.

As shown in Figure 1, the absorption maximum at 326 nm of polyamide **5** film decreased gradually, indicating that the NBD residue was being isomerized to the corresponding QC group under photoirradiation. The UV spectrum change of this polyamide also showed the appearance of two isosbestic points at 248 and 291 nm, meaning that the photochemical valence isomerization from the NBD residue to the corresponding QC group in the main chain of polyamide **5** occurred without any side reaction in the film state.

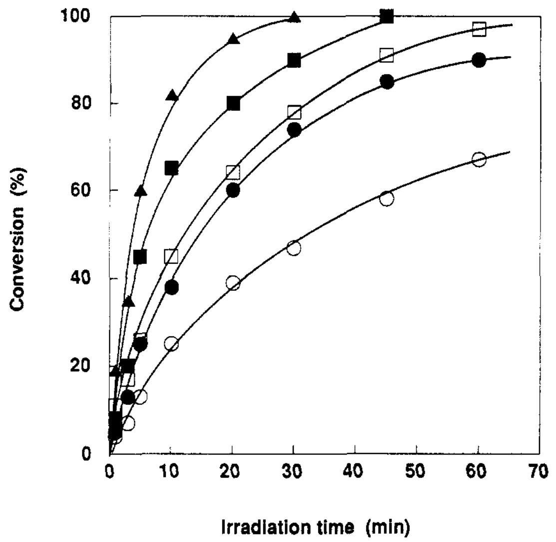


Figure 2. Photochemical valence isomerization of the NBD residues in polyamides in dichloromethane solution (1.0 × 10^{-4} mol/L): (▲) polyamide **5**; (■) polyamide **6**; (□) polyamide **3**; (●) polyamide **4**; (○) polyamide **1**.

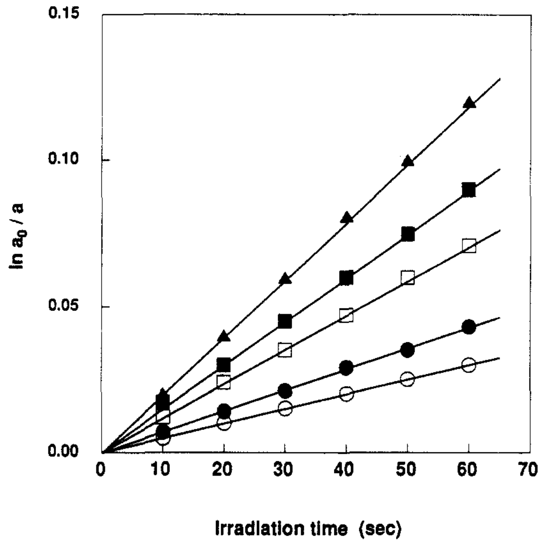


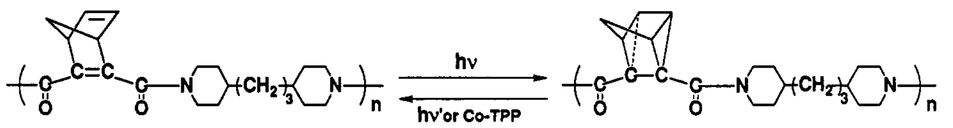
Figure 3. Rate of photochemical reaction of the NBD residues in polyamides in dichloromethane solution (1.0 × 10^{-4} mol/L): (▲) polyamide **5**; (■) polyamide **6**; (□) polyamide **3**; (●) polyamide **4**; (○) polyamide **1**.

Table 6. First-Order Rate Constant of Photochemical Valence Isomerization of the NBD Residues in Polyamides under Photoirradiation

polym no.	additive (amt, mol %)	in the solution 10^3k_{obsd}, s^{-1}	at the film state, 10^3k_{obsd}, s^{-1}
1	none	0.47	0.09
3	none	1.17	1.00
4	none	0.69	0.57
5	none	1.94	1.66
6	none	1.44	1.29
1	DABP (5)	1.60	
1	MK (5)	1.57	
5	Co-TPP (10)		1.54
5	Co-TPP (20)		1.15
5	Co-TPP (30)		0.80

The changes of UV spectra of polyamides **1–6** were estimated in the film state under air and in dichloromethane solution under nitrogen upon long time photoirradiation, and the conversions from NBD residues to QC groups in the polymers were calculated from the degree of decreases of optical densities of the polymers. As shown in Figure 2, polyamides **5** and **6** containing NBD residues with aromatic *N*-phenylcarbamoyl groups had higher photochemical reactivities than polyamides **3** and **4** containing NBD residues with aliphatic *N*-alkylcarbamoyl groups in the dichloromethane solution. Interestingly

Scheme 4



enough, polyamides 3 and 4 prepared from the reaction with primary diamines also showed a higher reactivity than polyamide 1 prepared from the reaction with secondary diamine DPP under the same irradiation conditions.

As shown in Figure 3, it was found that the observed rates of photochemical reaction of the NBD residues in the polymer main chains obeyed first-order kinetics, as did the rate of photochemical reaction of the pendant NBD moieties[11] in the polymer in the dichloromethane solution, and the rate constants of the above polyamides are summarized in Table 6.

The rates of photochemical reaction of the NBD residues in the polyamides in the initial stage were also measured in the film state, and the observed rates of the reaction of the NBD residues in the polymers also obeyed first-order kinetics. As summarized in Table 6, the observed rate constants of polyamides exhibit the following order: polyamide 5 > polyamide 3 > polyamide 6 > polyamide 4 > polyamide 1, in which the order of polyamides 3 and 6 was different from that of the photochemical reaction in the dichloromethane solution. These results mean that the photochemical reactivity of the NBD residue in the polyamide main chain in the solution corresponded mainly to the optical density in the NBD residues at each wavelength, although the reaction rate of the polyamide was affected by the light source used.[18,19] On the other hand, the reaction rate of the polyamides with NBD residues may also have been affected by the T_g of each polymer at the film state in the same way as the reaction rate of the photosensitive polymer.[23]

Since the rate of photochemical reaction of the NBD residue in polyamide 1 was lower than that of aromatic polyamides 5, the photosensitization of polyamide 1 was examined in the dichloromethane solution. As summarized in Table 6, the rate of the reaction of polyamide 1 was extremely enhanced by the addition of 5 mol % DABP and MK. The same results have been obtained[18] on the photochemical reaction of polyamide 1 with the above sensitizers in the film state. These results suggest that the NBD residue in polyamide 1 was effectively sensitized by the addition of appropriate photosensitizers (Scheme 4).

The photochemical reaction of polyamide 5, which had the highest photochemical reactivity among the prepared polyamides, was performed with Co-TPP catalyst in the film state. As summarized in Table 6, the rate of photochemical reaction of the NBD residue in polyamide 5 decreased with increasing catalyst concentration. It may be that the main reason is a filter effect due to the Co-TPP catalyst, which has strong absorptions at 265, 410, and 527 nm.[14b]

Catalytic and Photochemical Reversion of the Resulting QC Groups in the Polyamide. When the catalyst Co-TPP dissolved in dichloromethane was added to the photoirradiated polymer solution in dichloromethane, the produced QC groups in the polyamides reverted smoothly to the corresponding NBD residues (Scheme 4), and it was found that the observed rates of catalytic reversion of QC groups in the polymer main chains obeyed first-order kinetics, as did the rate of catalytic reversion of pendant QC groups in the polymers[11] in the dichloromethane solution. As summarized in Table 7, the QC group in polyamide 3 having a flexible polymer main chain showed the highest rate of reversion. Furthermore, the rate of catalytic reversion of the produced QC groups in the polyamides took the following order: polyamide 3 > polyamide 5 > polyamide 6 > polyamide 4 > polyamide 1. This might be due to the steric hindrance of the polymer main chain caused by the rate of catalytic reversion of the QC groups in the polyamides.

Table 7. First-Order Rate Constant of Catalytic Reversion of QC Groups in Polyamides in the Dichloromethane Solution[a]

polym no.	$10^4 k_{obsd}$, s^{-1}	polym no.	$10^4 k_{obsd}$, s^{-1}
1	1.50	5	3.23
3	3.60	6	3.03
4	1.70		

[a] The catalytic reversion of the QC group in the polymer was carried out in dichloromethane solution (1.0×10^{-4} mol/L) using Co-TPP catalyst (3.0×10^{-5} mol/L).

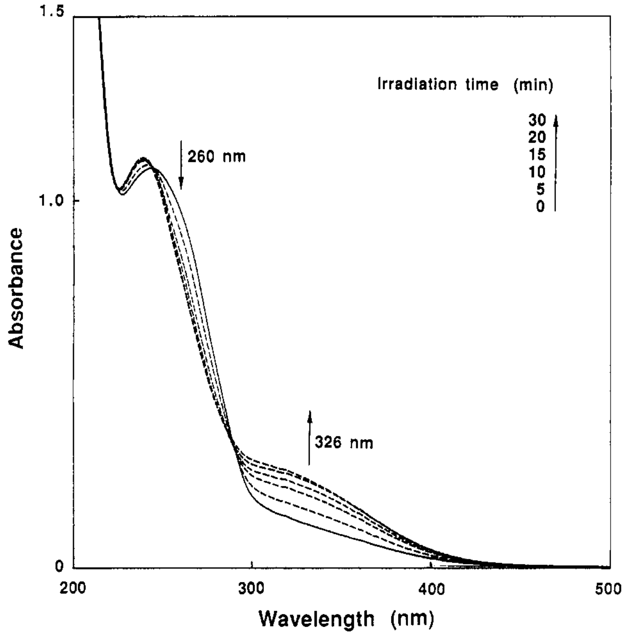


Figure 4. Change in the UV spectrum of polyamide 5 with the QC group upon irradiation with 265-nm light in the film state.

As shown in Figure 4, the UV spectrum of the photoirradiated polyamide 5 containing the QC group in the main chain reverted to that of the corresponding NBD residue with about 75% conversion, and with two isosbestic points at 248 and 291 nm, when the QC group in the polyamide film on the quartz cell was irradiated with 265-nm light through a monochromator for 30 min. This means that photochemical reversion of the produced QC group in the polymer main chain occurred without any side reaction upon irradiation at suitable wavelengths.

Considering the above result, the photochemical reversion of the QC group in the photoirradiated polyamide 5 was done under irradiation with UV light of different wavelengths, which was performed with a xenon lamp fitted with a monochromator. As shown in Figure 5, the observed rate of the reversion upon irradiation at 260 nm was faster than the rates upon irradiation at other wavelengths, and the rate of reversion of the produced QC

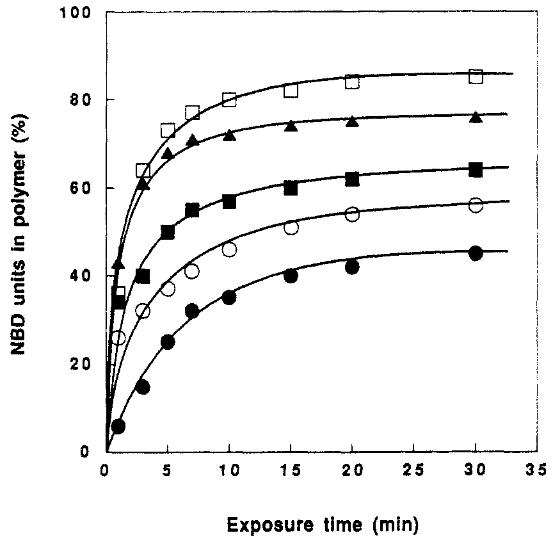


Figure 5. Rate of photochemical reversion of the QC group in polyamide **5** in the film state: (□) 260 nm; (▲) 265 nm; (■) 270 nm; (○) 255 nm; (●) 235 nm.

Table 8. First-Order Rate Constant of Photochemical Reversion of the QC Group in Polyamide 5 in the Film State

wavelength, nm	10^3k_{obsd}, s^{-1}	wavelength, nm	10^3k_{obsd}, s^{-1}
235	0.23	265	3.33
255	2.08	270	3.00
260	3.55		

groups in the polyamides took the following order: 260 nm > 265 nm > 270 nm > 255 nm > 235 nm. This means that the rate of photochemical reversion of the QC group in the polyamide **5** was related to the absorption maxima of the QC group at $\lambda = 260$ nm.

Finally, this result also suggests that although the observed rates of the reversion obeyed first-order kinetics in the initial stage (Table 8), the conversion process of the QC groups reached saturation upon each irradiation after about 30 min. However, a detailed correlation between the degree of conversion of the QC group and the irradiated wavelength could not be drawn from this data alone.

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