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Design of Multifunctional Polymeric Photosensitizers Containing Pendant (Nitroaryl)oxy Groups and Quaternary Onium Salts for Photochemical Valence Isomerization of Potassium 3-Phenyl-2,5-norbornadiene-2-carboxylate

Tadatomi Nishikubo,* Tatsuo Kawashima, Katsumi Inomata, and Atsushi Kameyama

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221 Japan

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ABSTRACT: Photochemical valence isomerization of potassium 3-phenyl-2,5-norbornadiene-2-carboxylate (PNC) was carried out using soluble or insoluble multifunctional polymeric photosensitizers containing both pendant (nitroaryl)oxy groups as photosensitizer moieties and pendant quaternary ammonium or phosphonium salts as substrate-attracting groups. These photosensitizers were prepared by partial substitution reaction of poly(*p*-(chloromethyl)styrene) or insoluble chloromethylated poly(styrene) bead with appropriate amounts of potassium 4-nitro-1-naphthoxide or 4-nitrophenoxide using a phase-transfer catalyst followed by an addition reaction of the remaining chloromethyl groups in the polymers with some tertiary phosphines or amines. The rates of the photochemical valence isomerization of PNC in the presence of multifunctional polymeric photosensitizers were significantly higher than those of PNC with low molecular weight photosensitizers in methanol. The efficiency of the multifunctional polymeric photosensitizers was strongly affected by the kind of photosensitizing moiety and substrate-attracting group, the content of pendant photosensitizing moiety in the polymer chain, and the photosensitizer concentration in the reaction system. It was found that the polymeric photosensitizer containing 11.8 mol % of a pendant 4-nitro-1-naphthoxy moiety as a photosensitizing group and a pendant benzyltributylphosphonium salt as a substrate-attracting group has the highest efficiency for the valence isomerization of PNC among the prepared multifunctional polymeric photosensitizers.

Introduction

Polymeric photosensitizers containing pendant photosensitizing groups such as benzophenone,[1-4] acetophenone,[5,6] or rose bengal[7-9] moieties have been widely used in various photochemical reactions such as isomerization, dimerization, and oxidation of organic compounds in solution. However, the efficiency of these polymeric photosensitizers is no better than that of the corresponding low molecular weight photosensitizers except for that reported in a recent study[10] by Neckers et al. Although Hautala et al. has reported[11] the photochemical valence isomerization of norbornadiene (NBD) to quadricyclane (QC), which is a very important step in the solar energy storage process and which uses the cross-linked poly(styrene) bead or silica gel containing pendant 4-(*N,N*-dimethylamino)benzophenone moiety as a photosensitizing group, the efficiencies of his polymeric photosensitizers were lower than those of the corresponding low molecular weight photosensitizers. It is known that the mobility of the photosensitizing group bonded to the polymer backbone is definitely restricted, and the self-quenching between neighboring photosensitizing groups in the polymer chain occurs frequently in ordinary polymeric photosensitizer systems.

Recently, we have proposed[12-17] the concept of multifunctional polymeric photosensitizers, in which both pendant photosensitizing moieties and substrate-attracting groups play the coordinating role. These new multifunctional polymeric photosensitizers have higher efficiencies than the corresponding low molecular weight photosensitizers on the photoisomerizations of cinnamic acid and sorbic acid derivatives because the reactant is attracted to the vicinity of the polymer chain by the substrate-attracting groups and energy is transferred effectively from the excited photosensitizing moiety in the polymer to the reactant.

This article reports on the successful photochemical valence isomerization of potassium 3-phenyl-2,5-norbornadiene-2-carboxylate (PNC) to the corresponding QC derivative in the presence of some designed multifunctional polymeric photosensitizers containing both pendant (nitroaryl)oxy groups as photosensitizer moieties and pendant quaternary ammonium or phosphonium salts as substrate-attracting groups. Furthermore, the effects on the valence isomerization of PNC in this reaction system of such factors as a kind of photosensitizing moiety and substrate-attracting group, content of pendant photosensitizing moiety in the polymer, kind of reaction medium, and photosensitizer concentration are investigated in detail.

Experimental Section

Materials. The solvents were purified in the usual way prior to use. Commercial tripropylamine (TPA), tributylamine (TBA), trihexylamine (THA), tripropylphosphine (TPP), tributylphosphine (TBP), and trihexylphosphine (THP) were used without further purification. The phase-transfer catalyst, tetrabutylammonium bromide (TBAB), was recrystallized twice from ethyl acetate. 3-Phenyl-2,5-norbornadiene-2-carboxylic acid was synthesized by Diels–Alder reaction as follows: Phenylpropionyl chloride (12.3 g, 0.075 mmol) and cyclopentadiene (30 mL, 0.36 mmol) were allowed to react in the presence of 0.2 g of picric acid at room temperature for 1 h and then refluxed for 1 h. Excess cyclopentadiene was evaporated, and the residue was dissolved in toluene. The material in solution was extracted with aqueous solution of sodium hydrogen carbonate, and the aqueous phase was neutralized with sulfuric acid to precipitate the product. It was filtered, washed several times with water, and dried in vacuo. The crude product was recrystallized from hexane as reported previously:[18] yield 52.8%; mp 135–136 °C. PNC, potassium 4-nitro-1-naphthoxide (PNN), and potassium 4-nitrophenoxide (PNP) were prepared by reaction of potassium hydroxide with corresponding the acid, naphthol, or phenol in methanol and recrystallized. Poly(*p*-(chloromethyl)styrene) (PCMS; the re-

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Table I
Conditions and Results of the Substitution Reaction of PCMS with the Potassium Salt of Photosensitizer Compounds[a]

run no.	PCMS, mmol	photosensitizer compound (mmol)	solvent, mL	yield, g	DF,[b] mol %	η red,[c] dL/g
1	10	PNN (0.5)	20	1.26	3.4	0.19
2	10	PNN (1.0)	20	1.37	8.2	0.25
3	50	PNN (7.5)	100	7.52	11.8	0.27
4	10	PNN (2.0)	20	1.48	16.8	0.30
5	10	PNN (3.0)	20	1.60	24.8	0.42
6	10	PNN (4.0)	20	1.72	33.5	0.44
7	10	PNP (1.5)	20	1.47	14.5	0.43

[a] The reaction was carried out with 10 mol % of TBAB to PCMS in DMF at 30 °C for 24 h. [b] Degree of functionalization, which was estimated by UV spectrum. [c] Measured at a concentration of 0.5 g/dL in DMF at 30 °C.

Table II
Conditions and Results of the Substitution Reaction of PCMS-3C with the Potassium Salt of a Photosensitizer Compound[a]

run no.	PCMS-3C bead, mmol	photosensitizer compound (mmol)	yield, g	Cl content in polymer, mg/g	DF,[b] mol %
8	20	PNN (1.0)	3.43	187.9	5.0
9	20	PNN (2.0)	3.55	168.0	10.0
10	20	PNN (3.0)	3.64	156.8	13.1
11	20	PNN (4.0)	3.82	145.1	16.5

[a] The reaction was carried out in the presence of 10 mol % of TBAB to PCMS-3C in 50 mL of DMF at 80 °C for 48 h. [b] Degree of functionalization, which was determined by elemental analysis of chlorine.

duced viscosity of the polymer in DMF was 0.16 dL/g, measured at a concentration of 0.5 g/dL at 30 °C) was prepared in 71.4% yield by radical polymerization of *p*-(chloromethyl)styrene (which was provided from Seimi Chemical Co., Ltd., and distilled twice under reduced pressure) (61.05 g, 0.40 mol) by using AIBN (0.66 g, 4.0 mmol) in toluene (80 mL) at 60 °C for 5 h and then at 80 °C for 3 h under flowing nitrogen, followed by precipitation in methanol and reprecipitation twice from THF into methanol and drying at 60 °C under reduced pressure. The macroreticular chloromethylated poly(styrene) bead cross-linked with 3% divinyl benzene (PCMS-3C; 209.7 mg/g as chlorine, provided by Mitsubishi Kasei Co., Ltd.) was washed in hot water, methanol, and twice in boiling acetone and then dried at 60 °C under reduced pressure.

Apparatus. UV spectra were recorded on the Shimazu Models UV-240 and UV-2100S spectrophotometers.

Typical Procedure for the Synthesis of a Polymeric Photosensitizer Containing Pendant Chloromethyl Groups and Photosensitizing Groups. Polymeric photosensitizers containing pendant chloromethyl groups and photosensitizing groups were synthesized by partial substitution reaction of PCMS or PCMS-3C with appropriate amounts of PNN or PNP using TBAB as a phase-transfer catalyst in DMF according to the method reported previously.[11,16] The conditions and results are summarized in Tables I and II, respectively.

Typical Procedure for the Synthesis of a Multifunctional Polymeric Photosensitizer Containing both Pendant Photosensitizing Groups and Substrate-Attracting Groups. Multifunctional polymeric photosensitizers containing both pendant photosensitizing groups and substrate-attracting groups were also synthesized by addition reaction of polymers having both pendant chloromethyl groups and photosensitizing groups with 50% larger amounts of tertiary phosphines or amines as reported previously.[11,16] The conditions and results are summarized in Tables III and IV, respectively.

Measurement of Adsorption of PNC to an Insoluble Multifunctional Polymeric Photosensitizer Bead. PCN (3.76 mg, 1.5 × 10^{-4} mol/L) was dissolved in 100 mL of water or methanol, and then the solution was stirred for 30 min. The multifunctional photosensitizer; P3C($NN_{13.1}$–BTBP) (10.9 mg, 2.54 × 10^{-4} mol/L as substrate-attracting group), which has 13.1 mol % of pendant 4-nitro-1-naphthoxy (NN) moieties and 73.9 mol % of pendant benzyltripropylphosphonium chloride (BTPP) residues, was added into the solution with magnetic stirring. The degree of adsorption of PNC was determined by decrease of the absorption maximum at 290 nm of PNC in the solution using UV a spectrophotometer.

Photochemical Reaction of PNC Using a Soluble Multifunctional Polymeric Photosensitizer. PNC (3.76 mg, 1.5 × 10^{-4} mol/L) and photosensitizer P($NN_{11.8}$–BTPP) (5.95 mg, 2.25 × 10^{-5} mol/L as photosensitizing group), which contains 11.8 mol % of pendant NN moieties as the photosensitizing group and 88.2 mol % of pendant BTPP residues as the substrate-attracting group, were dissolved in 100 mL of water and then stirred for 30 min under nitrogen. The photochemical reaction of the solution was carried out in a cylindrical Pyrex glass photochemical reactor with water jacket immersion and thermometer at 30 °C using a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) through a filter (Toshiba UV-33) at a distance 36 cm, in which the intensity of the irradiated light was kept always at 0.63–0.66 mW/cm^2 (366 nm), in nitrogen atmosphere with stirring. The degree of conversion of PNC to the corresponding QC derivative was determined by decrease of the absorption maximum at 290 nm of PNC in the solution using a UV spectrophotometer.

Photochemical Reaction of PNC Using an Insoluble Multifunctional Polymeric Photosensitizer Bead. PNC (3.76 mg, 1.5 × 10^{-4} mol/L) was dissolved in water (100 mL), and then P3C($NN_{13.1}$–BTPP) (6.50 mg, 3.0 × 10^{-5} mol/L as photosensitizing group) having 13.1 mol % of pendant NN moieties and 73.9 mol % of pendant BTPP residues was added to the solution. The solution containing polymer bead was stirred for 1 h under nitrogen, and then the photochemical reaction was performed under the same irradiation conditions applied to the above photochemical reaction. The reaction of PNC in solution was also periodically analyzed by UV spectrometer.

Determination of the Quantum Yield of the Photochemical Reaction of PNC in the Presence of a Multifunctional Polymeric Photosensitizer. An aqueous solution composed of PNC (1.5 × 10^{-4} mol/L) with some multifunctional polymeric photosensitizer (2.25 × 10^{-5} mol/L as photosensitizing group) or without any photosensitizer dissolved in water (3 mL) was charged into a rectangular quartz cell. The solution in the quartz cell was irradiated at 366 nm with monochromator (JASCO Model CT-10) fitted with a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) under nitrogen, and then the degree of conversion of PNC was monitored by UV spectrophotometer. The light intensity was determined by ammonium ferrioxalate actinometry.[19]

Results and Discussion

Syntheses of Multifunctional Polymeric Photosensitizers Containing both Nitroaryl Moieties and Quaternary Onium Residues. Soluble and insoluble polymeric photosensitizers containing various amounts of pendant 4-nitro-1-naphthoxy (NN) or 4-nitrophenoxy (NP) moieties and pendant chloromethyl (CM) group were synthesized by partial substitution reactions of PCMS or PCMS-3C with PNN or PNP using 10 mol % (to the CM group in the polymer) of TBAB as a phase-transfer catalyst (PTC) in DMF at 30 °C for 24 h or at 80 °C for 48 h, respectively. The results are summarized in Tables I and II. The substitution reaction of the pendant CM groups in soluble PCMS with PNN and PNP proceeded smoothly with high conversions under mild reaction conditions. The reaction of the CM groups in the cross-linked PCMS-3C with PNN also proceeded with high conversions under the given reaction conditions, although the reactivity of CM groups in the cross-linked polystyrene bead was essentially lower than that of CM groups in soluble PCMS under the same conditions.

The further introduction of a substrate-attracting group on to the above polymeric photosensitizers was carried

Table III
Conditions and Results of the Addition Reaction of Partially Substituted PCMS by PNN or PNP with Tertiary Phosphines or Amines[a]

run no.	ClMe group in polymer, (mmol)	phosphine or amine (mmol)	solvent, mL	temp, °C	yield, g	Cl content in polymer, mg/g	onium salt[b] in polymer, mol %	η red,[c] dL/g
12	P(CMS-NN$_{3.4}$) (5.0)	TPP (7.5)	10	50	1.40	109.6	96.6	1.34
13	P(CMS-NN$_{8.2}$) (5.0)	TPP (7.5)	10	50	1.48	104.3	91.8	1.44
14	P(CMS-NN$_{11.8}$) (7.5)	TPP (11.3)	15	50	2.34	100.3	88.2	1.43
15	P(CMS-NN$_{11.8}$) (2.5)	TBP (3.8)	5	60	0.74	93.1	81.7	1.28
16	P(CMS-NN$_{11.8}$) (2.5)	THP (3.8)	5	80	0.78	74.4	87.8	1.14
17	P(CMS-NN$_{11.8}$) (5.0)	TPA (7.5)	20	80	1.37	105.5	87.8	1.30
18	P(CMS-NN$_{11.8}$) (2.5)	TBA (3.8)	5	80	0.65	93.6	88.2	
19	P(CMS-NN$_{11.8}$) (2.5)	THA (3.8)	10	80	0.73	76.5	88.2	
20	P(CMS-NN$_{16.8}$) (5.0)	TPP (7.5)	10	50	1.64	94.6	83.2	1.49
21	P(CMS-NN$_{24.8}$) (2.5)	TPP (3.8)	5	60	0.82	85.7	75.2	1.51[d]
22	P(CMS-NN$_{33.5}$) (2.5)	TPP (3.8)	10	60	0.99	76.0	66.5	1.53[d]
23	P(CMS-NP$_{14.5}$) (2.5)	TPP (3.8)	5	50	0.83	99.7	85.5	0.87

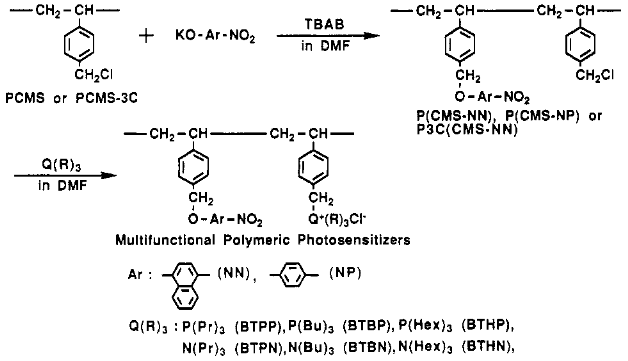
[a] The reaction was carried out in DMF for 48 h. [b] Quaternary onium salt in the polymer was calculated from elemental analysis of chlorine. [c] Measured at a concentration of 0.5 g/dL in water at 30 °C. [d] Measured at a concentration of 0.5 g/dL in methanol at 30 °C.

Table IV
Conditions and Results of the Addition Reaction of Partially Substituted PCMS-3C by PNN with Tertiary Phosphines[a]

run no.	polymer bead	tertiary phosphine	temp, °C	yield, g	Cl content in polymer, mg/g	onium salt[b] in polymer, mol %
24	P3C(CMS-NN$_{5.0}$)	TPP	60	0.83	101.6	82.0
25	P3C(CMS-NN$_{10.0}$)	TPP	60	0.84	95.6	76.9
26	P3C(CMS-NN$_{13.1}$)	TPP	60	0.89	91.8	73.9
27	P3C(CMS-NN$_{13.1}$)	TBP	60	0.80	82.9	73.8
28	P3C(CMS-NN$_{13.1}$)	THP	80	0.92	70.0	72.1
27	P3C(CMS-NN$_{16.5}$)	TPP	60	0.96	87.6	70.5

[a] The reaction was carried out with 2.5 mmol of P3C(CMS-NN) (as chloromethyl group) and 3.8 mmol of tertiary phosphine in 10 mL of DMF for 120 h. [b] Quaternary onium salt in the polymer was calculated from elemental analysis of chlorine.

Scheme I



out by the addition reactions of the series of P(CMS–NN), P(CMS–NP), and P3C(CMS–NN) containing both pendant CM groups with 1.5 times larger amounts of tertiary phosphines such as TPP, TBP, and THP or tertiary amines such as TPA, TBA, and THA at 50–80 °C for 48 or 120 h, respectively. The results are summarized in Tables III and IV.

Introducing trialkylphosphine onto P(CMS–NN) depended on the alkyl length of the phosphines. The phosphines TPP and TBP were effectively introduced to the polymers at 50 and 60 °C, respectively, and THP at 80 °C, to yield the corresponding multifunctional polymeric photosensitizer series such as P(NN–BTPP)s, P(NN–BTBP), and P(NN–BTHP). This means that the reactivity of tertiary phosphines towards pendant CM groups in P(CMS–NN)s decreases with increasing number of carbon atoms in the alkyl chain due to their steric hindrance.[14] The reaction of P(CMS–NP) with TPP took place to give the corresponding polymer P(NP–BTPP) at 50 °C.

The reactions of P(CMS–NN) with tertiary amines such as TPA, TBA, and THA gave the corresponding polymers such as P(NN–BTPA)s, P(NN–BTBA), and P(NN–BTHA) at the relatively high temperature of 80 °C, because the reactivity of tertiary amines toward pendant CM groups in the polymer was lower than that of tertiary phosphines.[14]

Furthermore, it was found that multifunctional polymeric photosensitizers containing 3.4–16.8 mol % of pendant sensitizing groups and 96.6–81.7 mol % of pendant BTPP, BTBP, BTPA, or BTBA groups were soluble in water as well as in methanol. However, multifunctional polymeric photosensitizers with 24.8–33.5 mol % of pendant photosensitizing groups and 75.2–66.5 mol % of pendant BTPP groups were only soluble in methanol and not in water. Multifunctional polymeric photosensitizer with 11.8 mol % of pendant photosensitizing groups and 87.8 mol % of pendant BTHP or 88.2 mol % of pendant BTHA groups were soluble in methanol and acetone but insoluble in water. This result indicates that the solubility of these polymeric photosensitizers in water and in organic solvents was strongly affected by the degree of quaternarization of the pendant CM group, the degree of introduction of pendant photosensitizing group, and the kind of substrate-attracting group in the polymer.

The reactions of insoluble P3C(CMS–NN)s with TPP, TBP, and THP were also performed at 60–80 °C for 120 h to give the corresponding multifunctional polymeric photosensitizer beads such as P3C(NN–BTPP), P3C(NN–BTBP), and P3C(NN–BTHP). In this case, the reaction time was longer than of P(CMS–NN)s with tertiary phosphines, because the reactivity of pendant CM groups in the cross-linked poly(styrene) bead was lower than that of the CM groups of linear PCMS.[14,16]

As a result, soluble and insoluble multifunctional polymeric photosensitizers containing suitable amounts of pendant photosensitizing groups and substrate-attracting groups were prepared with high degree of conversion.

Adsorption and Ion-Exchange Reaction between an Insoluble Multifunctional Polymeric Photosensitizer Bead and PNC. The efficiency of substrate-attracting groups in multifunctional polymeric photosensitizers was evaluated using PNC and an insoluble bead

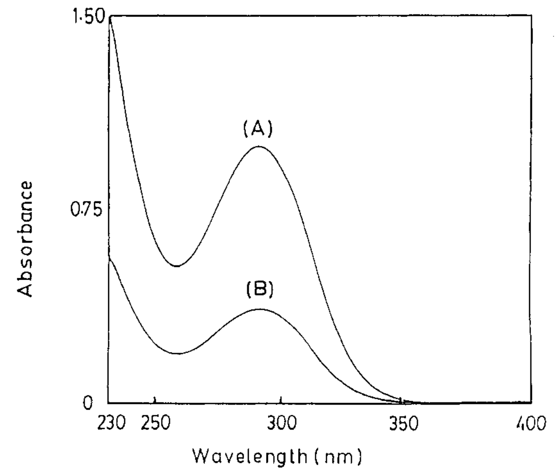


Figure 1. Change of UV spectrum of PNC (1.5 × 10^{-4} mol/L) by addition of polymer bead P3C(NN$_{13.1}$–BTPP) containing 13.1 mol % of pendant NN moiety and 73.8 mol % of pendant BTPP residue (2.54 × 10^{-4} mol/L as substrate-attracting group) in water: (A) before addition of polymer bead; (B) after addition of polymer bead.

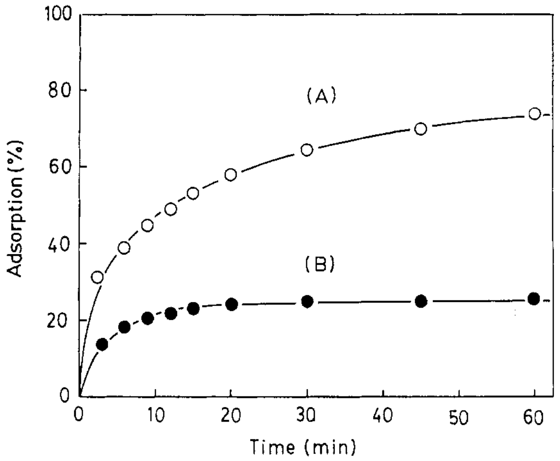


Figure 2. Rate of adsorption of PNC (1.5 × 10^{-4} mol/L) to polymer bead P3C(NN$_{13.1}$–BTBP) (2.54 × 10^{-4} mol/L as substrate-attracting group): (A) in water; (B) in methanol.

containing both a pendant NN moiety and BTPP group in water and in methanol, respectively. As shown in Figure 1, the absorption maximum (290 nm) in the UV spectrum of PNC in water decreased strongly with addition of insoluble multifunctional polymeric photosensitizer bead P3C(NN$_{13.1}$–BTPP), meaning that the PNC was adsorbed on the polymer bead.

Figure 2 shows the correlation between degree of adsorption and the time both in water and methanol. This result indicates that PNC was strongly adsorbed to the multifunctional polymeric photosensitizer bead, and then the ion-exchange reaction between the pendant BTBP group in the polymer bead and PNC occurred more effectively in water than in methanol. Furthermore, this result suggests that the state of equilibrium of the ion-exchange reaction appeared at 20 min in methanol and at 60 min in water at room temperature.

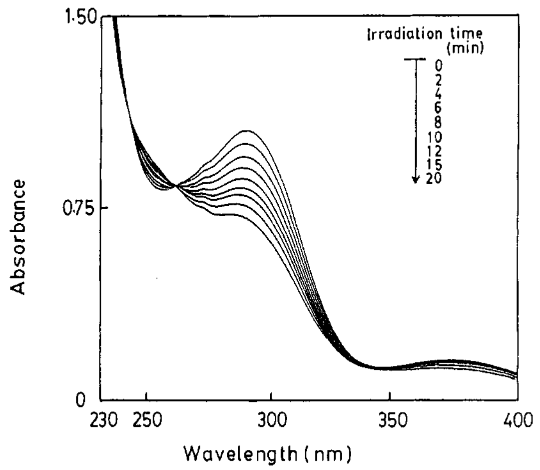


Figure 3. Change of UV spectrum of PNC (1.5 × 10^{-4} mol/L) in the presence of soluble polymer P(NN$_{11.8}$–BTPP) containing 11.8 mol % of pendant NN moiety and 88.2 mol % of pendant BTPP residue (2.25 × 10^{-5} mol/L as photosensitizing group) upon the irradiation with >330-nm light in water.

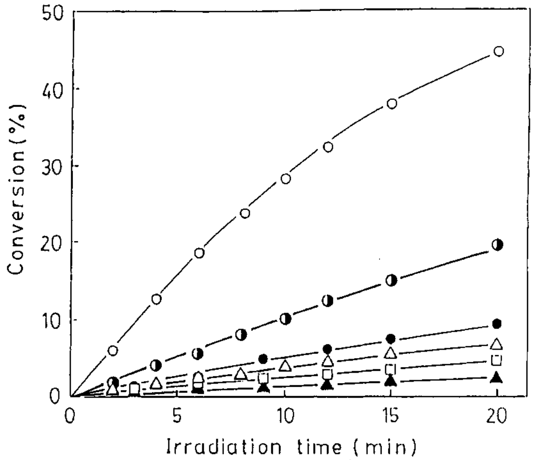
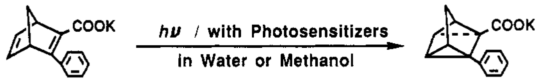


Figure 4. Rate of reaction of PNC (1.5 × 10^{-4} mol/L) using 15 mol % of photosensitizers upon the irradiation with >330-nm light in water: (○) with P(NN$_{11.8}$–BTPP); (◑) with P3C(NN$_{13.1}$–BTPP); (●) with 4-nitro-1-methoxynaphthalene; (△) with P(NP$_{14.5}$–BTPP); (□) without photosensitizer; (▲) with *p*-nitroanisole.

Scheme II



Photochemical Valence Isomerization of PNC Using Multifunctional Polymeric Photosensitizers. Although photochemical valence isomerization of methyl or benzyl esters of 3-phenyl-2,5-norbornadiene-2-carboxylic acid to the corresponding QC compounds has been reported recently[20,21] in organic solvent without photosensitizer, there is no report of the photosensitizing valence isomerization of NBD derivative in aqueous solution. As shown in Figure 3, the UV spectrum of PNC was gradually changed and two isosbestic points appeared at 244 and 266 nm when photoirradiation beyond 330-nm light was carried out in the presence of soluble multifunctional polymeric photosensitizer P(NN$_{11.8}$–BTPP) using a high-pressure mercury lamp with a glass filter. The absorption of PNC also decreased when an insoluble multifunctional photosensitizer bead P3C(NN$_{13.1}$–BTPP) was used in the irradiation under the same conditions. These results suggest that the photochemical valence isomerization of PNC would occurred selectively without any side reaction in the presence of multifunctional polymeric photosensitizers in aqueous solution.

As shown in Figure 4, the efficiency of multifunctional polymeric photosensitizers and the corresponding low molecular weight (LMW) photosensitizers was evaluated in methanol; 5 and 9 mol % of PNC (1.5 × 10^{-4} mol/L) were isomerized to the corresponding QC derivative under 20-min irradiation with >330-nm light without photosensitizer and with 15 mol % of LMW photosensitizer 4-nitro-

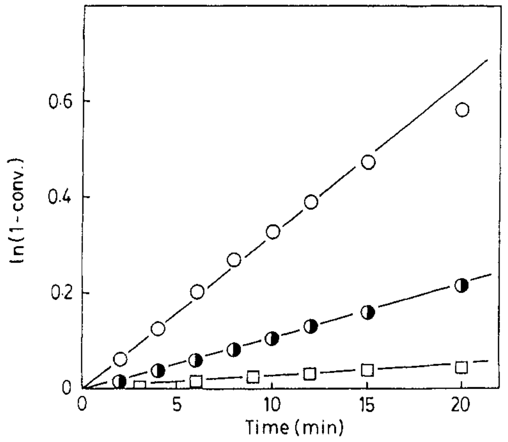


Figure 5. First-order dependence of the reaction of PNC (1.5 × 10^{-4} mol/L) using 15 mol % of photosensitizers upon the irradiation with >330-nm light in water: (○) with P(NN$_{11.8}$–BTPP); (◑) with P3C(NN$_{13.1}$–BTPP); (□) without photosensitizer.

1-methoxynaphthalene (absorption maximum; 361 nm in methanol), respectively. This indicates that the rate of photochemical reaction of PNC was slightly promoted by addition of 4-nitro-1-methoxynaphthalene.

On the other hand, 44 and 19 mol % of PNC were isomerized to the QC compound under the same irradiation conditions using 15 mol % of soluble multifunctional polymeric photosensitizer P(NN$_{11.8}$–BTPP) containing 11.8 mol % of pendant NN moieties (absorption maximum; 361 nm) and 88.2 mol % of pendant BTPP groups and insoluble poly(styrene) bead P3C(NN$_{14.5}$–BTPP) containing 14.5 mol % of pendant NN moieties and 73.8 mol % of pendant BTPP groups, respectively. Apparently, the photochemical isomerization of PNC was strongly enhanced by the multifunctional polymeric photosensitizers containing pendant NN moiety as the photosensitizing group, and the rate of reaction of PNC in this system was faster than with the corresponding LMW photosensitizers under the same irradiation conditions. Besides, the photosensitizing efficiency of soluble polymer P(NN$_{11.8}$–BTPP) was higher than that of insoluble bead P3C(NN$_{14.5}$–BTPP).

When the reaction of PNC was performed with 15 mol % of LMW photosensitizer *p*-nitroanisole (absorption maximum; 306 nm) under the same irradiation conditions, the rate of reaction of PNC decreased. However, with soluble multifunctional photosensitizer P(NP$_{14.5}$–BTPP) containing 14.5 mol % of pendant NP moieties (absorption maximum; 306 nm) and 85.5 mol % of pendant BTPP groups, the rate of reaction was slightly promoted.

These results suggest that substrate PNC was concentrated in the vicinity of the polymer chain due to the action of pendant substrate-attracting groups such as BTPP and that the energy transfer occurred effectively from pendant NN or NP moieties to the attracted PNC molecules. These results also indicate that the efficiency of the multifunctional polymeric photosensitizers was affected strongly by the correlation between the absorption range in the UV spectrum of pendant photosensitizer moiety and the wavelength of the irradiating light. That is, polymers containing pendant NN moieties have higher efficiency than the polymers containing pendant NP moieties under the same irradiation conditions.

Furthermore, Figure 5 shows that the observed rate of the valence isomerization of PNC with multifunctional polymeric photosensitizer obeyed first-order kinetics in the initial reaction stage. Accordingly, the efficiency of the multifunctional polymeric photosensitizers discussed below can be evaluated from the observed pseudo-first-order rate constant of the isomerization of PNC.

Table V
Quantum Yield of PNC with Multifunctional Polymeric Photosensitizer[a]

wavelength, nm	photosensitizer	chemical yield, %	quantum yield, ϕ
366	none	1.7	0.19
366	P(NN$_{11.8}$–BTPP)	10.2	0.42
405	none	0	0
405	P(NN$_{11.8}$–BTPP)	2.6	0.19

[a] The photochemical reaction was carried out with PNC (1.5 × 10^{-4} mol/L) and photosensitizer (2.25 × 10^{-5} mol/L) in water at room temperature for 10 min.

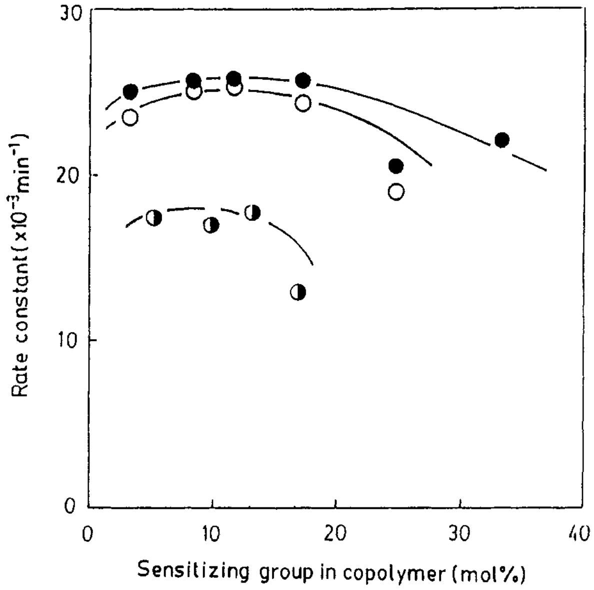


Figure 6. Correlation between the reaction rate of PNC (1.5 × 10^{-4} mol/L) and the content of pendant NN moiety in the polymeric photosensitizers: (●) with P(NN–BTPP)s (2.25 × 10^{-5} mol/L) in 25% methanolic aqueous solution; (○) with P(NN–BTPP)s (2.25 × 10^{-5} mol/L) in water; (◑) with P3C(NN–BTPP)s (3.0 × 10^{-5} mol/L) in water.

Quantum yields of the photoisomerization of PNC were measured both with polymeric photosensitizer P(NN$_{11.8}$–BTPP) and without any photosensitizer in water (Table V). The quantum yield of the reaction was 0.19 without photosensitizer and 0.42 with P(NN$_{11.8}$–BTPP) under irradiation with 366-nm light. When the irradiation was set at 405 nm, the quantum yield without photosensitizer was 0 and with P(NN$_{11.8}$–BTPP) was 0.19. These results indicate that the energy transfer occurred effectively from the multifunctional polymeric photosensitizers to the PNC molecules.

Correlations between the rate constant of PNC and the content of pendant NN moiety in soluble and insoluble multifunctional polymeric photosensitizers containing pendant BTPP residue as the substrate-attracting group are shown in Figure 6, in which the reaction was carried out in water (1.5 × 10^{-4} mol/L) or in 25% methanolic aqueous solution using 15 mol % of soluble photosensitizer or 20 mol % of insoluble photosensitizer bead, respectively. It seems that the efficiency was affected by the content of pendant photosensitizing moiety in the polymer chain. That is, the polymer containing about 5–20 mol % of pendant NN moiety had the highest photosensitizing efficiency for the isomerization of PNC among soluble photosensitizers. A similar trend was also found in the reaction with insoluble polymeric photosensitizer

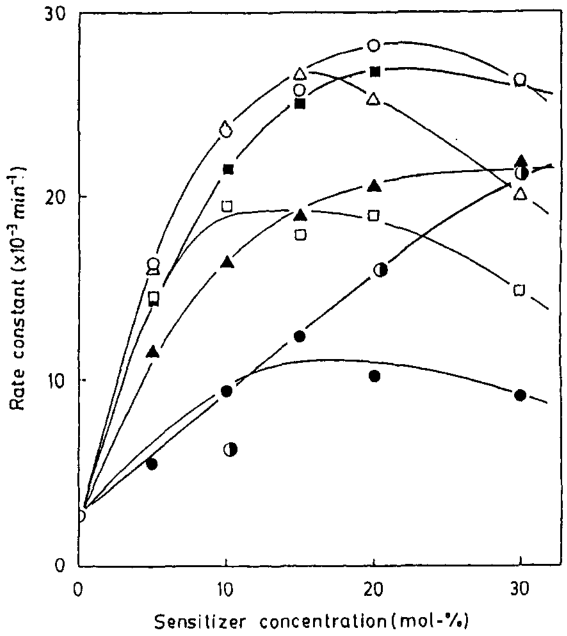


Figure 7. Effect of the photosensitizer concentration in the reaction of PNC (1.5×10^{-4} mol/L) in water: (□) P(NN$_{3.4}$–BTPP); (△) P(NN$_{8.2}$–BTPP); (○) P(NN$_{11.8}$–BTPP); (■) P(NN$_{16.8}$–BTPP); (▲) P(NN$_{24.8}$–BTPP); (●) P(NP$_{14.5}$–BTPP); (◑) P3C(NN$_{13.1}$–BTPP).

beads P3C(NN–BTPP)s.

This means that the introduction of large amounts of pendant photosensitizing groups caused self-quenching between the photosensitizing groups by their coaggregation due to hydrophobic interaction in the polymer chain. It also seems that the introduction of small amounts of pendant photosensitizing group in the polymer chain caused depression of the effective energy transfer from the photosensitizing group to the located PNC molecules at long distance, in which PNC was attracted by the substrate-attracting group BTPP in the polymer chain.

As shown in Figure 7, when the valence isomerization of PNC (1.5×10^{-4} mol/L) was carried out in the presence of 5–30 mol % of various multifunctional photosensitizers containing pendant BTPP residue as the substrate-attracting group in water, soluble photosensitizers P(NN$_{11.8}$–BTPP), P(NN$_{8.2}$–BTPP), and P(NN$_{16.8}$–BTPP) had higher efficiency than soluble photosensitizers P(NN$_{3.4}$–BTPP), P(NN$_{24.8}$–BTPP), and P(NP$_{14.5}$–BTPP) and insoluble bead P3C(NN$_{13.1}$–BTPP).

This result suggests that the efficiency of the photosensitizer was strongly affected by the degree of introduction of photosensitizing group as well as the polymer composition. That is, P(NN$_{11.8}$–BTPP) containing 11.8 mol % of pendant NN moiety had the highest efficiency, and the efficiency went down either with increasing or decreasing the amounts of pendant NN moiety in the polymer.

Figure 7 also shows that the rate of reaction of PNC was strongly affected by the photosensitizer concentration, and the highest rate of PNC was shifted to higher photosensitizer concentration with an increase in the degree of introduction of pendant photosensitizing moiety in the polymer chain. On the other hand, the rate of reaction of PNC increased gradually with an increase in the photosensitizer concentration, when insoluble photosensitizer bead P3C(NN$_{13.1}$–BTPP) was added. This means that the most suitable concentration of multifunctional polymeric photosensitizer depends on the polymer composition.

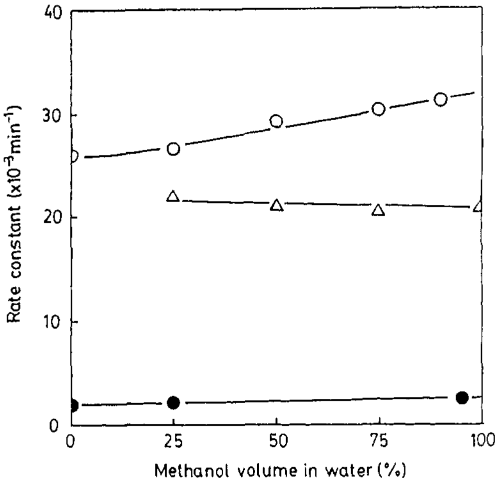


Figure 8. Effect of the amount of methanol in water in the reaction of PNC (1.5×10^{-4} mol/L) in the presence of polymeric photosensitizer (2.25×10^{-5} mol/L): (○) P(NN$_{11.8}$–BTPP); (△) P(NN$_{11.8}$–BTHP); (●) without photosensitizer.

The effect of reaction solvent on the photochemical reaction for PNC was examined. As shown in Figure 8, the rates of photochemical reactions of PNC without photosensitizer and with P(NN$_{11.8}$–BTHP) containing relatively hydrophobic substrate-attracting group were hardly affected by the methanol concentration. On the other hand, the rate of reaction of PNC increased gradually with an increase of methanol concentration, when P(NN$_{11.8}$–BTPP), which has relatively hydrophilic substrate-attracting group, was used as the polymeric photosensitizer. Furthermore, the rate with P(NN$_{11.8}$–BTPP) was higher than that with P(NN$_{11.8}$–BTHP). It seems that the photosensitizing efficiency was strongly affected by the conformation of the multifunctional polymeric photosensitizer, which would vary with the kind of reaction medium.

To evaluate the effect of the substrate-attracting group in the soluble polymer chain, the photochemical isomerization of PNC was performed with various multifunctional photosensitizers containing different substrate-attracting groups in 25% methanolic aqueous solution. As shown in Figure 9, P(NN$_{11.8}$–BTBP) containing pendant BTBP residue had higher efficiency than P(NN$_{11.8}$–BTPP) containing pendant BTPP residue and P(NN$_{11.8}$–BTHP) containing pendant BTHP residue among the polymers having quaternary phosphonium salts as the substrate-attracting group. It seems that pendant BTBP residue of P(NN$_{11.8}$–BTBP) has suitable characteristics as the substrate-attracting group for PNC in 25% methanolic aqueous solution. For the polymeric photosensitizers containing pendant quaternary ammonium salts, P(NN$_{11.8}$–BTPA) had the highest efficiency, and the efficiency of the polymeric photosensitizer decreased with an increase in the bulkiness and hydrophobicity of the pendant substrate-attracting group.

These results suggest that efficiency was also strongly affected by the kind of onium salt and the kind of alkyl group attached to the onium salts and that pendant quaternary phosphonium salts have higher efficiency than pendant quaternary ammonium salts as the substrate-attracting group for PNC in this system.

As shown in Figure 10, the efficiency of insoluble photosensitizer beads with some pendant quaternary phosphonium salts as the substrate-attracting groups was evaluated in 25, 50, and 75% methanolic aqueous solution, respectively. Photosensitizer bead P3C(NN$_{13.1}$–BTBP) containing pendant BTBP residue as the substrate-

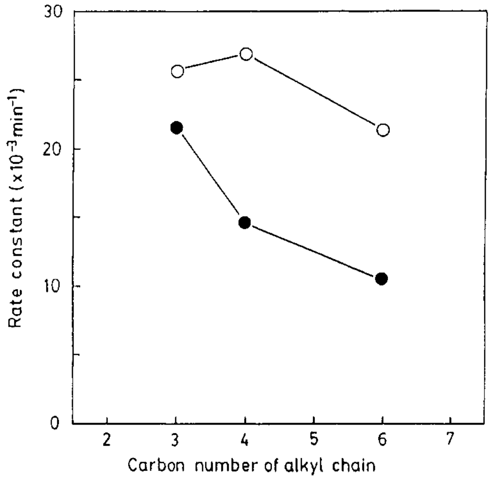


Figure 9. Correlation between the reaction rate of PNC (1.5×10^{-4} mol/L) and the carbon number of alkyl chain on the quaternary onium salt in the soluble polymeric photosensitizer containing 11.8 mol % of pendant NN moiety (2.25×10^{-5} mol/L as photosensitizing group) in 25% methanolic aqueous solution: (○) quaternary phosphonium salt; (●) quaternary ammonium salt.

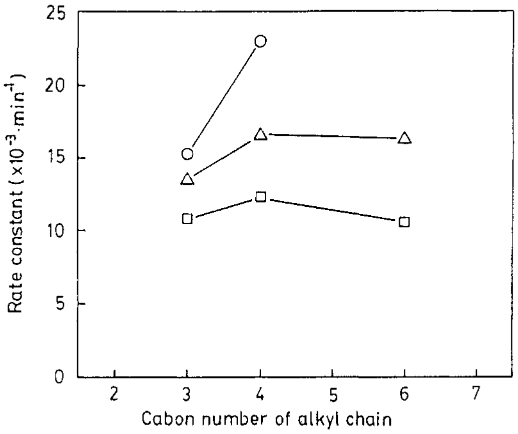


Figure 10. Correlation between the reaction rate of PNC (1.5 × 10^{-4} mol/L) and the carbon number of alkyl chain on the quaternary phosphonium salt in the insoluble polymeric photosensitizer bead containing 13.1 mol % of pendant NN moiety (4.5×10^{-5} mol/L as photosensitizing group): (○) in 25% methanolic aqueous solution; (△) in 50% methanolic aqueous solution; (□) in 75% methanolic aqueous solution.

attracting group had a higher efficiency than P3C(NN$_{13.1}$–BTPP) and P3C(NN$_{13.1}$–BTHP) under the same conditions. Figure 10 also shows that the efficiency of photosensitizer bead decreased with an increase of methanol concentration. This result means that a suitable combination of reaction medium and substrate-attracting group in the polymer bead will give the highest efficiency as the photosensitizer for the valence isomerization of PNC.

From all these results, it can be concluded that the efficiency of multifunctional polymeric photosensitizers for the photochemical valence isomerization of PNC is strongly affected by the kinds of photosensitizing moiety and substrate-attracting group, the content of photosensitizing moiety bonded to the side chain of polymer, and the photosensitizer concentration in the reaction system. Multifunctional polymeric photosensitizers P(NN$_{11.8}$–BTPP) and P(NN$_{11.8}$–BTBP) containing 11.8 mol % of pendant NN moieties and 88.2 mol % of pendant BTPP residues and 81.7 mol % of BTBP residues have the highest photosensitizing efficiency among the prepared polymeric photosensitizers. Furthermore, these results suggest that the multifunctional polymeric photosensitizers containing both pendant photosensitizing groups and substrate-attracting groups show great potential for use in solar energy conversion and storage systems based on the photochemical valence isomerization of NBD derivatives.

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