grafting efficiencies and also excellent reproducibility by making use of an advantage of the water-soluble nature of the partially deacetylated chitin. The polypeptide side-chain length, on which the solubility is greatly dependent, can be regulated easily. This method seems to be useful for preparation of various kinds of chitin/polypeptide hybrid materials.

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Registry No. γ-Methyl L-glutamate, 1499-55-4; γ-methyl L-glutamate NCA, 1663-47-4.

References and Notes

(1) Sannan, T.; Kurita, K.; Iwakura, Y. *Makromol. Chem.* **1976,** *177,* 3589.
(2) Kurita, K.; Sannan, T.; Iwakura, Y. *Makromol. Chem.* **1977,** *178,* 3197.
(3) Kurita, K.; Sannan, T.; Iwakura, Y. *Makromol. Chem.* **1977,** *178,* 2595.
(4) Sannan, T.; Kurita, K.; Iwakura, Y. *Polym. J.* (*Tokyo*) **1977,** *9,* 649.
(5) Kurita, K.; Ichikawa, H.; Ishizeki, S.; Fujisaki, H.; Iwakura, Y. *Makromol. Chem.* **1982,** *183,* 1161.
(6) Kurita, K.; Taniguchi, A.; Koyama, Y. *J. Appl. Polym. Sci.* **1986,** *31,* 1169.
(7) Kurita, K.; Taniguchi, A.; Koyama, Y. *J. Appl. Polym. Sci.* **1986,** *31,* 1951.
(8) Kurita, K.; Koyama, Y.; Murakami, K.; Yoshida, S.; Chau, G. *Polym. J.* (*Tokyo*) **1986,** *18,* 673.
(9) Kojima, K.; Yoshikuni, M.; Suzuki, T. *J. Appl. Polym. Sci.* **1979,** *24,* 1587.
(10) Shigeno, Y.; Kondo, K.; Takemoto, K. *J. Macromol. Sci., Chem.* **1982,** *A17,* 571.
(11) Kurita, K.; Kanari, M.; Koyama, Y. *Polym. Bull.* (*Berlin*) **1985,** *14,* 511.
(12) Aiba, S.; Minoura, N.; Fujiwara, Y. *Int. J. Biol. Macromol.* **1985,** *7,* 120.
(13) Hackman, R. H. *Aust. J. Biol. Sci.* **1960,** *13,* 568.
(14) Kurita, K.; Iwakura, Y. *Org. Synth.* **1980,** *59,* 195.

Study of Polymeric Photosensitizer. 2. Syntheses of Multifunctional Polymeric Photosensitizers Containing a Pendant Nitroaryl Group and a Quaternary Phosphonium Salt and Their Application to the Photochemical Reaction of Potassium Cinnamate

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ABSTRACT: Multifunctional polymeric photosensitizers containing both pendant nitroaryl groups as a photosensitizer moiety and pendant benzyltributylphosphonium chloride as a substrate-attracting group were synthesized by substitution reactions of poly((chloromethyl)styrene) (PCMS) with potassium salts of photosensitizing compounds by using phase-transfer catalysis followed by addition reactions of the resulting polymers with tributylphosphine (TBP) in *N*,*N*-dimethylformamide (DMF) under mild reaction conditions and by the addition reaction of PCMS with TBP followed by the substitution reaction of the potassium salt of the photosensitizing compound under the same reaction conditions. These reactions proceeded very smoothly to give the corresponding new multifunctional polymeric photosensitizers. One of the same polymeric photosensitizers was also prepared in 51% yield by radical copolymerization of the corresponding monomers by using azobis(isobutyronitrile) in DMF. These polymers were soluble in water and methanol, and the polymeric photosensitizers containing pendant benzyltributylphosphonium chloride as a substrate-attracting group and pendant 4-nitrophenoxy (PTBP-NP) or 4-(4-nitrophenoxy)butylate moieties as a chromophore showed higher photosensitization efficiency than the corresponding low molecular weight photosensitizer for trans–cis photoisomerization of potassium cinnamate in water. Furthermore, it was found that although the multifunctional polymeric photosensitizer PTBT-NP has excellent efficiency, the control of content of pendant photosensitizer moiety in the polymer and of concentration of the photosensitizer in the reaction system is very important to get high efficiency.

Introduction

It is well-known that photosensitizers have been widely used in photochemical reactions such as isomerization, dimerization, and oxidation of organic compounds in solution and in photocrosslinking or photodegradation reactions of several polymers in the film state. Polymeric photosensitizers have also been interesting from the viewpoint of solar energy storage and exchange processes. Moser and Cassidy[1] have reported cis–trans photoisomerization of *cis*-1,3-pentadiene by poly(vinyl phenyl ketone) (PVPK). Leermakers and James[2] have also reported photochemical balance isomerization of norbornadiene (NBD) to quadricyclane (QDC) and isomerization of piperylene using PVPK. The first photooxidation using polymer-based sensitizers containing pendant rose bengal moiety has been reported by Blossey et al.[3-6] Recently, Schaap and co-workers[7,8] and Neckers and co-workers[9-13] have studied separately these photooxidations using several polymeric photosensitizers containing rose bengal moiety. Neckers et al.[14,15] also reported photodimerization of coumarin or indene, cycloaddition of benzo(*b*)thiophene to dichloroethylene, and isomerization of NBD to QDC using polymeric photosensitizer containing benzophenone moiety. Hautala et al.[16,17] have proposed a solar energy storage process using a NBD–QDC system with heterogeneous photosensitizers such as the crosslinked polystyrene and silica gel having pendant 4-(*N*,*N*-dimethylamino)benzophenone moiety. However, the efficiency of all these polymeric photosensitizers was generally comparable to or slightly lower than the corresponding low

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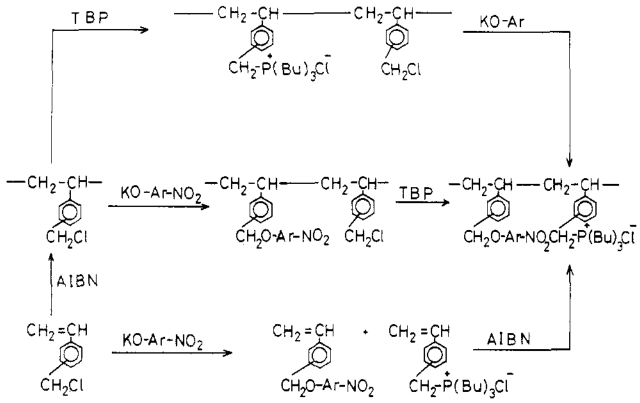
Scheme I



molecular weight photosensitizers used so far.

Recently, we have considered the complementarity of functional groups and the effect of reaction media in enzymes, which are typical polymeric catalysts, and the concentration effect and the transportation of phase-transfer catalyst (PTC). With this background, we synthesized[18] multifunctional polymeric photosensitizers containing pendant nitroaryl moieties as a chromophore and pendant tertiary amine as a substrate-attracting group. The multifunctional polymeric photosensitizer obtained showed higher activity than the corresponding low molecular weight photosensitizer in a photochemical reaction of methyl cinnamate in tetrahydrofuran (THF).

This article reports on the successful syntheses of multifunctional polymeric photosensitizers (see Scheme I) containing pendant nitroaryl moieties as a chromophore and a pendant quaternary phosphonium salt as a substrate-attracting group and investigates the photochemical reaction of potassium cinnamate by using those multifunctional polymeric photosensitizers in water.

Experimental Section

Materials. The solvents were purified in the usual way prior to use. Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol at 40 °C. Chloromethylated styrene (CMS) (mixture of 40% meta and 60% para) and methacrylic acid (MA) were distilled twice under reduced pressure. Poly((chloromethyl)styrene) (PCMS; the reduced viscosity of the polymer in DMF was 0.15 dL/g, measured at a concentration of 0.5 g/dL at 30 °C) was prepared in 62% yield by radical polymerization of CMS (305.26 g, 2 mol) by using AIBN (3.28 g, 0.02 mol) in benzene (400 mL) at 60 °C for 5 h and then 80 °C for 3 h under flowing nitrogen, followed by one precipitation in methanol and two reprecipitations from acetone into methanol, and drying at 50 °C under reduced pressure. Commercial tributylphosphine (TBP) was used without further purification. The phase-transfer catalyst (PTC) tetrabutylammonium bromide (TBAB) was recrystallized twice from THF. Potassium 4-nitrophenoxide (PNP), potassium 4-nitro-1-naphthoxide (PNN), potassium (4-nitrophenoxy)acetate (PNPA), potassium 4-(4-nitrophenoxy)butylate (PNPB), potassium cinnamate (PCIN); λ_{max} 268 nm in water), and potassium solrbate (PSB; λ_{max} 253 nm in water) were prepared by reaction of potassium hydroxide with the corresponding phenol, naphthol, or acids in methanol and were then recrystallized.

Apparatus. Infrared (IR) spectra were measured on the JASCO Model A-202 spectrophotometer. UV spectra were recorded on the Shimazu Model UV-240 spectrophotometer. The ^{1}H NMR analyses were performed on the JEOL Model PS-100 spectrometer.

Substitution Reaction of PCMS with the Potassium Salt of Photosensitizing Compounds. Typical examples of the reaction of PCMS with the potassium salt of the photosensitizing compound are as follows:[19,20]

Typical Procedure for the Substitution Reaction of PCMS with PNP. PCMS (1.53 g, 10.0 mmol) was dissolved in 20 mL of DMF, and PNP (0.36 g, 2.0 mmol) and TBAB (0.32 g, 1.0 mmol) as a PTC were added to the solution. The mixture was stirred at 30 °C for 24 h and then poured into water. The obtained polymer was purified by reprecipitating twice from THF into water and from THF into methanol and finally dried in vacuo at 50 °C. The yield of the recovered polymer (PCMS-NP) was 1.77 g. The degree of substitution was 19.2 mol %, calculated from elemental analysis of chlorine (166.2 mg/g) and UV absorption (305 nm in THF). The reduced viscosity of the polymer in DMF was 0.27 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1520 and 1340 ($-NO_2$ stretching), and 1260 cm^{-1} (C–O–C stretching). The ^{1}H NMR spectrum ($CDCl_3$) showed δ 4.2 (CCH_2Cl), 5.0 (CCH_2O), and 6.1–8.4 (aromatic protons).

Typical Procedure for the Substitution Reaction of PCMS with PNN. The reaction of PCMS (1.53 g, 10.0 mmol) with PNN (0.46 g, 2.0 mmol) was carried out by using TBAB (0.32 g, 1.0 mmol) in DMF (20 mL) at 30 °C for 24 h, and the reaction product was purified by the procedure described above. The yield of final polymer (PCMS-NN) was 1.62 g. The degree of substitution of the polymer was 18.5 mol %, calculated from elemental analysis of chlorine (159.7 mg/g) and UV absorption (362 nm in THF). The reduced viscosity of the polymer in DMF was 0.78 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1520 and 1320 ($-NO_2$ stretching), and 1280 cm^{-1} (C–O–C stretching). The ^{1}H NMR spectrum ($CDCl_3$) showed δ 4.2 (CCH_2Cl), 5.0 (CCH_2O), and 6.1–8.8 (aromatic protons).

Substitution Reaction of PCMS with PNPA. To PCMS (1.53 g, 10.0 mmol) in DMF (20 mL) were added PNPA (0.59 g, 2.5 mmol) and TBAB (0.32 g, 1.0 mmol). The mixture was stirred at 30 °C for 24 h and then poured into water. The reaction product was purified by reprecipitating twice from THF into water and from THF into methanol and then dried in vacuo at 50 °C. The yield of final polymer (PCMS-NPA) was 1.81 g. The degree of substitution of the polymer was 21.0 mol %, calculated from elemental analysis of chlorine (150.3 mg/g) and UV absorption (300 nm in THF). The reduced viscosity of the polymer in DMF was 0.25 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1760 (C=O stretching of ester), 1520 and 1350 ($-NO_2$ stretching), and 1260 cm^{-1} (C–O–C stretching).

Substitution Reaction of PCMS with PNPB. PCMS (1.53 g, 10.0 mmol) was allowed to react with PNPB (0.52 g, 2.0 mmol) in the presence of TBAB (0.32 g, 1.0 mmol) in DMF (20 mL) at 30 °C for 24 h. The yield of final polymer (PCMS-NPB) was 1.59 g. The degree of substitution was 19.5 mol %, calculated from elemental analysis of chlorine (150.7 mg/g) and UV absorption (307 nm in THF). The reduced viscosity of the polymer in DMF was 0.22 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1740 (C=O stretching of ester), 1510 and 1340 ($-NO_2$ stretching), and 1260 cm^{-1} (C–O–C stretching).

Typical Procedure for the Addition Reaction of PCMS-NP with TBP. The reaction of PCMS-NP$_{19.2}$ (0.86 g, 4.0 mmol as chloromethyl group) with TBP (1.21 g, 6.0 mmol) was carried out in DMF (10 mL) at 30 °C for 24 h, and then the reaction mixture was poured into ether. The obtained polymer was purified by reprecipitating twice from methanol into ether, filtered, and dried in vacuo at 50 °C. The yield of final polymer (PTBP-NP) was 1.26 g. The TBP content in the polymer was 80.8 mol %, calculated from elemental analysis of chlorine (86.4 mg/g). The reduced viscosity of the polymer in DMF was 1.09 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The UV spectrum showed the λ_{max} at 317 nm in water. The ^{1}H NMR spectrum (DMSO-d_6) showed δ 0.9 (CCH_3) and 6.6–8.4 (aromatic protons).

Typical Procedure for the Addition Reaction of PCMS-NN with TBP. PCMS-NN$_{18.5}$ (0.92 g, 4.0 mmol) as chloromethyl group) was made to react with TPB (1.21 g, 6.0 mmol) in DMF (10 mL) at 50 °C for 24 h, and the product was purified by the same procedure applied above. The yield of final polymer (PTBP-NN) was 1.25 g. The TBP content in the polymer was 79.8 mol %, calculated from elemental analysis of chlorine (83.6 mg/g). The reduced viscosity of the polymer in DMF was 2.56 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The UV spectrum showed the λ_{max} at 374 nm in water. The ^{1}H NMR spectrum (DMSO-$d_6{}^1$) showed δ 0.9 (CCH_3) and 6.2–8.8 (aromatic protons).

Addition Reaction of PCMS-NPA with TBP. The reaction of PCMS-NPA$_{21.0}$ (0.92 g, 4.0 mmol was chloromethyl group) with TBP (1.21 g, 6.0 mmol) was carried out in DMF (10 mL) at 30 °C for 24 h. The yield of final polymer (PTBP-NPA) was 1.19 g. The TBP content in the polymer was 79.0 mol %, calculated from elemental analysis of chlorine (80.9 mg/g). The reduced viscosity of the polymer in DMF was 0.88 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The UV spectrum showed the λ_{max} at 314 nm in water. The ^1H NMR spectrum ($CDCl_3$) showed δ 0.9 (CCH_3) and 6.0–8.2 (aromatic protons).

Addition Reaction of PCMS-NPB with TBP. The reaction was carried out as above on PCMS-NPB$_{19.5}$ (0.93 g, 4.0 mmol as chloromethyl group). The yield of final polymer (PTBP-NPB) was 1.16 g. The TBP content in the polymer was 72.5 mol %, calculated from elemental analysis of chlorine (84.9 mg/g). The reduced viscosity of the polymer in DMF was 0.97 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The UV spectrum showed the λ_{max} at 320 nm in water. The ^1H NMR spectrum ($CDCl_3$) showed δ 0.9 (CCH_3) and 6.0–8.3 (aromatic protons).

Typical Procedure for the Addition Reaction of PCMS with TBP. The addition reaction of PCMS (0.76 g, 5.0 mmol) with TBP (1.52 g, 7.5 mmol) was carried out in DMF (10 mL) at 30 °C for 24 h, and the reaction mixture was poured into ether. The obtained polymer was purified by reprecipitating twice from methanol into ether, filtered, and dried in vacuo at 50 °C. The yield of final polymer (PTBP) was 1.01 g. The TBP content in the polymer was 100 mol %, calculated from elemental analysis of chlorine (99.9 mg/g). The reduced viscosity of the polymer in DMF was 1.0 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The ^1H NMR spectrum ($CDCl_3$) showed δ 0.9 (CCH_3) and 6.0–7.8 (aromatic protons).

Addition Reaction of PCMS-TBP with PNP. PCMS-TBP$_{33.2}$ (1.10 g, 3.4 mmol as chloromethyl group), which was prepared by partial addition reaction of PCMS with TBP, was made to react with PNP (0.89 g, 5.0 mmol) in DMF (10 mL) at 80 °C for 24 h and then poured into water. The polymer was reprecipitated twice from THF into water, from THF into HCl acidic water, and from THF into methanol. The yield of final polymer (PTBP-NP) was 0.86 g. The NP content in the polymer was 66.8 mol %, calculated from elemental analysis of chlorine (40.8 mg/g) and UV absorption (317 nm in water). The reduced viscosity of the polymer in DMF was 0.86 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1520 and 1340 ($-NO_2$ stretching) and 1260 cm^{-1} (C–O–C stretching).

Synthesis of (4-Nitrophenoxymethyl)styrene (NPMS). NPMS (mp 61–70 °C, a mixture of meta and para) was synthesized by the reaction of CMS (15.3 g, 0.1 mol) with PNP (21.3 g, 0.12 mol) in DMF (50 mL) by using TBAB (3.2 g, 10 mmol) as a PTC at 30 °C for 24 h. The solution was poured into water, filtered, washed with water, and dried. The obtained crude product was recrystallized twice from methanol. The yield of NPMS was 96.9%. The IR (KBr) spectrum showed absorption peaks at 1630 (C=C), 1510 and 1320 ($-NO_2$), and 1260 cm^{-1} (C–O–C). The ^1H NMR spectrum ($CDCl_3$) showed δ 5.04 (CCH_2O), 5.2 and 5.7 (CH_2=C), 6.6 (C=CH), and 6.8–8.2 (aromatic protons). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.65; H, 5.13; N, 5.52.

Synthesis of (4-Nitro-1-naphthoxymethyl)styrene (NNMS). NNMS (mp 110–119 °C, a mixture of meta and para) was prepared in 64.1% yield by the reaction of CMS with PNN with the same method that was applied to the synthesis of NPMS and recrystallized twice from methanol. The IR spectrum (KBr) showed absorption peaks at 1620 (C=C), 1510 and 1320 ($-NO_2$), and 1260 cm^{-1} (C–O–C). The ^1H NMR spectrum ($CDCl_3$) showed δ 5.2 (CCH_2O), 5.3 and 5.7 (CH_2=C), 6.7 (C=CH), and 7.2–8.8 (aromatic protons). Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.50; H, 4.76; N, 4.52.

Synthesis of Tributyl(vinylbenzyl)phosphonium Chloride (VBPC). CMS (7.63 g, 50 mmol) was reacted with TBP (10.12 g, 50 mmol) at 30 °C for 1 h, and then the mixture was poured into hexane, filtered, washed with hexane, and dried in vacuo. The obtained crude product was recrystallized twice from the mixed solvent of benzene (50%) and hexane (50%). The yield of VBPC (mp 127–128 °C, a mixture of meta and para) was 37.7%. The IR spectrum (KBr) showed an absorption peak at 1640 cm^{-1} (C=C). The ^1H NMR spectrum ($CDCl_3$) showed δ 0.9 (CCH_3), 5.3 and 5.8 (CH_2=C), 6.7 (C=CH), and 7.3–7.7 (aromatic protons). Anal. Calcd for $C_{21}H_{36}ClP$: C, 71.06; H, 10.32. Found: C, 70.56, H, 10.13.

Radical Copolymerization of NPMS and VBPC. Radical copolymerization of NPMS (0.08 g, 0.3 mmol) and VBPC (0.96 g, 2.7 mmol) was carried out by using AIBN (0.005 g, 0.03 mmol) as an initiator in DMF (6 mL) at 60 °C for 4 h and then 80 °C for 2 h under flowing nitrogen. The polymer solution was precipitated into ether, reprecipitated twice from methanol into ether, filtered, and dried in vacuo at 50 °C. The yield of final polymer (PTBP-NP) was 50.5%. The NPMS unti in the copolymer was 14.5 mol %, calculated from UV absorption (317 nm in water) and elemental analysis of chlorine (85.6 mg/g). The reduced viscosity of the polymer in DMF was 0.23 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1520 and 1340 ($-NO_2$ stretching) and 1260 cm^{-1} (C–O–C stretching).

Radical Copolymerization of NPMS and MA. NPMS (1.99 g, 7.8 mmol), MA (6.08 g, 70.6 mmol), and AIBN (0.13 g, 0.78 mmol) were dissolved in DMF (20 mL), and then the polymerization was carried out at 60 °C for 5 h and then 80 °C for 3 h under flowing nitrogen and precipitated into methanol. The obtained polymer was purified by reprecipitating twice from THF into ether, filtered, and dried in vacuo at 50 °C. The yield of final polymer (PMA-PNP) was 71.0%. The NPMS unit in the copolymer was 10.8 mol %, calculated from UV absorption (305 nm in THF). The reduced viscosity of the polymer in DMF was 0.17 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The potassium salt of this polymer (PPMA-NP) was prepared by neutralizing PMA-NP with potassium hydroxide in methanol, evaporating the methanol, and drying in vacuo at 50 °C.

Typical Procedure for Photochemical Reaction by Method A. PCIN (2.24 mg, 3.0 × 10^{-5} mol/L) and polymeric photosensitizer PTBP$_{90.8}$-NP$_{19.2}$ (2.12 mg, 3.0 × 10^{-6} mol/L as the photosensitizer unit in the polymer) were dissolved 400 mL of water. Irradiation of this polymer solution was then performed at 30 °C in a small conventional photochemical reactor, consisting of a four-necked reaction vessel (400 mL) with a Pyrex water jacket immersion vessel and a 100-W high-pressure mercury lamp (Ushio Electric Co., UM-102), under nitrogen atmosphere with magnetic stirring. Nitrogen gas was bubbled through the solution for 60 min before UV irradiation, and then the nitrogen gas stream was passed very slowly through the reaction mixture during exposure. The rate of disappearance of the absorption maximum at 268 nm of *trans*-PCIN was measured by UV spectrophotometer.

Typical Procedure for Photochemical Reaction by Method B. The photochemical reaction of PCIN (2.24 mg, 3.0 × 10^{-5} mol/L) using PTBP$_{80.8}$-NP$_{19.2}$ (2.12 mg, 3.0 × 10^{-6} mol/L as the photosensitizer unit in the polymer) was carried out at 30 °C by use of a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) through a filter (Toshiba UV-37) and a Pyrex glass filter at a distance of 30 cm in nitrogen atmosphere with magnetic stirring.

Results and Discussion

Syntheses of a Multifunctional Polymeric Photosensitizer Containing a Pendant Photosensitizer Moiety and a Substrate-Attracting Group. Polymeric photosensitizers containing pendant 4-nitrophenoxy or 4-nitro-1-naphthoxy moieties and the chloromethyl groups were synthesized by the partial substitution reaction of pendant chloromethyl groups of PCMS with PNP, PNN, PNPA, or PNPB in DMF by using TBAB as a PTC under mild reaction conditions (Table I).

This result suggested that the reaction of PCMS with PNP, PNN, and PNPB proceeded almost quantitatively. On the other hand, the degree of functionalization (DF) with PNPA was lower than with the other photosensitizer compounds under similar conditions.

Multifunctional polymeric photosensitizers containing both a pendant photosensitizer moiety and the quaternary

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

polym no.	photosensitizer compd (amount, mmol)	yield, g	Cl in polymer mg/g	DF[b] mol %	η_{red},[c] dL/g
1	PNP (0.5)	1.42	213.9	4.9	0.26
2	PNP (1.0)	1.48	195.2	10.0	0.26
3	PNP (1.5)	1.71	178.7	15.2	0.27
4	PNP (2.0)	1.77	166.2	19.2	0.27
5	PNP (3.0)	1.45	132.6	31.0	0.27
6	PNP (4.0)	1.58	106.7	41.3	0.27
7	PNP (5.0)	1.90	85.2	50.8	0.27
8	PNP (6.0)	1.88	63.5	61.4	0.27
9	PNN (1.0)	1.37	190.4	9.9	0.18
10	PNN (2.0)	1.57	157.4	19.2	0.22
11	PNN (3.0)	1.68	128.4	28.8	0.23
12	PNN (4.9)	1.81	101.7	39.1	0.21
13	PNN (5.0)	1.87	79.5	49.0	0.19
14	PNPA (2.0)	1.62	165.3	16.5	0.26
15	PNPA (2.5)	1.81	150.3	21.0	0.25
16	PNPB (2.0)	1.59	150.9	19.5	0.22

[a] Each reaction was carried out in 10 mmol of PCMS by using 1.0 mmol of TBAB as a phase-transfer catalyst in 20 mL of DMF at 30 °C for 24 h. [b] Drgree of functionalization. [c] Measured at a concentration of 0.5 g/dL in DMF at 30 °C.

phosphonium salt as a substrate-attracting group were prepared by the addition reaction of pendant chloromethyl groups of the polymeric photosensitizers obtained as above with TBP in DMF at 30–80 °C (Table II).

This result suggested that the reactions of pendant chloromethyl groups in the polymer containing the pendant 4-nitrophenoxy moiety (PCMS-NP) or the polymer containing the pendant (4-nitrophenoxy)acetate moiety (PCMS-NPA) with TBP successfully proceeded with high conversion. However, the reactions of pendant chloromethyl groups in the polymer containing the pendant 4-nitro-1-naphthoxy moiety (PCMS-NN) or the polymer containing the pendant (4-nitrophenoxy)butylate moiety (PCMS-PNPB) with TBP did not proceed quantitatively under the same conditions. It seems that the addition reactions of pendant chloromethyl groups, especially the chloromethyl groups surrounded by the NN moieties, in PCMS-NN or PCMS-NPB were partially hindered by the bulky photosensitizer moieties.

Also the multifunctional polymeric photosensitizer containing the pendant NP moiety and pendant benzyltributylphosphonium chloride (PTBP-NP) was prepared by the partial addition reaction of chloromethyl groups of PCMS with TBP followed by the substitution reaction of the resulting polymer with PNP in DMF.

Photosensitizer monomers NPMS and NNMS were synthesized in 96.6 and 64.1% yields by the substitution reactions of PCMS with PNP and PNN by using phase-transfer catalysis in DMF under mild conditions, respectively.

The monomer VBPC containing the substrate-attracting group was prepared in 38% yield by the addition reaction of CMS with TBP at 30 °C for 1 h.

The same multifunctional polymeric photosensitizer PTBT-NP containing the pendant NP moiety and pendant benzyltributylphosphonium chloride was also synthesized in 49.5% yield by radical copolymerization of the corresponding monomers VBPC and NPMS by using AIBN as an initiator in DMF at 60 °C for 4 h and then 80 °C for 2 h under flowing nitrogen.

These results mean that the multifunctional polymeric photosensitizers containing both a pendant photosensitizer moiety and a substrate-attracting group can be prepared by the reactions of pendant chloromethyl groups of PCMS with potassium salts of photosensitizing compounds and TBP in DMF and by the radical copolymerization of the corresponding monomers by using AIBN in DMF.

The other type of polymeric photosensitizer containing the pendant NP moiety and the potassium carboxylate (PPMA-NP) was prepared by radical copolymerization of MA and NPMS by using AIBN in DMF followed by neutralizing the resulting polymer with potassium hydroxide in methanol.

Photochemical Reactions of PCIN and PSB Using Multifunctional Polymeric Photosensitizers. The photochemical reaction of PCIN (3.0×10^{-5} mol/L) with 10 mol % of polymeric photosensitizers PTBP$_{80.8}$-NP$_{19.2}$, PPMA$_{89.2}$-NP$_{10.8}$, or low molecular weight photosensitizer PNPB or without any photosensitizer was carried out in water through a Pyrex glass filter by method A. As shown in Figure 1, the rate of photochemical reaction of PCIN was greatly promoted by addition of the polymeric photosensitizer PTBP-NP, which has a pendant quaternary phosphonium salt. Although the rate of photochemical reaction of PCIN with low molecular weight photosensitizer PNPB was higher than that without photosensitizer, the rate of PCIN was depressed by the addition of polymeric photosensitizer PPMA-NP, which has a pendant carboxylate anion. This result clearly shows that a multifunctional polymeric photosensitizer containing both a pendant NP moiety as a photosensitizer and pendant benzyltributylphosphonium chloride moiety as a substrate-attracting group has higher efficiency than low molecular weight photosensitizer PBNP under the same conditions, because of the excellent intermolecular inter-

Table II
Conditions and Results of Addition Reaction of PCMS and Their Copolymers with TBP[a]

polym no.	ClMe group in polym (amount, mmol)	TBP, mmol	rctn condition temp, °C	rctn condition time, h	yield, g	TBP unit in polym, mol %	η_{red}[b]
17	PCMS-NP$_{4.9}$ (4.8)	7.1	30	24	1.04	95.1	1.07
18	PCMS-NP$_{10.0}$ (4.5)	6.8	30	24	0.90	90.0	1.06
19	PCMS-NP$_{15.2}$ (4.2)	6.4	30	24	1.01	84.8	1.01
20	PCMS-NP$_{19.2}$ (4.0)	6.0	30	24	1.26	80.8	1.09
21	PCMS-NP$_{31.0}$ (3.5)	5.3	30	48	0.99	69.0	1.11
22	PCMS-NP$_{41.3}$ (0.2)	0.8	80	24	1.26	52.7	1.00
23	PCMS-NP$_{50.8}$ (0.4)	2.4	80	24	1.06	37.3	1.19
24	PCMS-NN$_{10.2}$ (2.2)	4.5	30	48	0.48	89.8	0.81
25	PCMS-NN$_{19.2}$ (2.0)	4.0	30	48	0.52	80.8	0.81
26	PCMS-NN$_{28.8}$ (1.8)	3.6	80	24	0.66	71.2	0.73
27	PCMS-NN$_{39.1}$ (1.5)	3.1	80	24	0.69	55.5	0.70
28	PCMS-NN$_{49.0}$ (1.3)	2.6	80	24	0.70	28.8	0.63
29	PCMS-NPA$_{21.0}$ (4.0)	6.0	30	24	1.19	79.0	0.88
30	PCMS-NPB$_{19.5}$ (4.0)	6.2	30	24	1.16	75.1	0.97

[a] The reaction was carried out in 10 mL of DMF. [b] Measured at a concentration of 0.5 g/dL in DMF at 30 °C.

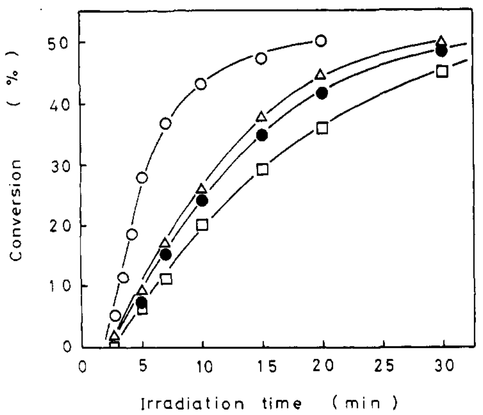


Figure 1. Rate of reaction of PCIN (3.0 × 10^{-5} mol/L) with 10 mol % of photosensitizer in water by method A: (○) with PTBP-NP$_{19.2}$; (△) with PNPB; (□) with PPMA-NP$_{10.8}$: (●) without photosensitizer.

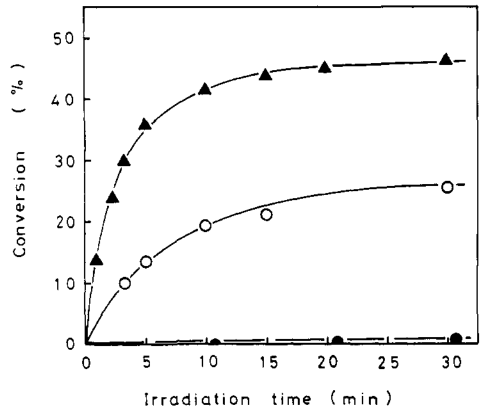


Figure 2. Rate of reaction of PCIN (3.0 × 10^{-5} mol/L) with 10 mol % of photosensitizer in water by method B: (▲) with PTBT-NP$_{19.2}$; (○) with PTBT-NN$_{19.2}$; (●) without photosensitizer.

action between PCIN and pendant phosphonium salt in the polymer. On the other hand, it seems that the polymeric photosensitizer PPMA-NP acts as a quencher, because the pendant NP moiety in this polymer might be excited by the irradiation of UV light; however, the energy of the excited NP moiety could not be transferred to PCIN due to the electrical repulsion between pendant carboxylate anion in the polymer and cinnamate anion in water. Therefore, if cinnamate compound has an anion-attracting group such as quaternary salt, PPMA-NP should have an excellent photosensitization efficiency.

The photochemical reaction of PCIN (3.0 × 10^{-5} mol/L) with PTBP$_{80.8}$-NP$_{19.2}$ (3.0 × 10^{-6} mol/L) or PTBP$_{80.0}$-NN$_{19.2}$ (3.0 × 10^{-6} mol/L) or without any photosensitizer was carried out in water through Pyrex glass and filter UV-37 by method B. As shown in Figure 2, although the reaction of PCIN with two polymeric photosensitizers proceeded, the reaction did not proceed without a photosensitizer. This is evidence that energy transfer occurred effectively from polymeric photosensitizers such as PTBP-NP and PTBP-NN to PCIN in water.

As shown in Figure 3, the UV spectrum of PCIN (3.0 × 10^{-5} mol/L) changed by irradiation of the light in the presence of PTBP$_{80.8}$-NP$_{19.2}$ (3.0 × 10^{-6} mol/L) in water, and the isobestic point appeared at 227 and 248 nm. This shows that very clean photochemical reaction of PCIN occurred in this reaction system.

Also the ^{1}H NMR spectrum of PCIN in deuteriated water showed signals at δ 6.05 (doublet) based on *cis*-CH=CH protons in addition to the signals at δ 6.45 (doublet) derived from *trans*-CH=CH protons by light irradiation in the presence of the same polymeric photosensitizer. However, the ^{1}H NMR spectrum did not show methin protons from the cyclobutane ring or the vinyl chain. These results suggest that only trans–cis isomerization of PCIN occurred in this reaction system.

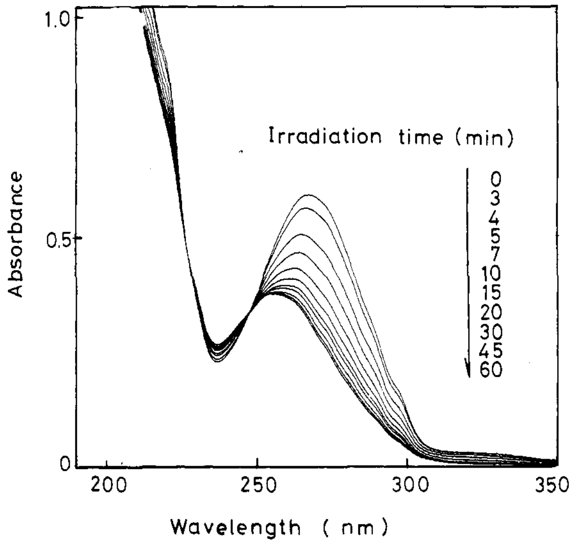


Figure 3. Change of UV spectrum of PCIN (3.0 × 10^{-5} mol/L) using photosensitizer PTBP-NP$_{4.9}$ (3.0 × 10^{-6} mol/L) in water by method A.

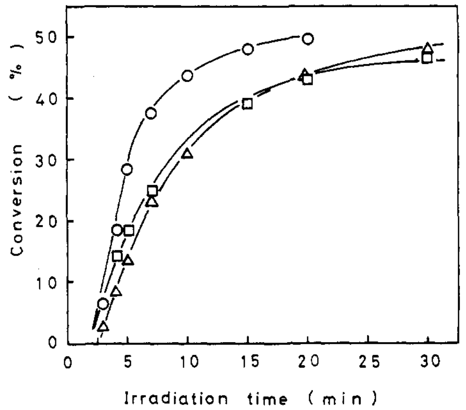


Figure 4. Rate of reaction of PCIN (3.0 × 10^{-5} mol/L) with 10 mol % of photosensitizer by method A: (○) with PTBP-NPB$_{19.5}$; (△) with PTBP-NPA$_{21.0}$; (□) with PTBP-NN$_{19.2}$.

As shown in Figure 2, trans–cis photoisomerization of PCIN was effectively promoted by PTBP-NN upon irradiation by method B; however, PPTBP-NN did not promote the photochemical reaction upon irradiation by method A. Furthermore, as shown in Figure 4, the photoisomerization reaction of PCIN (3.0 × 10^{-5} mol/L) was also greatly promoted by addition of PTBP-NPB. However, the efficiency of PTBP-NPA was lower than those of PTBP-NP and PTBP-NPB.

In addition, it was found that the reaction of PCIN was not promoted by addition of a polymer (PTBP) containing pendant benzyltributylphosphonium chloride or the low molecular weight photosensitizer PNPB when the irradiation was carried out under the same conditions (Figure 5).

Therefore, it may be concluded that PTBP-NP and PTBP-NPB are good multifunctional polymeric photosensitizers (see Scheme II), which have a higher efficiency than the low molecular weight photosensitizer PNPB for the trans–cis photoisomerization of PCIN in water.

Furthermore, it was interesting that the reaction of PCIN (3.0 × 10^{-5} mol/L) in water was greatly promoted by addition of 10 mol % of PTBP and PNPB (Figure 5).

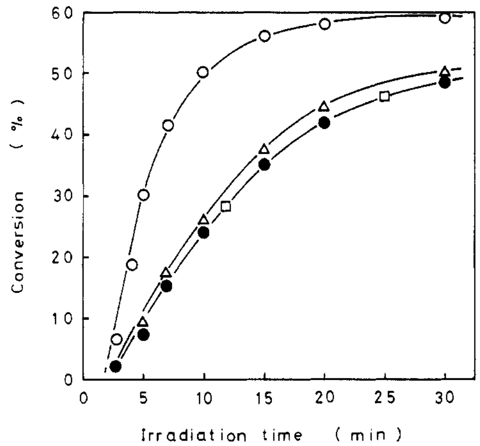
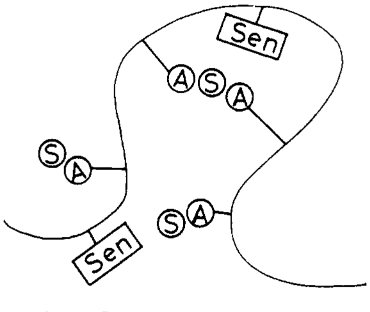
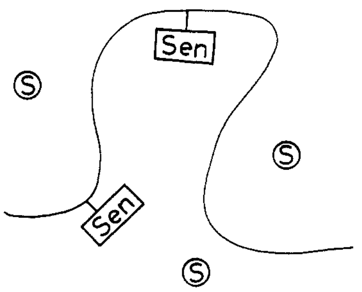


Figure 5. Rate of reaction of PCIN (3.0×10^{-5} mol/L) with 10 mol % of reagent in water by method A: (□) with PTBP; (△) with PNPB; (○) with PTBP + PNPB; (●) without reagent.

Scheme II



Multifunctional polymeric photosensitizer



Conventional polymeric photosensitizer

A: Substrate-attracting group
S: Substrate
Sen: Photosensitizer moiety

This means that PNPB was concentrated near polymer PTBP as well as PCIN in water, and then energy transfer occurred effectively from PNPB to the neighboring PCIN. Therefore, it may also be concluded that the PTBP-PNPB system is an interesting new multifunctional polymeric photosensitizer as well as the previously mentioned copolymer PTBP-NPB.

It is well-known[21] in phase-transfer catalysis that the affinity of the counteranion with a quaternary ammonium cation decreases as follows: $I^- > Br^- > Cl^- > CH_3CO_2^- > F^- > OH^-$.

Since the observed rate of photochemical reaction of PCIN in the above reactions obeyed first-order kinetics, as shown in Figure 6, the effect of the added ion on the rate of reaction was compared by using the rate constants of the reactions. Although the rate of reaction of PCIN (3.0×10^{-5} mol/L) with 10 mol % of polymeric photosensitizer PTBP-NP$_{19.2}$ in water was scarcely affected by the addition of KCl, the rate of reaction was extremely depressed by the addition of KBr and KI. On the other hand, the rate of reaction was increased by the addition of small amounts of KF.

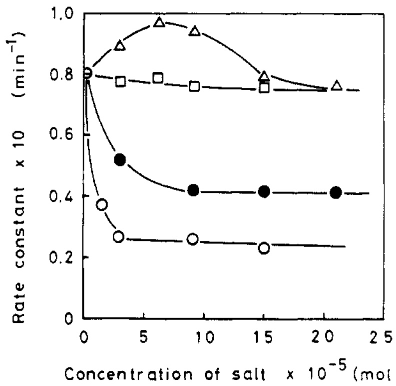


Figure 6. Change of reaction rate of PCIN (3.0×10^{-5} mol/L) with PTBP-NP$_{19.2}$ (3.0×10^{-6} mol/L) by addition of potassium halide: (△) with KF; (□) with KCl; (●) with KBr; (○) with KI.

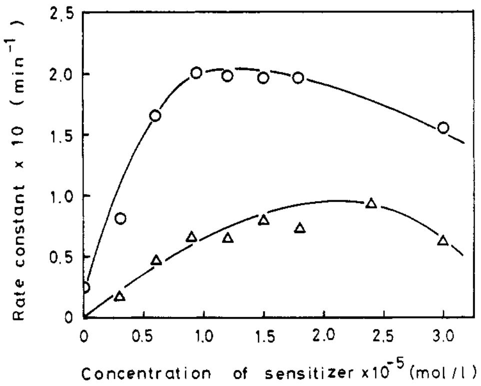


Figure 7. Correlation between the reaction rate of PCIN (3.0×10^{-5} mol/L) and the concentration of photosensitizer PTBP-NP$_{19.2}$ in water: (○) by method A; (△) by method B.

This result means that the anion-exchange reaction between PCIN and pendant quaternary phosphonium salt in the polymeric photosensitizer was interfered with by adding KBr and KI, because I^- and Br^- anions have higher nucleophilicity to the pendant phosphonium salts than does cinnamate anion. On the other hand, the rate of photochemical reaction of PCIN was promoted by the addition of some amounts of KF, because the content of the pendant phosphonium salt with cinnamate anion in the polymeric photosensitizer was increased by the salt effect of KF. Furthermore, F^- anion, which has a lower nucleophilicity than cinnamate anion, cannot prevent the anion-exchange reaction.

Although the rate of photochemical reaction of PCIN (3.0×10^{-5} mol/L) with use of PTBP-NP$_{19.2}$ increased with increasing photosensitizer content up to about 10 mol %, the rate of reaction gradually decreased with increase of the photosensitizer content when the irradiation was carried out by method A. On the other hand, the reaction had its highest rate near 20 mol % of the photosensitizer content when the irradiation was carried out by method B (Figure 7). This suggests that although some addition of polymeric photosensitizer promoted the photochemical reaction of PCIN, excess amounts of the polymeric photosensitizer either depressed the concentration effect of each substrate-attracting group in the polymer or obstructed the nonsensitizing reaction of PCIN by the self-quenching of the photosensitizer. Similar self-quenching has been found[13] in the photooxidation by other polymeric

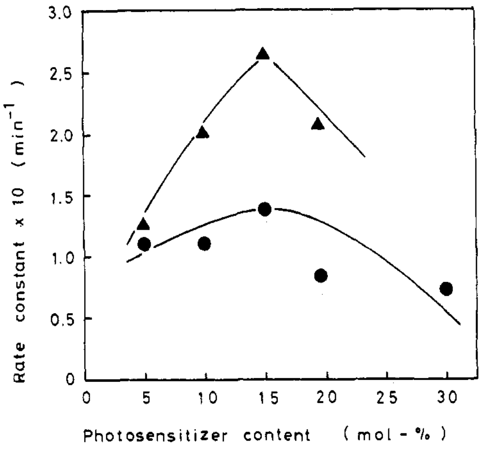


Figure 8. Correlation between the reaction rate of PCIN (3.0 × 10^{-5} mol/L) and the content of pendant photosensitizer group in the polymer in water by method A: (▲) with 3.0 × 10^{-6} mol/L of PTBP-NP; (●) with 1.2 × 10^{-5} mol/L of PTBP-NP.

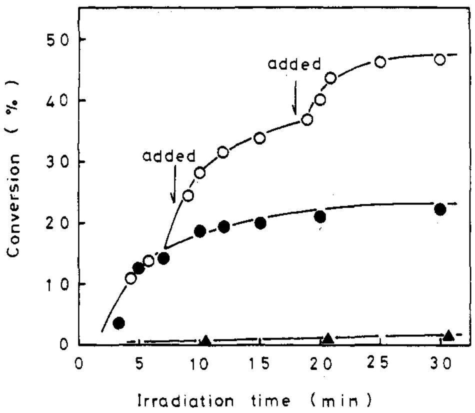


Figure 9. Rate of reaction of PSB (3.0 × 10^{-5} mol/L) with PTBP-$NP_{19.2}$ in water by method A: (●) with 10 mol % of the photosensitizer; (○) with total 30 mol % of the photosensitizer; (▲) without photosensitizer.

photosensitizers containing pendant rose bengal moiety.

The effect of content of pendant photosensitizer moiety in PTBT-NP on the rate of photochemical reaction of PCIN is shown in Figure 8. This polymeric photosensitizer had its highest rate at about 15 mol % of photosensitizer content, when the reactions were carried out with 10 or 40 mol % of photosensitizer concentration. This suggests that the introduction of large amounts of pendant photosensitizer moiety caused self-quenching between pendant photosensitizer moieties in the polymer. The same result has observed[22] in the photochemical reaction of self-sensitized photosensitive polymer containing pendant cinnamic ester and pendant 4-nitrophenoxy group as a photosensitizer in the diluted benzene solution. Neckers et al.[13] have also reported a similar result in photosensitization oxidation by a polymeric photosensitizer containing rose bengal.

Although the photochemical reaction of PSB (3.0 × 10^{-5} mol/L) proceeded slightly without photosensitizer in water, the reaction of PSB was greatly promoted by the addition of polymeric photosensitizer PTBP-$NP_{19.2}$ (Figure 9). This suggests that the multifunctional polymeric photosensitizer PTBP-NP was also effective for the photochemical reaction of PSB in water.

From all these results, it was concluded that although a multifunctional polymeric photosensitizer containing a pendant photosensitizer moiety and a substrate-attracting group has a higher photosensitization efficiency than the corresponding low molecular weight photosensitizer, the control of content of the pendant photosensitizer moiety in the polymer and of addition of photosensitizer into the reaction system is very important to get high efficiency.

Registry No. NPMS, 98457-90-0; CMS, 30030-25-2; PNP, 1124-31-8; NNMS, 98457-92-2; PNN, 88191-91-7; VBPC, 42808-25-3; TBP, 998-40-3; (NPMS)(VBPC) (copolymer), 114220-97-2; (NPMS)(MA) (copolymer, potassium salt), 114249-70-6; PCIN, 16089-48-8; PSB, 24634-61-5.

References and Notes

(1) Moser, R. E.; Cassidy, H. G. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 545.
(2) Leermakers, P. A.; James, F. C. *J. Org. Chem.* **1968**, *32*, 2898.
(3) Blossey, E. C.; Neckers, D. C.; Thayer, A. L.; Schaap, A. P. *J. Am. Chem. Soc.* **1973**, *95*, 1973.
(4) Schaap, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 3741.
(5) Neckers, D. C.; Blossey, E. C.; Schaap, A. P. Can. Patent 1044639, 1978; *Chem. Abstr.* **1979**, *90*, 213177h.
(6) Neckers, D. C.; Blossey, E. C.; Schaap, A. P. Can. Patent 1054971, 1979; *Chem. Abstr.* **1979**, *91*, 220263g.
(7) Schaap, A. P.; Thayer, A. L.; Zaklika, K. A.; Valenti, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4016.
(8) Handley, R. S.; Stern, A. J.; Schaap, A. P. *Tetrahedron Lett.* **1985**, *26*, 3183.
(9) Tamagaki, S.; Liesner, G. E.; Neckers, D. C. *J. Org. Chem.* **1980**, *45*, 1573.
(10) Lamberts, J. J. M.; Schumacher, D. R.; Neckers, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 5897.
(11) Paczkowski, J.; Neckers, D. C. *Macromolecules* **1985**, *18*, 1245.
(12) Paczkowski, J.; Neckers, D. C. *Macromolecules* **1985**, *18*, 2412.
(13) Peczkowska, B.; Paczkowski, J.; Neckers, D. C. *Macromolecules* **1986**, *19*, 863.
(14) Asai, N.; Neckers, D. C. *J. Org. Chem.* **1980**, *45*, 2903.
(15) Gupta, S. N.; Thijs, L.; Neckers, D. C. *Macromolecules* **1980**, *13*, 1037.
(16) Hautala, R. R.; Sweet, E. *Sol. Energy* **1977**, *19*, 503.
(17) Hautala, R. R.; King, R. B.; Kutal, C. *Solar Energy: Chemical Conversion and Storage*; Hamana: Clifton, NJ, **1979**; p 333.
(18) Uchida, J.; Nishikubo, T. *Nippon Kagaku Kaishi*, **1986**, 595.
(19) Iizawa, T.; Nishikubo, T.; Takahashi, E.; Hasegawa, M. *Makromol. Chem.* **1983**, *184*, 2297.
(20) Uchida, J.; Takahashi, E.; Iizawa, T.; Nishikubo, T. *Nippon Kagaku Kaishi* **1986**, 65.
(21) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*; Verlag Chemie: Weinheim, 1980; p 13.
(22) Nishikubo, T.; Uchida, J.; Takahashi, E.; Iizawa, T. *Makromol. Chem.* **1985**, *186*, 1555.