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Study of Polymeric Photosensitizers. 5. Synthesis of Multifunctional Photosensitizers Bonded on Cross-Linked Polymer Beads and Their Application for Photoisomerization of Potassium Sorbate

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ABSTRACT: Various new kinds of multifunctional polymeric photosensitizer beads, having excellent photosensitization efficiency, containing both a pendant benzophenone (BP) moiety as a photosensitizing group and pendant quaternary phosphonium or ammonium salts as the substrate-attracting groups were synthesized by the substitution reaction of the cross-linked (chloromethyl)polystyrene bead with potassium 4-benzoylphenoxide followed by the addition reaction of the resulting polymers with tertiary phosphines or amines and the radical copolymerization of (chloromethyl)styrene, 4-vinylbenzophenone, and small amounts of divinylbenzene followed by the addition reaction of the obtained polymer beads with tertiary phosphines or amines. The photosensitizing trans–cis isomerization of potassium sorbate (PSB) was carried out by using these multifunctional polymer beads in water or methanolic aqueous solution, and the resulting beads were evaluated for their photosensitization efficiency. This result indicates that the synthesized multifunctional photosensitizer beads have very high photosensitization efficiency for PSB, and the photosensitization efficiency of the polymer bead was strongly affected by the content of the pendant BP moiety, bulkiness or hydrophilicity of the substrate-attracting group, concentration of the photosensitizer bead, and reaction medium.

Introduction

Heterogenous polymeric photosensitizers have been widely used in the photochemical isomerization, dimerization, and oxidation of organic compounds, as well as in solar energy storage and exchange processes, because these photosensitizers can be separated easily from reaction mixtures or can be reused,[1] or they can be used in flow systems,[2] respectively.

Leermakers and James[3] have used small pieces of poly(vinyl phenyl ketone), which is like acetophenone, as a heterogeneous photosensitizer for photochemical cis–trans isomerization of *cis*-piperylene and the valence isomerization of norbornadiene (NBD) in isopentane. Blossey and Neckers have reported[4] introduction of benzophenone (BP) moiety into the cross-linked polystyrene bead and its application for the photochemical reactions of inden, tetrachloroethylene-cyclopentadiene, and coumarin. Blossey et al.[5,6] have also successfully utilized insoluble polymer-based rose bengal for the generation of singlet oxygen. Recently, Schaap et al.[7] and Neckers et al.[8–10] have studied separately this photooxidation system using various insoluble polymers having a rose bengal moiety. Kenly et al.[11] have reported the photooxidation of di-*n*-butyl sulfide by singlet oxygen using various immobilized photosensitizers in poly(vinyl chloride) or in cellulose acetate films. Hautala et al.[12] proposed a solar energy storage system using the photochemical reaction of NBD with insoluble photosensitizers such as cross-linked polystyrene or silica gel beads bound to a 4-(*N*,*N*-dimethylamino)benzophenone moiety as a chromophore. Many other heterogeneous polymeric photosensitizers have been reported[13–18] for the various photochemical reactions so far. However, the efficiency of all of these insoluble photosensitizers was generally lower than that of the corresponding low molecular weight photosensitizers used, with the exception of the recent work[19] of Neckers and his co-workers.

On the other hand, we have recently proposed[20,21] the concept of multifunctional polymeric photosensitizers composed of soluble polymers having both pendant substrate-attracting groups and photosensitizing groups. These polymers would have higher photosensitization efficiency than the corresponding low molecular weight photosensitizers.

This article reports on successful synthesis of multifunctional photosensitizers composed of the cross-linked polystyrene beads bound to quaternary phosphonium or ammonium salts as substrate-attracting groups and to BP

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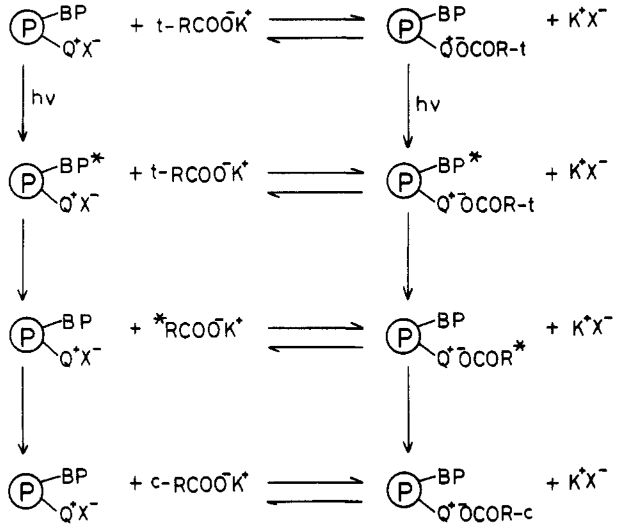
Scheme I



moiety as a photosensitizing group and investigates the photochemical reaction of potassium sorbate (PSB) by using those insoluble multifunctional polymeric photosensitizers in water or methanolic aqueous solution (Scheme I).

Experimental Section

Materials. The solvents were purified in the usual way prior to use. Benzoyl peroxide (BPO) was recrystallized twice from benzene at 40 °C. Chloromethylated styrene (CMS) (mixture of 40% meta and 60% para) was distilled twice under reduced pressure. Commercial triethylamine (TEA), triethylphosphine (TEP), tripropylphosphine (TPP), tributylphosphine (TBP), trihexylphosphine (THP), and trioctylphosphine (TOP) were used without further purification. Commercial 55% divinylbenzene (DVB) was used without further purification. Tetrabutylammonium bromide (TBAB) was recrystallized twice from THF. *trans*-PSB (λ_{max} 256 nm in water) and potassium 4-benzoylphenoxide (PBP) were prepared by the reactions of potassium hydroxide with sorbic acid or 4-hydroxybenzophenone in methanol, respectively, and then recrystallized. 4-Vinylbenzophenone (VBP; mp 50–51 °C (lit. 51–52 °C)[22]) was synthesized in 49% yield by the reaction of (4-benzoylbenzyl)triphenylphosphonium bromide with a 37% HCHO aqueous solution and an aqueous solution of sodium hydroxide as reported previously.[15] (Chloromethyl)polystyrene bead cross-linked with 3% DVB (PCMS-3C) (207.7 mg/g as chlorine) was provided by Mitsubishi Kasei Co. (Chloromethyl)polystyrene bead cross-linked with 1% DVB (PCMS-1C) (150.5 mg/g as chlorine) was prepared in 80.3% yield by the suspension copolymerization of CMS (51.8 g; 0.3 mol) with DVB (0.71 g; 3.0 mmol) in the presence of 98% saponified poly(vinyl alcohol) (PVA) (0.5 g) and 88% saponified PVA (0.02 g) in water (1 L) with BPO (0.73 g; 3 mmol) as radical initiator at 80 °C for 8 h under flowing nitrogen; filtered; washed twice each with water, methanol, and acetone; and dried under vacuum at 50 °C. Low molecular weight photosensitizer (4-benzoylbenzyl)triethylphosphonium bromide[23] (BTEPB) (mp 175–176 °C) was synthesized by the addition reaction of 4-(bromomethyl)benzophenone with TEP.

Apparatus. UV spectra were recorded on the Shimazu Model UV-240 spectrophotometer.

Typical Procedure for the Substitution Reaction of the Cross-Linked (Chloromethyl)polystyrene with the Potassium Salt of the Photosensitizing Compound. A typical example of the reaction of PCMS-1C or PCMS-3C with the potassium salt of the photosensitizing compound is as follows:

A mixture of 5.19 g (22 mmol as chloromethyl group) of PCMS-1C and 0.58 g (2.2 mmol) of PBP in 50 mL of DMF was stirred in the presence of 0.71 g (2.2 mmol) of TBAB as a phase-transfer catalyst (PTC) at 80 °C for 48 h. The polymer was filtered, washed three times each with water and acetone, and dried under vacuum at 50 °C to yield 5.51 g of polymeric photosensitizer (P-1). The degree of substitution of the polymer was 9.4 mol %, calculated from elemental analysis of chlorine (127.3 mg/g).

Typical Procedure for the Synthesis of the Cross-Linked Photosensitizer by the Suspension Copolymerization of VBP and CMS. A typical example of the suspension copolymerization of VBP and CMS for the synthesis of the cross-linked photosensitizer is as follows:

Suspension copolymerization of 1.04 g (5.0 mmol) of VBP, 6.79 g (45.5 mmol) of CMS, and 0.12 g (0.5 mmol) of DVB in 200/ mL of water was carried out in the presence of 98% saponified PVA (0.50 g) and 88% saponified PVA (0.02 g) using 0.12 g (0.5 mmol) of BPO at 80 °C for 8 h under following nitrogen. The polymer bead was filtered, washed three times each with water and acetone, and dried under vacuum at 50 °C. The yield of polymer bead (P-10) was 69.2%. The content of chlorine in the polymer was 121.2 mg/g.

Typical Procedure for the Synthesis of a Multifunctional Polymeric Photosensitizer Bead Having Both Pendant Photosensitizing and Substrate-Attracting Groups. Polymer bead P-1 (0.70 g; 2.5 mmol as chloromethyl group), containing 9.4 mol % of pendant BP moiety, which was prepared by partial substitution reaction of the chloromethyl group of PCMS-1C with PBP, was made to react with 0.5 g (3.8 mmol) of TEP in 10 mL of DMF at 60 °C for 120 h. The polymer bead was filtered, washed three times with methanol, and dried under vacuum at 50 °C. The yield of recovered polymer (P-13) was 0.84 g. The content of pendant benzyltriethylphosphonium chloride (BTEPC) in the polymer was 77.1 mol %, calculated from elemental analysis of chlorine (93.3 mg/g).

Measurement of Adsorption of PSB to a Multifunctional Polymer Bead. *trans*-PSB (5.41 mg; 9×10^{-5} mol/L) was dissolved in 400 mL of water and then a suitable amount (1×10^{-4}–7×10^{-4} mol/L as substrate-attracting group) of the multifunctional polymer bead was added into the solution with magnetic stirring. The degree of adsorption of PSB was measured by the disappearance of absorption maximum at 256 nm of PSB in the solution by UV spectrophotometry.

Photochemical Reaction of PSB Using a Multifunctional Polymeric Photosensitizer Bead. The photoisomerization of PSB (9×10^{-5} mol/L) was carried out with suitable amounts (9×10^{-6}–6.3×10^{-5} mol/L as pendant BP moiety) of the multifunctional polymer bead in a small conventional photochemical reactor, consisting of a four-necked reaction vessel (400 mL) with a Pyrex water Jacket immersion and a 100-W high-pressure mercury lamp (Ushio Electric Co., UM-102), at 30 °C under nitrogen atmosphere with magnetic stirring. Nitrogen gas was bubbled through the solution for 90 min before switching on the lamp; then the nitrogen gas stream was passed very slowly over the reaction solution during UV light irradiation. The rate of disappearance of the absorption maximum at 256 nm of *trans*-PSB was measured by UV spectrophotometer.

Results and Discussion

Syntheses of Multifunctional Polymeric Photosensitizer Beads Having both a Benzophenone Moiety and Substrate-Attracting Groups. A BP moiety as a photosensitizing group was introduced into the cross-linked polystyrene bead by two different methods. As summarized in Table I, the partial substitution reaction of the cross-linked (chloromethyl)polystyrene beads (PCMS-1C and PCMS-3C) with PBP was carried out with TBAB as a PTC in DMF at 80 °C for 48 h.

This result suggests that the reaction of PCMS-1C with PBP proceeded almost quantitatively. On the other hand, the degree of functionalization (DF) of PCMS-3C by PBP was lower than PCMS-1C.

BP moiety was also conducted into the cross-linked chloromethylpolystyrene bead by radical copolymerization of VBP, CMS, and 1% DVB (Table II). This result suggests that the yield of bead increased with increasing the ratio of VBP in the charged monomers. However, the degree of introduction of VBP unit in the cross-linked copolymer bead could not be determined by general analytical methods. Therefore, the VBP unit in the polymer

Table I
Conditions and Results of the Substitution Reaction of Chloromethylpolystyrene Beads with PBP[a]

polym	PCMS bead, mmol	PBP, mmol	TBAB, mmol	DMF, mL	yield, g	Cl in polym, mg/g	DF,[b] mol %
P-1	PCMS-1C (22.0)	2.2	2.2	50	5.51	127.3	9.4
P-2	PCMS-1C (22.0)	3.3	2.2	50	5.80	114.9	15.1
P-3	PCMS-1C (22.0)	4.4	2.2	50	6.32	103.9	20.6
P-4	PCMS-3C (17.6)	1.8	1.8	40	3.11	174.8	8.8
P-5	PCMS-3C (17.6)	2.6	1.8	40	3.10	157.1	14.1
P-6	PCMS-3C (17.6)	3.5	1.8	40	2.97	144.3	18.7

[a] The reaction was carried out at 80 °C for 48 h. [b] Degree of functionalization.

Table II
Conditions and Results of Suspension Copolymerization of VBP and CMS[a]

polym	VBP, mmol	CMS, mmol	yield, %	Cl in polym, mg/g	VBP in polym,[b] mol %
P-7	0.5	49.0	67.6	145.7	1.0
P-8	1.5	48.0	68.6	129.0	3.0
P-9	2.5	47.0	69.7	132.2	5.0
P-10	5.0	44.5	69.2	121.2	10.0
P-11	7.5	42.0	75.0	119.5	15.0
P-12	10.0	39.5	85.6	105.6	20.0

[a] The copolymerization was carried out with 1% DVB in 200 mL of water in the presence of 98% saponified PVA (0.50 g) and 88% saponified PVA (0.02 g) using 0.5 mmol of BPO at 80 °C for 8 h. [b] Supposed from charged VBP concentration.

bead was estimated from amounts of the charged VBP, because the soluble VBP–CMS copolymer having almost the same ratio with the charged monomer ratio has been synthesized[23] by radical copolymerization in benzene.

Several multifunctional photosensitizers of the cross-linked polystyrene bead bound to quaternary phosphonium or ammonium salts as substrate-attracting groups and to BP moiety as a photosensitizing group were prepared by the addition reaction of the pendant chloromethyl group in some cross-linked polystyrene beads containing a benzophenone moiety with tertiary phosphines or amines.

As summarized in Table III, the addition reactions of pendant chloromethyl groups in the partially functionalized PCMS-1C (P-1, -2, and -3) and PCMS-3C (P-4, -5, and -6) with 1.5 times higher amounts of tertiary phosphines were carried out in DMF for 120 h. The addition reaction of P-1, which has 9.4 mol% of pendant BP moiety, with TEP, TPP, and TBP proceeded with high conversion to give the corresponding polymers P-13, P-14, and P-15 containing 77.1, 71.7, and 76.6 mol% of pendant BTEPC, benzyltripropylphosphonium chloride (BTPPC), and benzyltributylphosphonium chloride (BTBPC), respectively, when the reaction was carried out at 60 °C. On the other hand, the reactions of P-1 with THP and TOP were carried out at 80 °C, because the reactivity decreased[24] with increasing the carbon number of alkyl chain in tertiary phosphines, and gave the corresponding polymers P-16 and P-17 containing 86.3 and 78.6 mol % of pendant benzyltrihexylphosphonium chloride (BTHPC) and benzyltrioctylphosphonium chloride (BTOPC), respectively.

The reactions of P-2 and P-3 with TEP, TPP, and TBP also gave the corresponding polymers (P-18–23) with high conversions at 60 °C. This result indicates that the degree of quaternalization of pendant chloromethyl group in the cross-linked polymer bead was not affected by the content of pendant BP moiety.

The addition reactions of pendant chloromethyl groups in P-4, P-5, and P-6, which are 3% cross-linked polymer beads and contain corresponding amounts of pendant BP

Table III
Conditions and Results of the Addition Reaction of Partially Substituted PCMS Beads by PBP with Tertiary Phosphines[a]

polym	starting polym	$P(R)_3$	temp, °C	yield, g	BP in polym, mol %	Cl in polym, mg/g	phosphonium unit in polym, mol %
P-13	P-1	TEP	60	0.84	9.4	93.3	77.1
P-14	P-1	TPP	60	0.94	9.4	87.2	71.7
P-15	P-1	TBP	60	0.94	9.4	78.6	76.6
P-16	P-1	THP	80	1.20	9.4	64.0	86.3
P-17	P-1	TOP	80	1.40	9.4	58.8	78.6
P-18	P-2	TEP	60	0.98	15.1	90.5	72.2
P-19	P-2	TPP	60	1.04	15.1	79.3	72.4
P-20	P-2	TBP	60	1.20	15.1	73.8	78.7
P-21	P-3	TEP	60	0.91	20.6	80.6	64.5
P-22	P-3	TPP	60	1.07	20.6	74.1	67.2
P-23	P-3	TBP	60	1.19	20.6	73.0	64.7
P-24	P-4	TEP	60	0.67	8.8	117.8	75.0
P-25	P-4	TPP	60	0.65	8.8	100.8	81.9
P-26	P-4	TBP	60	0.87	8.8	91.2	80.7
P-27	P-4	THP	80	1.03	8.8	75.3	82.3
P-28	P-4	TOP	80	0.83	8.8	64.5	82.6
P-29	P-5	TEP	60	0.73	14.1	103.6	79.2
P-30	P-5	TPP	60	0.88	14.1	93.1	78.9
P-31	P-5	TBP	60	0.91	14.1	83.4	78.9
P-32	P-5	THP	80	1.13	14.1	73.0	74.9
P-33	P-5	TOP	80	1.27	14.1	62.0	77.4
P-34	P-6	TEP	60	0.81	18.4	103.3	66.5
P-35	P-6	TPP	60	0.97	18.4	91.0	67.6
P-36	P-6	TBP	60	1.09	18.4	99.6	74.9
P-37	P-6	THP	80	1.18	18.4	67.4	74.5
P-38	P-6	TOP	80	1.07	18.4	56.5	71.1

[a] The reaction was carried out with 5 mmol of polymer (as chloromethyl group) and 7.5 mmol of tertiary phosphine 10 mL of DMF for 120 h.

Table IV
Conditions and Results of the Addition Reaction of the CMS–VBP Copolymer Bead with Tertiary Phosphine or Amine[a]

polym	starting polym	$P(R)_3$ or $N(R)_3$	yield, g	VBP in[b] copolym, mol %	Cl in copolym, mg/g	onium unit in copolym, mol %
P-39	P-7	TEP	1.87	1.0	102.4	85.5
P-40	P-9	TEP	2.08	5.0	82.0	89.3
P-41	P-10	TEP	2.25	10.0	86.2	88.1
P-42	P-11	TEP	2.11	15.0	86.8	79.6
P-43	P-12	TEP	1.94	20.0	79.9	71.8
P-44	P-7	TEA	1.70	1.0	107.3	77.5
P-45	P-9	TEA	1.92	5.0	90.3	87.0
P-46	P-10	TEA	2.11	10.0	91.8	82.1
P-47	P-11	TEA	1.89	15.0	79.9	72.6
P-48	P-12	TEA	1.81	20.0	98.2	70.2
P-49	P-11	TPP	1.04	15.0	65.3	73.4
P-50	P-11	TBP	1.20	15.0	65.1	79.7
P-51	P-11	THP	1.38	15.0	78.0	53.2

[a] The reaction was carried out with 5 mmol of polymer (as chloromethyl group) and 7.5 mmol of tertiary phosphine or amine in 10 mL of DMF at 80 °C for 120 h. [b] Supposed from the charged VBP concentration.

moiety, with TEP, TPP, THP, and TOP proceeded with high conversion to give the corresponding polymers (P-24–38) bound to benzyltrialkylphosphonium chlorides. This result means that the degree of quaternalization of the pendant chloromethyl group in the polymer bead was not affected by the degree of cross-linking up to 3% under the same reaction conditions.

The addition reactions of pendant chloromethyl groups of the cross-linked copolymers CMS–VBP (P-7, -9, -10, -11, and -12), which have about 1, 5, 10, 15, and 20 mol % of pendant BP moiety, with TEP and TEA were carried out in DMF at 80 °C for 120 h (Table IV).

This result suggests that the corresponding multifunctional photosensitizers (P-39–48) containing pendant BTEPC or benzyltriethylammonium chloride (BTEAC) were obtained with high conversion, although the reactivity of TEA was lower than that of TEP for the pendant chloromethyl group in the same polymer beads.

Adsorption and Ion Exchange Reaction between Multifunctional Polymeric Photosensitizer Bead and PSB in Water. It has been proposed[21] that the high efficiency of soluble multifunctional polymeric photosensitizers containing both a pendant photosensitizing group and the substrate-attracting group is attributable to the attraction effect of the polymer for the substrate, although the efficiency has not been measured by spectrophotometry in the reaction between the soluble polymeric photosensitizer and potassium cinnamate in water. However, as shown in Figure 1, the absorption maximum of the UV spectrum of PSB in water decreased dramatically when small amounts of the polymer bead containing quaternary salt were added into the solution.

As shown in Figure 2, the rate of decrease of PSB in water was measured by addition of the polymer bead (P-24). This suggests that the ion exchange reaction between the polymer bead and PSB had reached substantial equilibrium in 60 min in water.

Correlation between the amounts of adsorbed PSB on the polymer beads and concentration of substrate-attracting group in the polymer bead was determined. As shown in Figure 3, although total amounts of the adsorbed PSB increased with increasing amounts of added polymer bead, the adsorption efficiency of the quaternary salt in the polymer declined with increase in total amount of the added quaternary salt. This result means that the efficiency of the quaternary salt in the polymer bead is not affected by the content of pendant BP moiety and the degree of cross-linking of the bead.

Photochemical Reaction of PSB Using a Multifunctional Polymeric Photosensitizer Bead. It is known[25] that trans–cis isomerization proceeded preferentially in the photochemical reaction of PSB in water. As shown in Figure 4, the absorption maximum of the UV spectrum of *trans*-PSB in water decreased strongly under irradiation by the high-pressure mercury lamp in the

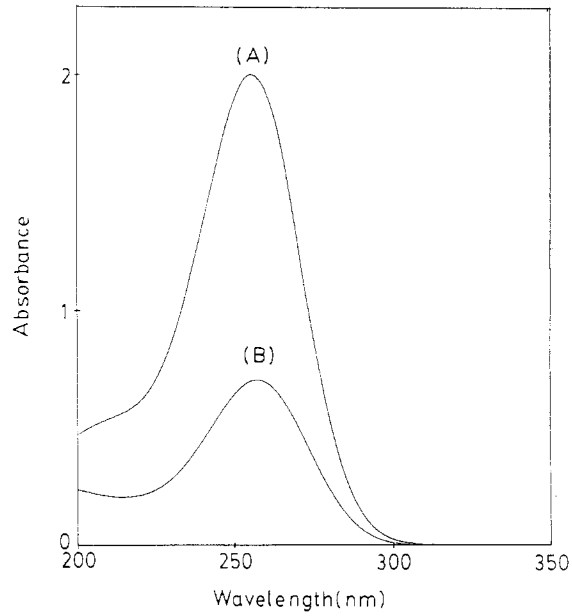


Figure 1. Change of UV spectrum of PSB (9×10^{-5} mol/L) in water: (A) before addition of polymer bead; (B) after addition of P-24 having 8.8 mol % of pendant BP moiety and 75.0 mol % of pendant BTEPC (3.1×10^{-4} mol/L as substrate-attracting group).

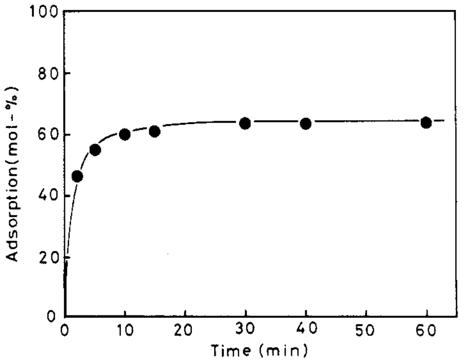


Figure 2. Rate of adsorption of PSB (9×10^{-5} mol/L) to polymer bead P-24 having 8.8 mol % of pendant BP moiety and 75.0 mol % of pendant BTEPC (3.1×10^{-4} mol/L as substrate-attracting group) in water.

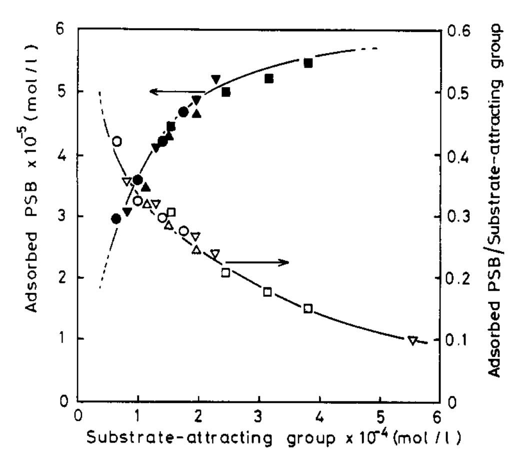


Figure 3. Correlation between the adsorbed PSB and the concentration of the substrate-attracting group in the polymer bead in water: (▽, ▼) P-40 having 5.0 mol % of pendant BP moiety and 89.3 mol % of pendant BTEPC; (□, ■) P-41 having 10.0 mol % of pendant BP moiety and 88.1 mol % of pendant BTEPC; (△, ▲) P-42 having 15.0 mol % of pendant BP moiety and 79.6 mol % of pendant BTEPC; (○, ●) P-43 having 20.0 mol % of pendant BP moiety and 71.8 mol % of pendant BTEPC.

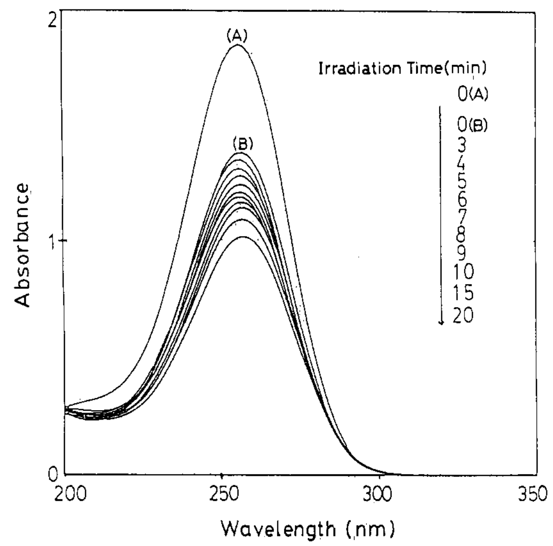


Figure 4. Change of UV spectrum of PSB (9 × 10^{-5} mol/L) on the polymer bead P-26 having 8.8 mol % of pendant BP moiety and 80.7 mol % of pendant BTBPC (2.7 × 10^{-5} mol/L as photosensitizing group) with irradiation of a high-pressure mercury lamp in 50% methanolic aqueous solution: (A) before addition of polymer bead; (B) after addition of polymer bead.

presence of multifunctional polymeric photosensitizer bead. This suggests that photosensitizing trans–cis isomerization of PSB occurred effectively in water when using the polymer bead.

As shown in Figure 5, although the rate of photochemical reaction of PSB was only slightly promoted by addition of low molecular weight photosensitizer BTEPB, the rate of reaction of PSB was increased significantly by addition of the multifunctional polymeric photosensitizer bead when the reaction was carried out in water. Figure 5 also shows that the efficiency of the polymer bead was strongly affected by the contents of photosensitizing group or substrate-attracting group. Furthermore, it was found that the observed rate of PSB with the polymeric photosensitizer bead obeyed first-order kinetics in the initial reaction stage.

Accordingly, the effect of photosensitizer content in the polymer bead was examined. As shown in Figure 6, a 3% cross-linked bead P-24, which contained 8.8 mol % of pendant BP moiety and 75.0 mol % of pendant BTEPC, had higher photosensitization efficiency than 3% cross-linked P-29 and P-34 containing 14.1 and 18.4 mol % of pendant BP moiety, respectively. In addition, the efficiency of 1% cross-linked P-13 containing 9.1 mol % of pendant BP moiety and 77.1 mol% of pendant BTEPC fell between that of P-24 and P-29.

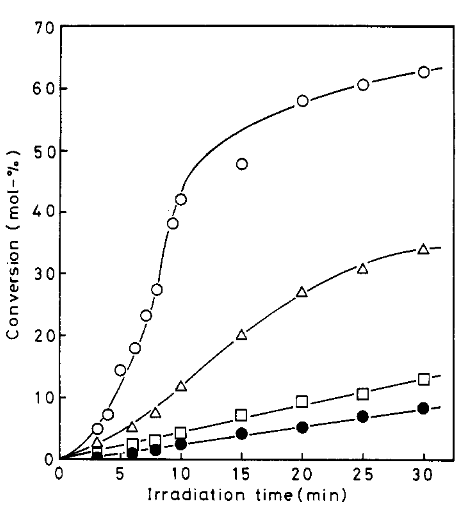


Figure 5. Rate of reaction of PSB (9 × 10^{-5} mol/L) using the polymer bead (2.7 × 10^{-5} mol/L as photosensitizing group) in water: (○) P-24 having 8.8 mol % of pendant BP moiety and 75.0 mol % of pendant BTEPC; (△) P-34 having 18.4 mol % of pendant BP moiety and 66.5 mol % of pendant BTEPC; (□) low molecular weight BTEPB; (●) without photosensitizer.

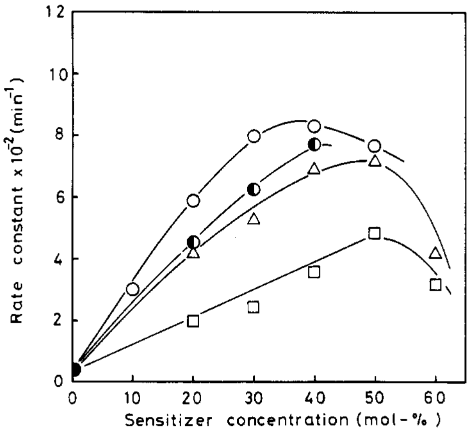


Figure 6. Correlation between the reaction rate of PSB (9 × 10^{-5} mol/L) and the concentration of polymer bead (as photosensitizing group) containing pendant BTEPC in water: (○) P-24 having 8.8 mol % of pendant BP moiety; (◐) P-13 having 9.4 mol % of pendant BP moiety; (△) P-29 having 14.1 mol % of pendant BP moiety; (□) P-34 having 18.4 mol % of pendant BP moiety.

This means that photosensitization efficiency of the polymer bead was strongly affected by the content of the photosensitizing group in the bead, because introduction of large amounts of photosensitizing group either decreased the degree of introduction of the substrate-attracting group in the polymer bead or depressed the effective energy transfer from the photosensitizing group to the substrate PSB by the self-quenching between photosensitizing groups. However, the efficiency was scarcely affected by the degree of cross-linking up to 3%.

Furthermore, P-24 showed the highest efficiency at 40 mol % of photosensitizer concentration to PSB, and P-29 and P-34 showed the highest efficiency, about 50 mol % of photosensitizer concentration. This result suggests that although the large amounts of polymer bead added, which were suspended in the reaction system, acted as filter for the photochemical reaction, the addition of proper quantities of the multifunctional polymeric photosensitizer bead

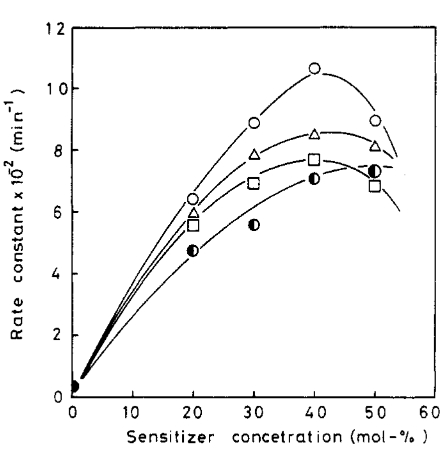


Figure 7. Correlation between the reaction rate of PSB (9×10^{-5} mol/L) and the concentration of polymer bead (as photosensitizing group) containing pendant BTEPC or BTEAC in water: (○) P-43 having 20 mol % of pendant BP moiety and 71.8 mol % of pendant BTEPC; (△) P-42 having 15 mol % of pendant BP moiety and 79.6 mol % of pendant BTEPC; (□) P-41 having 10 mol % of pendant BP moiety and 88.1 mol % of pendant BTEPC; (◐) P-48 having 20 mol % of pendant BP moiety and 70.2 mol % of pendant BTEAC.

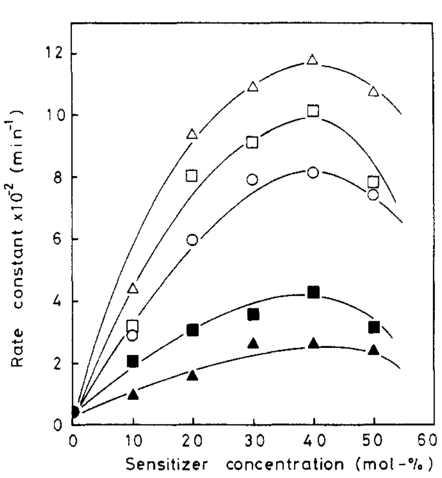


Figure 8. Correlation between the reaction rate of PSB (9×10^{-5} mol/L) and the concentration of polymer bead having 8.8 mol % of pendant BP moiety in water or in 50% methanolic aqueous solution: (△) P-24 having pendant BTEPC in water; (□) P-25 having pendant BTPPC in water; (○) P-26 having pendant BTBPC in water; (■) P-26 having pendant BTBPC in the methanolic solution; (▲) P-27 having pendant BTHPC in the methanolic solution.

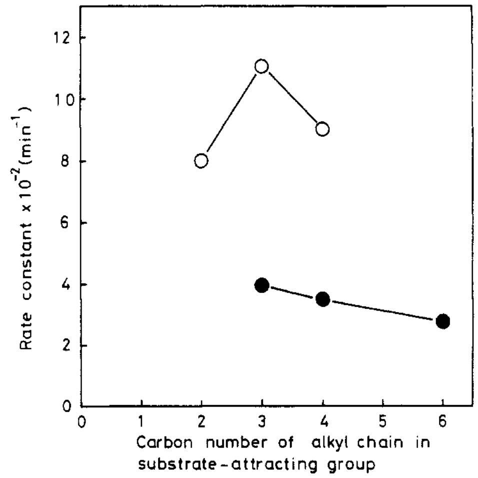


Figure 9. Correlation between the reaction rate of PSB (9×10^{-5} mol/L) and the carbon number of alkyl chain on the quaternary phosphonium salt in the polymer bead having 8.8 mol % of pendant BP moiety (2.7×10^{-5} mol/L as photosensitizing group): (○) in water; (●) in 50% methanolic aqueous solution.

would promote effectively the photochemical reaction.

On the other hand, as shown in Figure 7, 1% cross-linked P-43, which was prepared by radical copolymerization of CMS and VBP followed by addition reaction of the resulting polymer bead with TEP, containing about 20 mol % of pendant BP moiety and 71.8 mol % of pendant BTEPC, had higher photosensitization efficiency than P-42 and P-41 containing about 15 and 10 mol % of pendant BP moiety, respectively. This result is in contrast to that of Figure 6. It may be supposed that although the BP moiety was introduced preferentially near the surface of the polymer bead by the first substitution reaction of the cross-linked (chloromethyl)polystyrene beads (PCMS-1C, PCMS-3C), the BP moiety was homogeneously distributed in the polymer bead prepared by the radical copolymerization of VBP and CMS. That is, the amounts of active photosensitizing group on the surface of the beads P-41, -42, and -43 are very small, and large amounts of BP moiety distributed inside of the polymer bead do not act as photosensitizer for PSB.

Furthermore, the photosensitization efficiency of P-48 containing about 20 mol % of pendant BP moiety and 70.2 mol % of pendant BTEAC was lower than that of P-43. This result could also be explained by a quenching due to quaternary ammonium, which would not occurr or would be less efficient in the case of phosphonium.

The photosensitizing reaction of PSB was examined by using various polymer beads containing 8.8 mol % of pendant BP moiety and similar amounts (75–82 mol %) of five different substrate-attracting groups. As shown in Figure 8, the efficiency of polymer bead P-25 having pendant BTPPC was higher than those of polymer beads P-24, -26, and -27 having pendant BTEPC, BTBPC, or BTHPC, respectively. This suggests that the photosensitizing efficiency of the polymer bead was strongly affected by the bulkiness or the hydrophilicity of substrate-attracting group on the bead. Figure 8 also show that each photosensitizer bead has the highest efficiency at 40 mol % concentration for PSB.

Furthermore, it was found that the rate of photosensitizing isomerization of PSB was strongly affected by the reaction medium; that is, the rate of reaction of PSB with P-26 in water was surprisingly higher than that of PSB in 50% methanolic aqueous solution. This has to do either with the polymer solvent interaction or with the respective solubility of PSB in water or alcohol.

Correlation between the rate of reaction of PSB and the carbon number of alkyl group of the quaternary phosphonium salt of the polymer beads prepared by the polymer reaction of PCMS-3C is shown in Figure 9. Figure 10 shows the efficiency of the polymer beads containing 15 mol % of VBP unit, which were synthesized by the radical copolymerization of CMS and VBP followed by the addition reactions of the resulting polymer beads with the some phosphines, in water and in 50% methanolic aqueous solution. Polymer bead P-42 having pendant BTEPC as a substrate-attracting group has higher efficiency than the polymer beads P-49, -50, and -51 having pendant BTPPC, BTBPC, or BTHPC, respectively, and the efficiency gradually depressed with increase in the bulkiness or the hydrophobicity of substrate-attracting group on the polymer bead.

It was thought that, basically, a multifunctional polymeric photosensitizer bead having tiny or hydrophilic quaternary salt as the substrate-attracting group should have higher efficiency than the polymer bead having bulky or hydrophobic quaternary salt for the photochemical

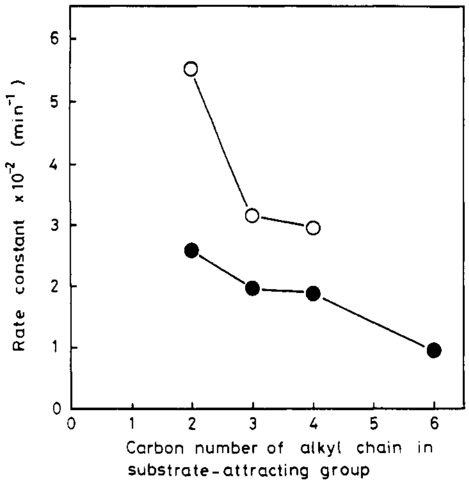
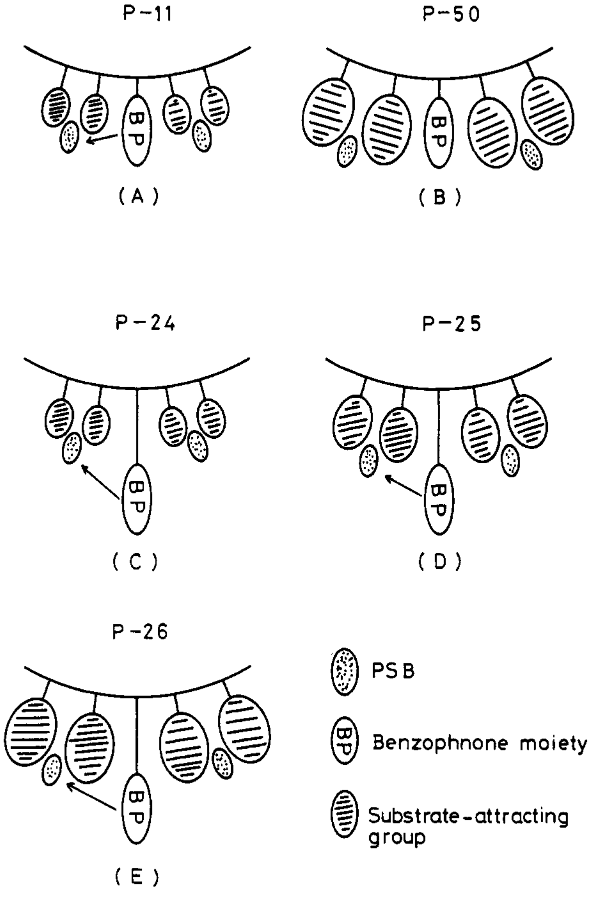


Figure 10. Correlation between the reaction rate of PSB (9 × 10^{-5} mol/L) and the carbon number of alkyl chain on the quaternary phosphonium salt in the polymer bead having 15.0 mol % of pendant BP moiety (2.7 × 10^{-5} as photosensitizing group): (○) in water, (●) in 50% methanolic aqueous solution.

Scheme II



reaction of PSB, because adsorption of PSB on the surface of the polymer bead and the ion exchange reaction between PSB and the substrate-attracting group on the bead occur smoothly (Scheme IIA,B) whereas the BP moiety on P-24, -25, -26, and -27 was bonded on the polymer bead with the benzyloxy group as the spacer. That is, the photosensitizing groups of P-24, -25, -26, and -27 have longer distances from the surface of the polymer bead than those of P-42, -49, -50, and -51. More effective energy transfer to PSB from the BP moiety on P-25 occurred than that from P-24 and -26, because suitable distances were maintained between the pendant BP moiety and the pendant BTPPC on the bead P-25 (Scheme IIC–E).

From these results, it was concluded that various multifunctional polymeric photosensitizer beads, which have a pendant BP moiety as the photosensitizing group and quaternary phosphonium or ammonium salts as the substrate-attracting groups, were synthesized by the substitution reaction of the cross-linked (chloromethyl)polystyrene bead with PBP using a phase transfer catalyst, followed by the addition reaction of the resulting polymers with tertiary phosphines or amines, and the radical copolymerization of CMS, VBP, and small amounts of DVB followed by the addition reaction of the obtained copolymer beads with the phosphines or amines using the same method applied to the above reactions. The synthesized multifunctional polymeric photosensitizer beads showed very high photosensitization efficiency for the photoisomerization of PSB.

Registry No. VBP, 3139-85-3; PTEPB, 122093-57-6; *trans*-PSB, 24634-61-5; *cis*-PSB, 122093-58-7; HCHO, 50-00-0; (4-benzoylbenzyl)triphenylphosphonium bromide, 55274-11-8; (4-bromomethyl)benzophenone, 32752-54-8.

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