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A Novel Approach to Chemical Functionalization of Polymer Film Surfaces by Aromatic Compounds via Photoinduced Electron Transfer

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ABSTRACT: Photoirradiation of a poly(2-hydroxyethyl methacrylate) (PHEMA) film with an acetonitrile solution of arylalkene or arylcyclopropane (S, aryl group; phenanthryl or pyrenyl group) in the presence of dimethyl terephthalate (DMTP) as an electron acceptor gave an aryl-modified polymer surface. Introduction of the aryl group to the film was confirmed by UV–vis absorption, fluorescence, X-ray photoelectron, and secondary ion mass spectroscopy. Mechanistic investigations indicated that a key intermediate of the photoreaction was the cation radical of S produced by one-electron transfer from the excited singlet state of S to DMTP. In addition to the factors controlling the photoreaction, properties of the modified polymer surface and micrometer fluorescent patterning of the film are also reported.

Introduction

A contribution of the surface to chemical/physical properties of a material is expected to become more important when the size of a material is reduced from centimeters or millimeters (as a bulk material) to micrometers or submicrometers, since a surface/volume ratio increases with decreasing size.[1] Interfacial interactions may also be dependent on the size of materials. Since it has been well recognized that surface properties play essential roles for functions of various materials, such as printing, painting, adhesive, lubricant, biocompatible materials, and so forth,[2] control of surface properties in the micrometer dimension will provide a new class of functionalized materials.

For control of surface properties and/or introduction of functionalities onto material surfaces in the micrometer dimension, conventional methods such as graft polymerization, corona-plasma discharge, chemical etching, and so on[2] cannot be applied owing to poor spatial resolution of the methods. For spatial resolution to be attained, use of microfabrication techniques represented by photolithography, scanning tunneling miocroscopy, and so on[3] is favorable. However, introduction of arbitrary chemical functions onto material surfaces will be very difficult since molecular mechanisms of reactions are not well controlled in these techniques. Among various methods, photochemical reactions are superior to other methods because a variety of chemical functions will be introduced to material surfaces by an appropriate choice of reactants. Furthermore, spatial patterns will be easily prepared on material surfaces by photoirradiation through a photomask or by scanning a focused light source. Actually, photochemical methods have been applied to prepare a chemically-functionalized patterned surface on a fluoropolymer film[4] or an ITO-coated glass plate[5] with the spatial resolution of ~100 μm. Recently, we also succeeded in simultaneous microfabrication and modification of a polymer film by laser ablation and reported that a fluorescent dye could be introduced to the film surface in a positive or negative micropattern (resolution ~2 μm).[6] In this case, however, the nature of the chemical bonding connecting the dye to the film was quite ambiguous. Clearly, new methods should be developed to introduce chemical functions on material surfaces with well-defined chemical structure and high spatial resolution.

A key reaction employed in the present study is the photochemical polar addition of alcohol to the radical cation of arylalkene or arylcyclopropane (S) produced by one-electron transfer from the excited state of S to an electron acceptor. In a homogeneous solution, it has been reported that a photoreaction of 1,1-diphenylethene[7] or 1-methyl-2-phenylcyclopropane[8] with methanol in the presence of a photosensitizer (Sens) gives an ether derivative in a regioselective manner (Scheme I). Furthermore, Dinnocenzo et al. recently reported that nucleophilic addition of the arylcyclopropane radical cation proceeded with complete inversion of the carbon center.[9] Therefore, we expect that the photoreaction of S with –OH groups in polymers brings about a functionalized surface with well-defined chemical bonding of the aryl group to the polymer (Scheme II). Since –OH groups are very common for various materials, such as cellulose, metal oxides, and so forth, the method will possess versatile applications.

In the present study, PHEMA films were used as a material with an –OH surface. For arylalkenes and arylcyclopropanes as S, we prepared a series of derivatives containing a pyrenyl, phenanthryl, or naphthyl group (Figure 1). These aromatic chromophores are known to act as an electron or excitation energy transfer sensitizer for a variety of reactions, so that aryl-modified polymer films will serve as heterogeneous photosensitizers or photocatalysts as well. In this paper, we show general features and mechanisms of the heterogeneous photoreaction between S and a PHEMA film. Characterization of the modified films and application of the method to micrometer fluorescent patterning of a film are also reported.

Experimental section

Chemicals. PHEMA (Aldrich) and acetonitrile (Nacalai, spectroscopic grade) were used without further purification. Dimethyl terephthalate (DMTP; Tokyo Kasei) was recrystallized repeatedly from methanol. 1-Cyanonaphthalene (1-CN; Tokyo Kasei) was purified by column chromatography (silica gel/*n*-hexane) followed by fractional distillation in vacuum. Preparations of the arylalkenes and arylcyclopropanes are as follows.

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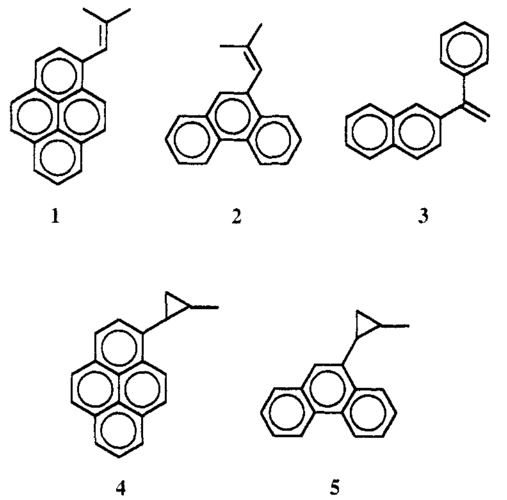
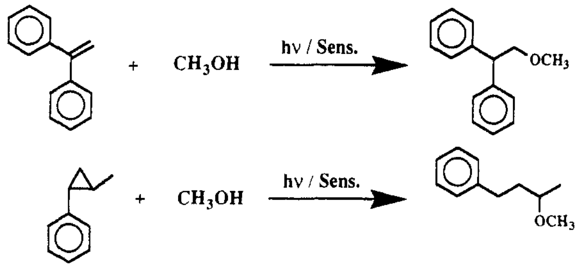
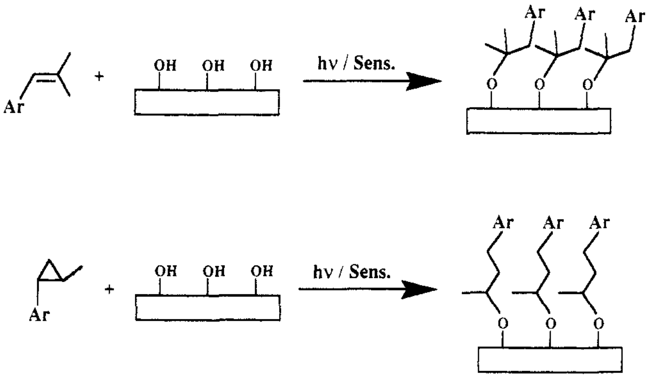


Figure 1. Structures and abbreviations of arylalkenes (1–3) and arylcyclopropanes (4, 5).

Scheme I



Scheme II



1-(1-Pyrenyl)-2-methylpropene (1). 2-Propylmagnesium bromide in diethyl ether (5 M, 20 mL) was added to an ethereal solution (50 mL) of 1-pyrenylaldehyde (Aldrich, 3.6 g), and the mixture was stirred for 1 h at a reflux temperature. After the reaction was allowed to stand for a further 12 h at room temperature, a saturated aqueous solution of ammonium chloride (20 mL) was added to the mixture. The mixture was then extracted with benzene, and the organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residues were dissolved in pyridine (50 mL). The pyridine solution was refluxed in the presence of *p*-toluenesulfonyl chloride (3.0 g) for 7 h. The solution was extracted with benzene/*n*-hexane (1:1, 20 mL) and the organic layer was washed with water repeatedly. After removal of the solvents, the residues were subjected to silica gel/*n*-hexane column chromatography. 1 was obtained in 20% yield (0.8 g): mp < 40 °C; 270-MHz ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 3 H), 2.10 (s, 3 H), 6.94 (s, 1 H), 7.83–8.24 (m, 9 H); MS (30 eV) 256 (M^+).

1-(9-Phenanthryl)-2-methylpropene (2). A 17-mL aliquot of *n*-butyllithium in *n*-hexane (Nacalai, 1.6 M) was added to an ether solution (80 mL) of 9-bromophenanthrene (Aldrich, 4.5 g) at −30 °C under a N_2 stream, and the mixture was allowed to warm to 0 °C. After the mixture was cooled to −20 °C, an ethereal solution (20 mL) of 2-methylpropionaldehyde (Nacalai, 2 mL) was added and the reaction was allowed to stand for a further 15 h under stirring. A saturated aqueous ammonium chloride solution (20 mL) was then added to the mixture at 5 °C, and the organic layer was washed with enough water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residues were purified by column chromatography on silica gel (*n*-hexane/benzene = 1/1, v/v) to give 1-(9-phenanthryl)-2-methylpropan-1-ol. Recrystallizations of the crude product from *n*-hexane/benzene (9/1, v/v) gave 3.6 g (75% yield) of white crystals: mp = 98.0–98.6 °C; 60-MHz ^{1}H NMR ($CDCl_3$) δ 1.0 (d, 6 H, J = 8 Hz), 2.0 (br, 1 H), 2.3 (m, 1 H), 5.1 (d, 1 H, J = 6 Hz), 7.4–8.8 (m, 9 H); MS (30 eV) 250 (M^+).

1-(9-Phenanthryl)-2-methylpropan-1-ol (1.55 g) was refluxed in 25% H_2SO_4 (20 mL) for 3 h. The mixture was then treated with 100 mL of *n*-hexane/benzene (9/1, v/v) after neutralization of the solution with an aqueous NaOH solution. The organic layer was washed with enough water and concentrated in vacuum to precipitate 1-(9-phenanthryl)-2-methylpropene. The precipitates were collected by filtration and subjected to column chromatography on silica gel/*n*-hexane. 2 (0.7 g, 45% yield) was further purified by vacuum distillation (200 °C, <1 mmHg). 2 (colorless crystal): mp = 51–53 °C; 270-MHz ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 3 H), 2.05 (s, 3 H), 6.65 (s, 1 H), 7.53–8.72 (m, 9 H); MS (30 eV) 232 (M^+).

1-(2-Naphthyl)-1-phenylethene (3). A mixture of 2-acetylnaphthalene (Nacalai, 8.5 g) and phenylmagnesium bromide (2.9 M, 18 mL) in absolute diethyl ether was refluxed for 6 h. After a saturated aqueous ammonium chloride solution (50 mL) was added to the mixture, the organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residues were purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2, 1/1, v/v). The crude product was refluxed in 20% H_2SO_4 (20 mL) for 1 h. After cooling, the mixture was extracted with 50 mL of benzene. Removal of the solvent gave 1-(2-naphthyl)-1-phenylethene as a yellow oil, which was purified by column chromatography on silica gel, followed by recrystallizations from methanol. Colorless crystals (5.8 g, 63% yield): mp = 55–56 °C; 270-MHz ^{1}H NMR ($CDCl_3$) δ 5.55 (d, 1 H, J = 1.0 Hz), 5.59 (d, 1 H), 7.33–7.41 (m, 5 H), 7.43–7.50 (m, 3 H), 7.78–7.85 (m, 4 H).

1-Methyl(1-pyrenyl)cyclopropane (4). 1-Pyrenylaldehyde (3.0 g) dissolved in a mixture of benzene/methanol/acetone (3/3/5, v/v, 110 mL) containing 0.5 g of NaOH was stirred for 1 h. Hydrazine hydrate (30 mL) was added to the mixture. After distillation of the solvents, 0.5 g of NaOH was added and the mixture was heated to 230 °C until gas evolution ceased. The reaction mixture was then allowed to cool to room temperature and extracted with 100 mL of benzene. The benzene layer was washed with enough water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residues were subjected to column chromatography on silica gel/*n*-hexane. The crude product was purified by vacuum distillation (200–230 °C, <1 mmHg) to give 2.4 g (72% yield) of 1-methyl(1-pyrenyl)cyclopropane (4) as a yellow oil:[10] 270-MHz ^{1}H NMR ($CDCl_3$) δ 0.64–1.47 (m, 6 H), 2.24–2.63 (m, 1 H), 7.66–8.53 (m, 9 H); MS (30 eV) 256 (M^+).

1-Methyl-2-(9-phenanthryl)cyclopropane (5). 5 was obtained by procedures analogous with those for the preparation of 4 using 9-phenanthrylaldehyde (3.02 g) as a starting material: colorless oil (2.45 g, 79% yield); 270-MHz ^{1}H NMR ($CDCl_3$) δ 0.58–1.44 (m, 3 H), 1.97–2.39 (m, 1 H), 7.46–8.69 (m, 9 H); MS (30 eV) 232 (M^+).

Photoreaction of PHEMA Film. A PHEMA film was spin-coated onto a quartz disk (29.5-mm diameter and 1-mm thickness) from a methanol solution of the polymer (10 mg/mL) and dried for 2–3 days at room temperature. The thickness of the film was estimated to be ca. 20 nm by a scanning electron microscope. The film on the quartz disk was washed in boiling benzene for 4 h to remove impurities and dried at ambient temperature prior to the experiments.

The PHEMA film on the quartz disk was fixed with a Teflon cell using a rubber O-ring, as illustrated in Figure 2. For fluorescence patterning experiments, a photomask was placed between the quartz disk and the Teflon cell. A 2-mL aliquot of an acetonitrile solution containing appropriate amounts of S and DMTP was poured into the cell and purged with a N_2 stream for 5 min. The cell was then sealed with another set of a quartz disk

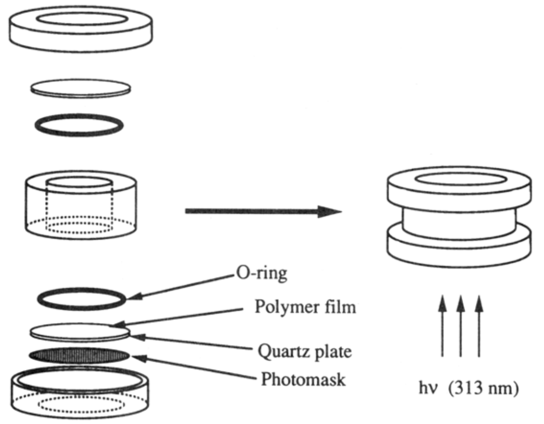


Figure 2. Teflon cell used for heterogeneous photoreaction of a PHEMA film.

and an O-ring. The film was irradiated from the bottom side of the cell to facilitate photoreactions at the film/solution boundary (Figure 2). A light source was a 500-W super high-pressure Hg lamp (Wacom, BMO 500D1), and 313-nm light was isolated by a combination of UV-D33S (Toshiba) and aqueous $K_2Cr_2O_7$ solution filters. After the photoreaction, the sample quartz disk was immersed in acetonitrile for several hours to remove unreacted compounds and dried in air prior to spectroscopic measurements.

Apparatus. Absorption and fluorescence (uncorrected) spectroscopy were performed with Shimadzu UV-3100S and Hitachi F-4010 spectrometers, respectively. ^{1}H NMR spectra were recorded on a JEOL JNM-PMX60SI or JNM-GX270 spectrometer with TMS as an internal standard. Mass spectra were obtained by a JEOL JMS-DX303H mass spectrometer. XPS measurements were performed by a VG Scientific Model ESCALAB MKII spectrometer. Mg $K\alpha$ radiation (1253.6 eV) operated at 10 kV and 20 mA was used as an X-ray excitation source. The carbon 1s binding energy (284.6 eV) for the trace amount of hydrocarbon originally present in air was used to calibrate the binding energy. Reproducibility of the binding energy between the measurements was 0.1 eV. Elemental analysis was carried out by a survey scan method, as reported elsewhere.[11]

Static secondary ion mass spectroscopy (static SIMS) was performed with a PHI/Perkin-Elmer 6300 quadrupole secondary ion mass spectrometer. Both positive and negative secondary ion mass spectra were obtained by bombardment of a xenon primary ion beam operated at 7 keV and 0.15 nA. The sputtering angle of the beam to the film was set at 60°, and the analyzed area was 1.5 mm in diameter. Charge-up of the sample during ion bombardment was compensated for by an electron spray. The spectra were analyzed on the basis of the literature values for PHEMA[12] as well as on the mass spectra of the starting materials and model compounds. Dynamic secondary ion mass spectroscopy (dynamic SIMS) was conducted with an Atomika A-DIDA 3000 ion mass spectrometer. Cs^+ generated at 12 keV and 15.8 nA was used as a primary ion source. Rastering and analyzing areas on a sample film were 400 × 400 and 80 × 80 μm, respectively. Charge-up was compensated for by an electron spray (0.6 kV and 3.0 A). Negative ions of m/z = 1, 12, 16, and 28 corresponding to H^-, C^-, O^-, and Si^-, respectively, were counted in counts per second (counts/s) as secondary ions. Depth profiles of the ions were estimated on the basis of the time profile of each anion and the etching rate.

Results and Discussion

A. Photoreaction of Aromatic Alkene or Cyclopropane with PHEMA Film. General Features. A photoreaction of a PHEMA film with an acetonitrile solution of the alkene (**1**–**3**: $(1–50) \times 10^{-3}$ M) or cyclopropane (**4**, **5**: $(5–7) \times 10^{-2}$ M) was performed in the presence of DMTP ($(1–5) \times 10^{-3}$ M) as an electron acceptor. A simple calculation based on the effective film diameter (irradiated area, 18 mm), thickness of the film (20 nm), and specific gravity (1.15–1.25) of PHEMA indicates that $\sim 1.9 \times 10^{-8}$ mol of the hydroxy group is involved in the effective volume of the film, so that the mole number of the reactant (**1**–**5** = $(2–14) \times 10^{-6}$ mol/2 mL) in the reaction system will be enough for the heterogeneous photoreaction.

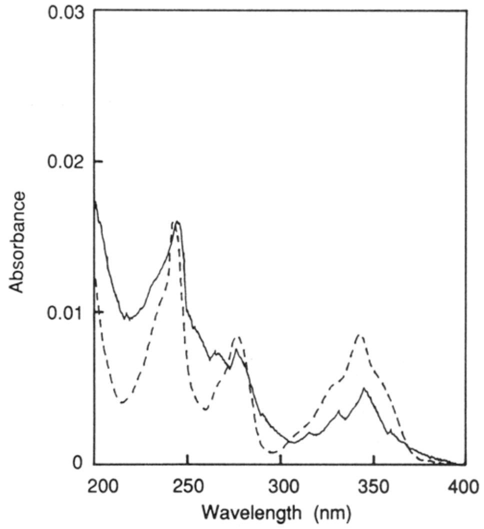


Figure 3. Absorption spectra of the **1**-modified PHEMA film (—; [**1**] = 2×10^{-2} M, [DMTP] = 5×10^{-3} M, t = 40 min) and **1** (- - -; in acetonitrile). The absorbance of **1** is normalized to that of the film at 245 nm.

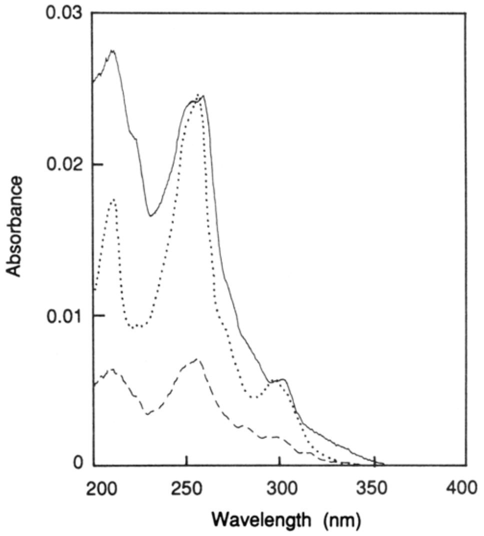


Figure 4. Absorption spectra of the **2**-modified PHEMA film (—, t = 100 min; - - -, t = 30 min; [**2**] = 1×10^{-2} M, [DMTP] = 5×10^{-3} M) and **2** (···; in acetonitrile). The absorbance of **2** is normalized to that of the film for t = 100 min at 265 nm.

Introduction of the aromatic chromophores to the film was checked spectroscopically. A typical example of the absorption spectrum of the film reacted with **1** or **2** is shown in Figure 3 or 4, respectively, together with that of **1** or **2** in acetonitrile. In these figures, absorption by the PHEMA film itself was subtracted from the observed spectrum, so that absorption is essentially ascribed to the chromophore introduced onto the film. The modified film exhibited several absorption bands similar to the relevant arylalkene. Although the spectrum of the film is slightly broader than that of **1** or **2**, the spectrum is well characterized as the pyrenyl or phenanthryl chromophore introduced to the film owing to close spectral similarities between the film and alkene. It is worth noting that any absorption and fluorescence originated from S is not observed in the wavelength region studied for the film exposed to the reaction mixture in the dark, indicating that simple adsorption of S to the film does not account

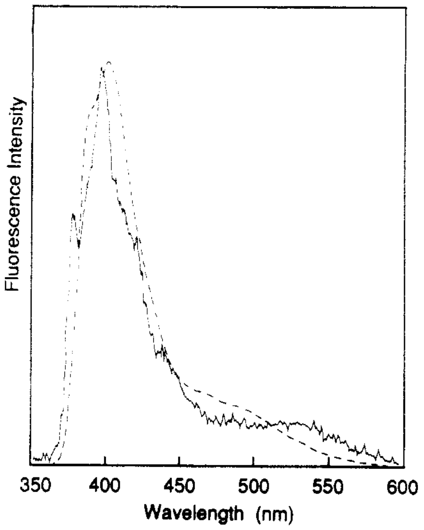


Figure 5. Fluorescence spectra of the 1-modified PHEMA film (—) and 1 (- - -; in acetonitrile). Fluorescence intensities are normalized to those at the maximum wavelength (λ_{excit} = 330 nm).

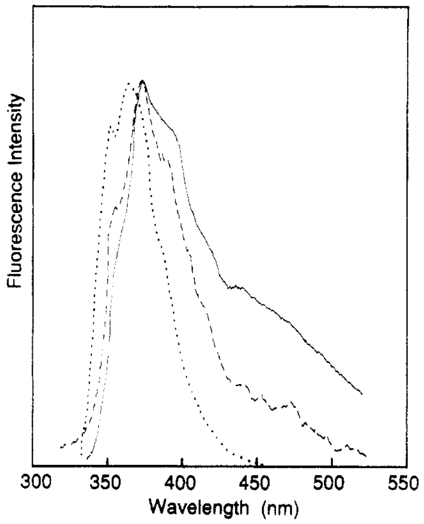


Figure 6. Fluorescence spectra of the 2-modified PHEMA film (—, t = 100 min; - - -, t = 30 min) and 2 (···; in acetonitrile). Fluorescence intensities are normalized to those at the maximum wavelength (λ_{excit} = 330 nm).

for the present results.

Fluorescence spectra corresponding to the data in Figures 3 and 4 are shown in Figures 5 and 6, respectively. Generally, arylalkene shows a broad and structureless fluorescence owing to internal rotation of the vinyl group around the carbon(aromatic)–carbon(vinyl) bond,[13] whereas arylalkane exhibits a structured fluorescence. Indeed, although 1 in acetonitrile showed a structureless fluorescence at 350–550 nm, the 1-modified film exhibited a structured fluorescence around 400 nm. Also, the fluorescence band around 400 nm is shifted to the higher energy as compared with that of 1 (Figure 5). The results suggest that the double bond in 1 reacts with a –OH group in the film. The broad fluorescence band of the 1-modified film around 530 nm will be ascribed to excimer fluorescence, as discussed again later. The fluorescence spectrum of the 2-modified film also shifts to the longer wavelength by ~10 nm relative to that of 2 (Figure 6). The photoreaction leads to a decrease in the fluorescence intensity ratio of the first to second vibrational bands as well as to a change in the vibrational spacing between the two bands (~860 and ~1360 cm^{-1} for 2 and the modified film, respectively). The relatively large shift of the maximum wavelength and the changes in the vibrational structure of the fluorescence will be explained by the reaction of 2 with the PHEMA film. Analogous results were obtained for the photoreaction of the film with the arylcyclopropane, as confirmed by characteristic absorption and fluorescence of the modified films.[14]

Control experiments were performed to obtain mechanistic information on the present functionalization reaction. The principal results are as follows.

(1) Fluorescence of 1 or 2 is efficiently quenched by DMTP in acetonitrile. The Stern–Volmer quenching constant, K_{SV}, was determined to be 870 or 370 M^{-1} s^{-1} for 1 or 2, respectively. The excited state of an aromatic compound is well-known to act as an electron donor, so that electron transfer from the excited state of 1 or 2 to DMTP is expected. Since photoinduced electron transfer from 1 to DMTP is highly exothermic (free energy change <–10 kcal/mol),[15] fluorescence quenching is acribed to the electron transfer mechanism.[16]

(2) Functionalization of a PHEMA film by 1 or 2 proceeded when DMTP was replaced by 1-CN, as confirmed by spectroscopic measurements of the modified film. However, the photoreaction in the absence of an electron acceptor (DMTP or 1-CN) did not give the modified film.

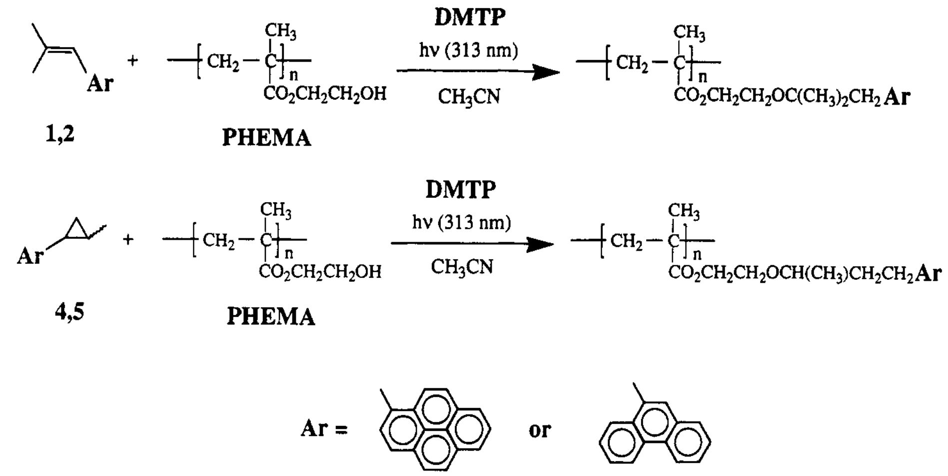
(3) Addition of a strong electron donor, triethylamine (8×10^{-3} M), suppressed the heterogeneous photoreaction.

All these results clearly prove that the present functionalization reaction involves the radical cation of S as a key intermediate, which is produced by photoinduced one-electron transfer from the excited singlet state of S to an electron acceptor (DMTP or 1-CN). In a homogeneous acetonitrile solution, the formation of pyrene radical cation and DMTP radical anion has been experimentally shown by nanosecond laser photolysis.[17] Inhibition of the photoreaction by triethylamine is due to hole transfer from the cation radical to the amine. Furthermore, the cation radicals of arylalkenes and arylcyclopropanes are known to react with alcohol to give relevant ether derivatives.[7–9,18–20] We suppose that the cation radical of 1, 2, 4, or 5 reacts with the –OH group in the PHEMA film, as shown in Scheme III. It is worth noting that fluorescence of 3 is quenched by DMTP in acetonitrile, so that the cation radical of 3 is expected to be produced. However, the naphthyl group was not introduced to the PHEMA film. A possible reason for this will be discussed later in detail.

Factors Controlling the Functionalization Reaction. As a characteristic feature of the present functionalization reaction, the amount of S introduced to the film can be controlled by several factors: photoirradiation time (t) and the concentration of S ([S]) or an electron acceptor ([DMTP]). Figures 7 and 8 demonstrate the effects of [DMTP] and [2] on the absorbance of the phenanthryl chromophore in the film at 252 nm (A_{252}), respectively.

A_{252} increases almost linearly with an increase in [DMTP] at [2] = 5×10^{-3} M and t = 40 min (Figure 7). This is easily understood by the fact that an increase in [DMTP] leads to that in an electron transfer quenching efficiency (QE) of the excited singlet state of 2 by DMTP. Since K_{SV} (2–DMTP) is 340 M^{-1} s^{-1}, 42% of the excited singlet state of 2 is quenched by DMTP (QE = 42%) at [DMTP] = 2.1×10^{-3} M, as estimated from the Stern–Volmer equation: $QE = 100(1 - I/I_0)$ where $I_0/I = 1 + K_{SV}$ [DMTP]. The results support the electron transfer mechanism for the present photoreaction. The amount of S in the film can be controlled by [DMTP] and, therefore, QE at constant [S].

Scheme III



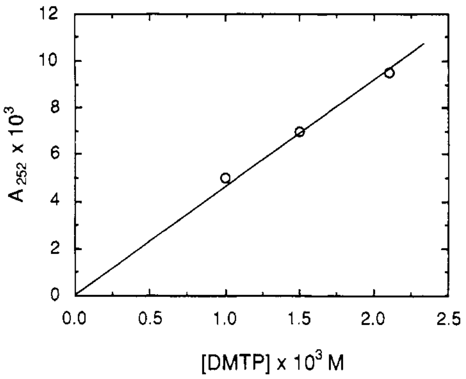


Figure 7. Dependence of the absorbance of the 2-modified PHEMA film at 252 nm (A_{252}) on [DMTP]. [2] = 5×10^{-3} M, t = 40 min.

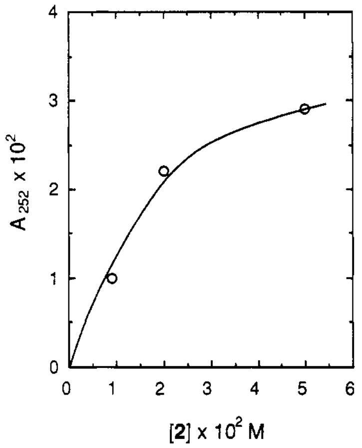


Figure 8. Dependence of the absorbance of the 2-modified PHEMA film at 252 nm (A_{252}) on [2]. [DMTP] = 5×10^{-3} M, t = 40 min.

A_{252} also increases with increasing [2] but tends to level off at [2] > 2×10^{-2} M^{-1} (Figure 8; [DMTP] = 5×10^{-3} M and t = 40 min). Since [DMTP] is much lower than [2], an increase in [2] does not directly lead to a linear increase in the concentration of the cation radical of 2. A high concentration of 2 also results in deactivation of the excited state through intermolecular interactions such as concentration quenching, excimer formation, excited-state annihilation, and so forth. Such intermolecular interactions of 2 compete with photoinduced electron transfer, so that a high concentration of 2 is not favorable for the functionalization reaction. These will be the main reasons for leveling off of A_{252} in Figure 8.

At $t < 50$ min, A_{252} increases almost linearly with t, while A_{252} levels off at $t > 50$ min (Figure 9). In this experiment, [2]/[DMTP] is constant, so that a change in QE is not the reason for the result. As described in the preceding section, the mole number of the hydroxy group in the effective volume of the PHEMA film is $\sim 1.9 \times 10^{-8}$ mol. If all the hydroxy groups are reacted with 2, A_{252} should reach 0.6, assuming the film thickness of 20 nm (optical path) and $\epsilon_{252} = 3.2 \times 10^4$ M^{-1} cm^{-1} (value for the alkane model compound of 2). However, XPS and SIMS measurements of the modified film suggest that S is introduced to the film surface (~7 nm) in every three monomer units of the polymer, as discussed later in detail. If this is the case, A_{252} is ca. one-ninth of 0.6, ~0.07. Qualitatively, the value is in good agreement with the observed A_{252} at $t = \infty$ (0.04–0.05, Figure 9). Therefore, the present heterogeneous photoreaction will be localized to the surface layer of the film. We suppose that leveling-off of the time conversion profile at $t > 50$ min will be acribed to a decrease in the reaction efficiency of the radical cation toward the film owing to relatively high surface coverage of the film by S, as well as to the poor solubilizing power of acetonitrile to a PHEMA film (discussed again later).

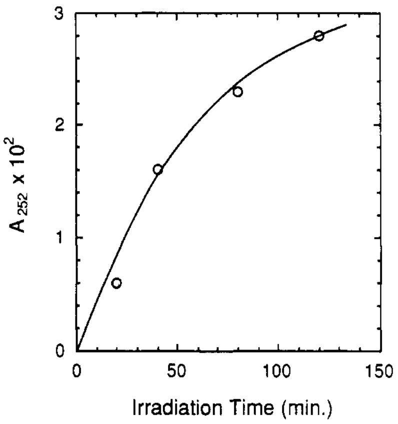


Figure 9. Time-conversion profile for the photoreaction of 2 and a PHEMA film. [2] = 1×10^{-2} M, [DMTP] = 5×10^{-3} M.

The amount of the chromophore introduced to the film is governed by t, [S], and [DMTP] in a complex manner. At the present stage of investigation, we have not optimized these conditions to attain a maximum efficiency of the photoreaction. However, the present discussion indicates that the maximum efficiency will be obtained under the condition of QE = 100%.

Model Reaction in Homogeneous Solution. We studied DMTP-sensitized photoreactions of 2 and 5 with methanol as model reactions. Typically, 2 or 5 (ca. 50 mg)

Scheme IV

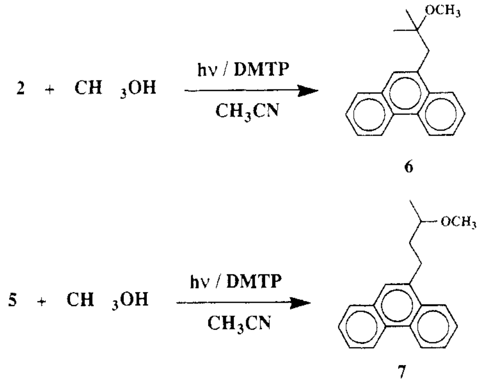


Table I
Quantum Yields of the Photoreaction[a]

S	$10^{-8}\Phi$	10^{-2}[S], M	10^{-3}[DMTP], M	[DMTP]/[S]
1	5.5	1.9	4.9	0.26
2	14	1.1	5.0	0.45
4	4.7	5.2	25	0.48
5	17	2.7	25	0.93

[a] The molar extinction coefficients determined for the pyrenyl and phenanthryl model compounds (2.8×10^4 M^{-1} cm^{-1} at 342 nm and 3.0×10^4 M^{-1} cm^{-1} at 252 nm, respectively) were used for calculation of the quantum yields.

dissolved in acetonitrile/methanol/benzene (2/1/0.5 mL) was irradiated at 313 nm in the presence of DMTP (10 mg) after purging the mixture with a N_2 stream for 10 min. Product analysis was made by ^{1}H NMR and mass spectroscopy. Photoirradiation of the mixture gave a methanol adduct of **6** (56% yield) or **7** (20% yield) as a major product (Scheme IV). It is worth emphasizing that **6** and **7** is produced regioselectively as expected from analogous photoreactions of arylalkenes or arylcyclopropanes.[7-9,18,19] The chemical structure of **6** satisfactorily agreed with that of the authentic sample synthesized by regioselective addition of 9-phenanthryllithium to 1,1-dimethyloxirane, followed by methylation of the resulting alcohol. Surface functionalization of a PHEMA film by S will proceed in a regioselective manner analogous to Scheme IV.

Quantum Yield Measurements. The number of S introduced to the film cannot be determined since the exact functionalized depth in the film (i.e., optical path length for absorption measurement) is unknown. Therefore, we estimated a quantum yield of the heterogeneous photoreaction (Φ) on the basis of surface coverage of the film by S (α), which corresponds to the concentration of the chromophore in a unit area. α was calculated by $\alpha = A/1000\epsilon$, where A and ϵ are absorbance and molar extinction coefficient at the wavelength measured, respectively. The incident light intensity at 313 nm (I) was determined by ferrioxalate chemical actinometry.[21] Φ was thus calculated by $\Phi = \alpha/I = A/1000\epsilon I$, as reported previously.[22] The results are summarized in Table I. Φ was on the order of 10^{-7}–10^{-8}, which was 10^2–10^3 times smaller than that for the homogeneous photoreaction of S with methanol (Scheme IV).

The data in Table I cannot be directly compared with each other since [S] and [DMTP] are different between the reaction systems. Qualitatively, however, the following discussion can be made. The QE values of the systems for **4** and **5** will be larger than those for **1** and **2**, respectively, as expected from [DMTP]/[S]. Nonetheless, Φ values are almost comparable for both sytems if the aromatic chromophore attached to S is identical: **1** vs **4** or **2** vs **5**. The reactivity of the cation radical toward the –OH group is higher for the arylalkenes, **1** and **2**, as compared with that for the cyclopropanes, **4** and **5**. This will be explained in terms of positive charge density at the reactive carbon center of the cation radical. Namely, the positve charge is delocalized over the double bond via direct vinylic conjugation for the alkenes while it is delocalized over the cyclopropane ring mainly by hyperconjugation. Generally, cation radicals of alkenes are more reactive than those of cyclopropanes. The reactivity of the cation radical is also influenced by the aromatic substituent. The stronger the aromaticity of the substituent, the more delocalization of the positive charge over the molecule. Table I indicates that the phenanthryl derivatives (**2** and **5**) exhibit higher reactivities as compared with the pyrenyl derivatives (**1** and **4**).

On the other hand, the naphthylalkene **3** was not introduced to a PHEMA film, but photoirradiation gave a dimeric product of **3**. This is markedly contrasting to the photoreaction of **3** and DMTP in acetonitrile/methanol (7/3, v/v), by which a methanol adduct of **3** is obtained in a quantitative yield. Mattes and Farid have reported that both the methanol adduct formation and dimerization of the radical cation of 1,1-diphenylethene proceed at a diffusion-controlled rate, and these reactions compete with each other depending on the concentration of methanol and the alkene.[18] In order to suppress dimerization of **3**, we performed the photoreaction of **3** with a PHEMA film at a lower concentration of **3** ($=1 \times 10^{-4}$ M). However, **3** was not introduced to the film. The β-position of the double bond in **1** or **2** is substituted by two methyl groups, so that dimerization or oligomerization of **1** and **2** is unfavorable. This is not the case for **3** in which substituents at the β-position of the double bond are hydrogen. Therefore, the cation radical of **3** will prefer dimerization with **3** to the reaction with the –OH group of a PHEMA film.

For efficient heterogeneous photoreactions, the lifetime and diffusion rate of a reactive species are quite important. Even if a reactive species is produced near the film/solution boundary, a short lifetime and/or fast diffusion (to the bulk solution phase) of the species will reduce a reaction efficiency. Surface properties of a polymer film to be functionalized will also play a key role. If a polymer film is swollen, a reactive species has enough chance to encounter a functional group in the film. In the present system, acetonitrile is a poor solvent for PHEMA. Although this is unfavorable for the present photoreaction, the condition is identical for all S studied. The diffusion rate of the radical cation of S will also be in the same order of magnitude in a given solvent. These discussions suggest that the absence of surface functionalization by **3** will be ascribed to the short lifetime of the radical cation of **3**. In order to understand factors governing the heterogeneous photoreaction in detail, time-resolved total internal reflection fluorescence/absorption spectroscopy, capable of elucidating photophysical and photochemical primary processes occurring at the film/solution interface,[23] is necessary and such approaches are the next target of the study.

B. Characterization of the Modified Films. Characterization by XPS and SIMS. Characterization of the modified films was performed by means of X-ray photoelectron spectroscopy (XPS) as well as of static and dynamic secondary ion mass spectroscopy (SIMS). High-resolution C_{1s}-XPS spectra of the **1**-modified film demonstrated that the C—H band intensity at 284.6 eV was much stronger than the C—O (286.6 eV) and C═O (288.6 eV) band intensities relative to that before the photore-

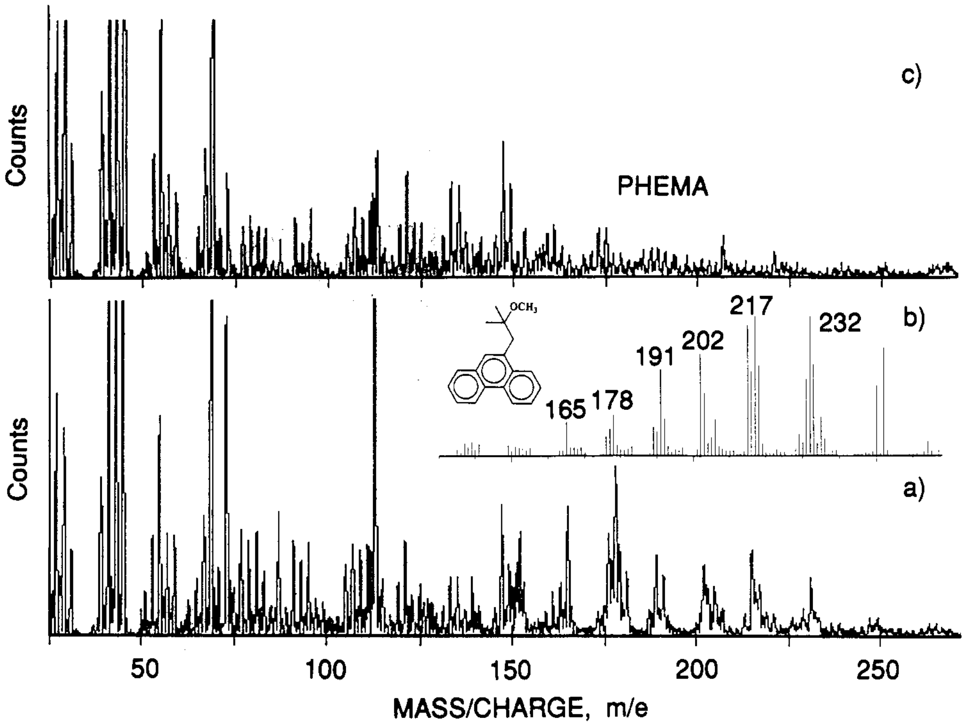


Figure 10. Static secondary ion mass spectra of the 2-modified PHEMA film: (a) [2] = 2×10^{-2} M, [DMTP] = 5×10^{-3} M, t = 40 min; (b) 6; (c) PHEMA film.

action.[24] Introduction of a π-electron system to the film was also confirmed by appearance of shake-up satellites around 290–294 eV. In order to obtain more quantitative information, we performed wide-scan XPS, by which C_{1s} and O_{1s} peaks were observed at 284.6 and 532.1 eV, respectively. Integration of the C_{1s} and O_{1s} peaks after correcting the instrumental sensitivity to each atom gave an atomic ratio of the 1-modified film of C/O = 2.8–3.3. For a PHEMA film itself, C/O is observed as 1.8–2.3 so that the composition of the 1-modified film is carbon-rich as compared with that of PHEMA. The calculated C/O ratios of the PHEMA and 1-modified films (structure in Scheme III) in a monomer unit are 2 and 8.7, respectively. If the OH group of the monomer unit is reacted with 1, C/O will increase by a factor of 4.35 = [C/O(modified)]/[C/O(PHEMA)], while the observed value is (2.8–3.3)/(1.8–2.3) = 1.4–1.6. These values suggest that 1 is introduced to the film surface in every three monomer units in average.

Figure 10 shows cationic static SIMS spectra. The spectrum of PHEMA does not show any significant peak at $m/e > 175$. For the 2-modified film, several peaks can be observed at m/e = 190–232, corresponding to the cationic fragments derived from 2. Indeed, the mass spectrum of 2 or a methanol adduct of 2 (2-methoxy-2-methyl-3-(9-phenanthryl)propane (6)) quite resembles that of the 2-modified film in the m/e region interested. The peak around $m/e \sim 232$ similar to the parent peak of 6 can be seen in the spectrum of the 2-modified film, while cationic fragments originated from DMTP (m/e = 194) are not observed in Figure 10a. Simple adsorption of 2 to the film will not explain the present results, which is also supported by the fact that the film exposed to the reaction mixture in the dark does not show any absorption and fluorescence characteristic to S, as described in the preceding section. Analogous results were obtained for other modified films, and all the results suggested that S was introduced to the PHEMA film via the ether bond, as illustrated in Scheme III.

Depth profiles of C/O and H/O atomic ratios in the films were estimated by dynamic SIMS (Figure 11). Since correction of the instrumental response for the sensitivity to each atom was difficult, we could not determine absolute values of C/O and H/O. Qualitatively, however, both C/O and H/O ratios of the 1-modified film with UV absorbance at 346 nm ($A_{346} = 5 \times 10^{-3}$) were larger than those of an unmodified film in the surface layer of $\sim$7 nm, though the ratios varied in the layer of 0–3 nm due to the artifacts of the present experimental conditions.[25] On the other hand, the film with $A_{346} = 1 \times 10^{-3}$ exhibited C/O and H/O depth profiles similar to those of a PHEMA film itself. Functionalization of S may proceed from the surface to the depth direction of the film. Assuming the functionalized depth (7 nm) and $A_{346} = 5 \times 10^{-3}$, the concentration of pyrene in the film was estimated to be 0.26 M.

Fluorescence Properties. For the 2-modified film, a fluorescence tail extends to 530 nm, and the fluorescence intensity around 450 nm increases with the increasing amount of 2 in the film (Figure 6). The broad fluorescence band around 450 nm is very similar to that reported for excimer fluorescence in poly(9-vinylphenanthrene) films.[26] Generally, phenanthrene does not form excimer even in concentrated solutions owing to the low stabilization energy for the excimer formation. A homogeneous solution of poly(9-vinylphenanthrene) also does not show excimer fluorescence. Observation of the excimer-like emission in the 2-modified film indicates that the phenanthryl chromophores are densely introduced to the film.

Similarly, the 1-modified film showed a broad and structureless excimer-like fluorescence around 530 nm in addition to the structured monomer fluorescence bands at 370–430 nm (Figure 5). Picosecond time-correlated single photon counting measurements of the film exhibited multicomponent decays for both monomer (378 nm) and excimer-like (500 nm) fluoresence. In a homegeneous solution, the pyrene excimer formation proceeds via a diffusion-controlled rate, and the time response of both monomer and excimer fluorescence can be analyzed by double exponential functions with common rate parameters.[27] The complex time response of the fluorescence from the film suggests nonuniform distribution and aggregation of the pyrenyl chromophores. Furthermore,

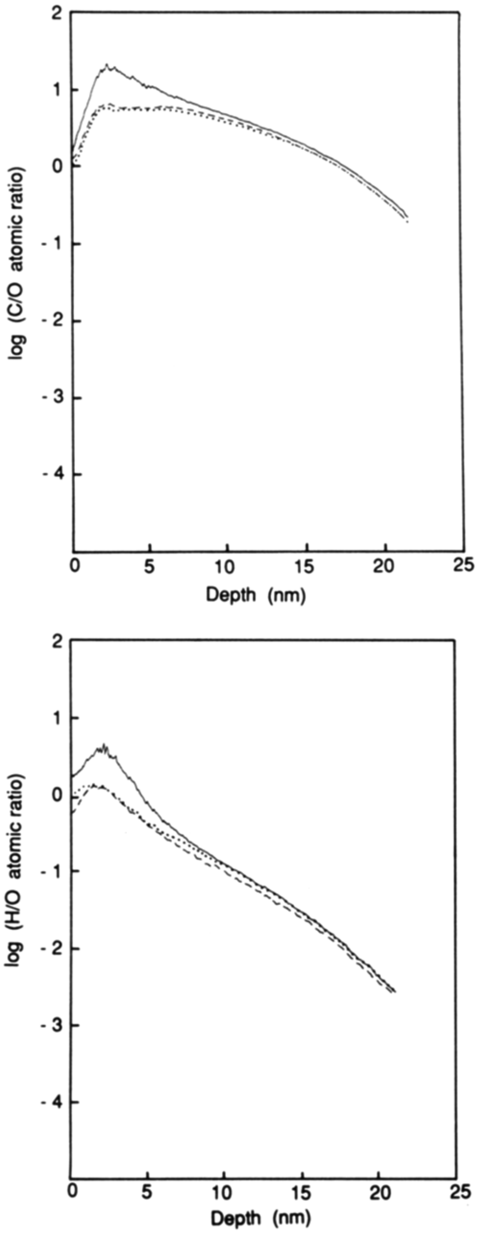


Figure 11. Depth profiles of the C/O (top) and H/O (bottom) intensity ratios for the 1-modified PHEMA films (—, A_{346} = 0.005; - - -, A_{346} = 0.001) and a PHEMA film (···).

the excimer-like fluorescence intensity is considerably weaker than the monomer fluorescence intensity, as expected from the concentration of pyrene in the film (~0.26 M). This will also be explained by the aggregation and resulting strong interactions between the chromophores in the ground state, which induces fast and efficient nonradiative decay of the excited state(s).

For application of the aryl-modified film as a heterogeneous photosensitizer or photocatalyst, aggregation of the chromophores is disadvantageous since it leads to a short excited lifetime of the chromophore. As discussed in the previous section, however, the amount of the chromophore in the film can be controlled by several factors such as *t*, [S], or [DMTP]. The modified layer in the film may also be controlled by an appropriate choice of a solvent after taking the degree of swelling of a polymer film with the solvent into account. Heterogeneous polymeric photosensitizers will be realized through such approaches.

C. Micrometer Patterning. We performed the photoreaction of the film through a photomask (a stainless alloy with 50-μm thickness; see also Figure 2). Photoirradiation of a PHEMA film and 4 through the photomask gave a fluorescent pattern on the film. A typical example of the fluorescent pattern on the film is shown in Figure 12a, which is comparable to the pattern of the original photomask used in the experiments (Figure 12b). Although the photograph in Figure 12a is ambiguous due to weak fluorescence from the film and a very thin modified layer (~7 nm), it is recognized that a micrometer-order pattern of 4 is produced on the film.

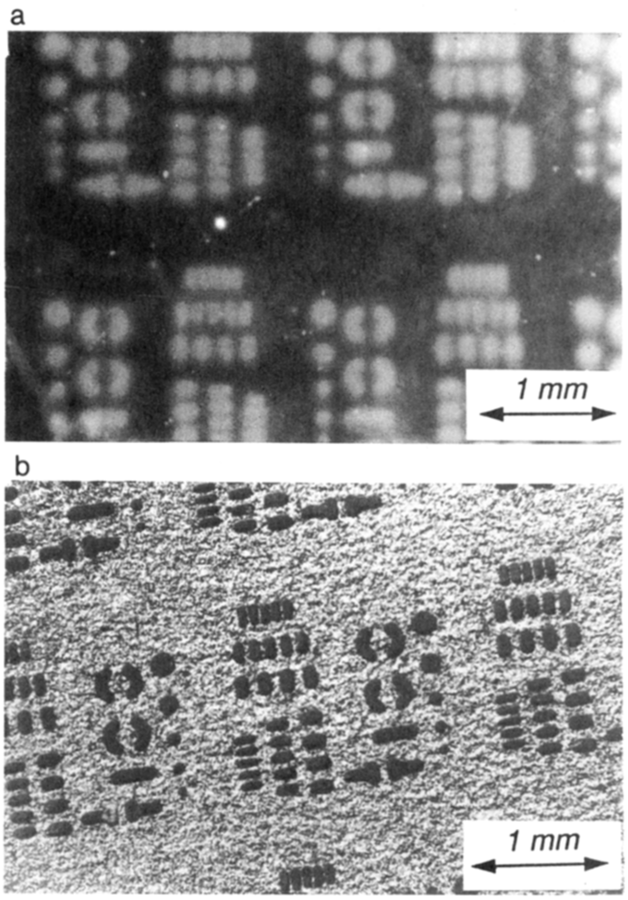


Figure 12. Micrometer fluorescent patterning of a PHEMA film: (a,top) fluorescence micropattern of the film ([4] = 5×10^{-2} M, [DMTP] = 5×10^{-2} M, *t* = 32 min); (b, bottom) photomask.

At the present stage of investigation, spatial resolution of the method is ~50 μm, as judged from the observed fluorescence and photomask patterns in Figure 12a,b, respectively. The resolution is better than that reported by Allmer and Feiring for photochemical modification of fluoropolymer film surface: 100 μm.[4] Spatial resolution of the pattern is not governed by the photoreaction employed but will be dependent on the experimental conditions, such as photoirradiation method, spatial homogeneity of the light source, thickness of the photomask, and so forth, while diffusion of a reactant molecule and the degree of swelling of a film will also come into play. Further optimization of the experimental conditions will improve the spatial resolution of the method.

Concluding Remarks

The present photochemical surface functionalization method is quite unique and novel, since (i) introduction of the chromophore proceeds in a regioselective manner and (ii) the amount of the chromophore introduced to the film can be controlled by photoirradiation time and the concentrations of S and DMTP. In particular, regioselective surface functionalization of a polymer film by an aromatic chromophore has never been explored, so that the present method will open new possibilities to prepare various functionalized materials. As an example, the arylcyclopropane, **4** or **5**, possesses an asymmetric carbon, so that asymmetricity will be added to the film surface if asymmetric **4** or **5** is used as a starting material.[9] We expect such materials will exhibit nonlinear optical or ferroelectric properties in addition to photochemical functions of the aromatic chromophore itself.

Finally, it is worth pointing out that, besides a PHEMA film, the photoreaction is applicable to functionalization of silylated glass surfaces with 3-hydroxypropyl or 3-mercaptopropyl groups. Surface functionalization of a poly(vinyl alcohol) film by S was also suggested from the characteristic fluorescence of the chromophore in the film after the photoreaction. Introduction of –OH groups to the material surfaces or conversion of surface functional groups to –OH can be easily done by conventional methods, so that a combination of the present photochemical reaction with surface pretreatment will be promising for functionalization of various material surfaces with arbitrary chromophores.

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