CHEMISTRY LETTERS, pp. 1945-1948, 1990.

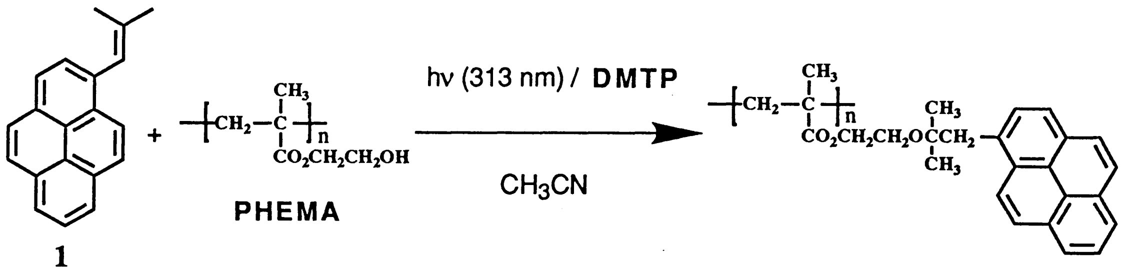
Photochemical Surface Modification of Poly(2-hydroxyethyl methacrylate) Film with 1-(1-Pyrenyl)-2-methylpropene

Nobuyuki ICHINOSE, Noboru KITAMURA,* and Hiroshi MASUHARA*†
Microphotoconversion Project, ERATO, JRDC,
15 Morimoto-Cho, Shimogamo, Sakyo-ku, Kyoto 606

Introduction of pyrenyl group to surface of a poly(2-hydroxyethyl methacrylate) (PHEMA) film was achieved by photoreaction of the film with an acetonitrile solution containing 1-(1-pyrenyl)-2-methylpropene and dimethyl terephthalate (DMTP). Spatial patterning of the film was also explored to show a possible application of the method to microfabrication with photo-functional molecules.

One of our research interests is to create a number of micrometer-order photo-functional sites on material surfaces and to control chemical processes occuring at the surface by laser pulses. To achieve this, surface functionalization should be accompanied by, i) high spatial resolution, ii) applicability of the technique to various photoresponsive molecules (S), and iii) well-defind chemical bonding of S to the surface. Although photoresist[1)] and surface graft polymerization[2)] techniques are sometimes applied to surface modification, these seem to be inadequate for the present purpose owing to complexities in chemical structures of the modified surface. In this study, photochemical polar addition of alcohol to aromatic olefin via photoinduced one-electron transfer[3)] was chosen for surface modification. We expect the photoreaction will proceed even in inhomogenous systems with high regioselectivity. Also, since -OH group is common for various materials such as cellulose, metal oxides, and so forth, photo-functional molecules will be introduced selectively to the -OH surface by the present method. As an example, we explored surface functionalization of PHEMA film with pyrene as S.

PHEMA films (20 nm thickness) were prepared on quartz plates by spin-coating of a methanol solution and used after washing with boiling benzene. Irradiation of the film at 313 nm (500 W super high-pressure Hg lamp with an aqueous $K_2Cr_2O_7$ solution filter and a Toshiba UV-D33S glass filter) was carried out from



(1)

---

† Permanent address: Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606.

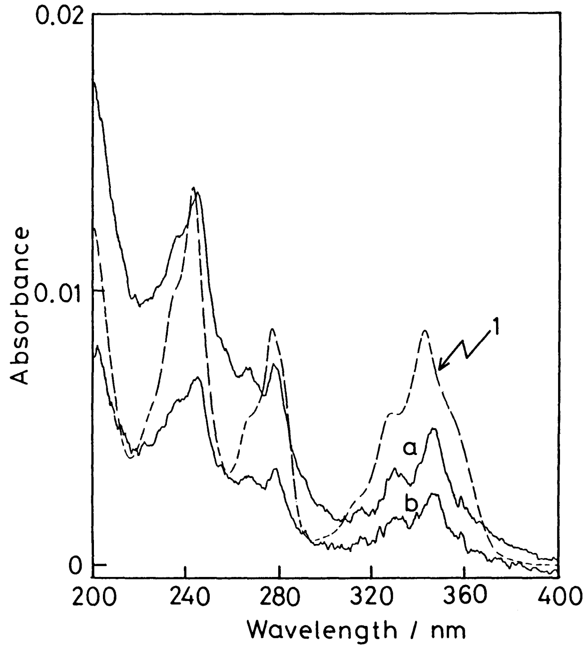


Fig. 1. UV-absorption spectra of the PHEMA films irradiated at 313 nm for 40 min with an acetonitrile solution of [DMTP] = 5 x 10^{-3} mol dm^{-3} and, a) [**1**] = 2 x 10^{-2} mol dm^{-3} or b) [**1**] = 2 x 10^{-3} mol dm^{-3}. Dashed line represents UV-absorption spectrum of **1** in acetonitrile. The absorbance at 245 nm is normalized to that of a).

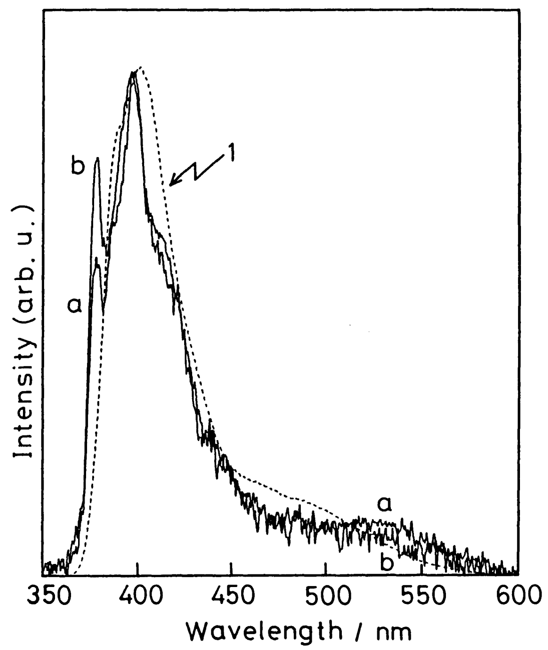
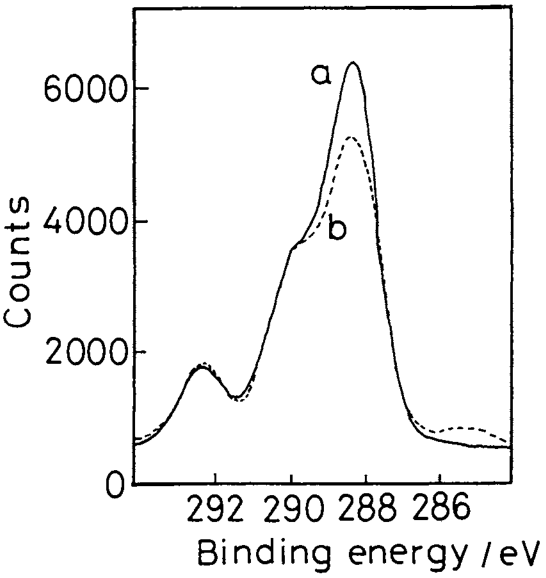


Fig. 2. Fluorescence spectra of the irradiated PHEMA films (excited at 330 nm). a) and b) corresponds to the samples in Fig. 1. Dotted line represents a fluorescence spectrum of **1** in acetonitrile. Fluorescence intensities of the spectra are normalized at their maximum wavelengths.

the quartz plate side for 30-60 min with a PHEMA film being in contact with an acetonitrile solution (ca. 2 cm^3) of 1-(1-pyrenyl)-2-methylpropene (**1**) (2-20 x 10^{-3} mol dm^{-3}) and DMTP (5 x 10^{-3} mol dm^{-3}). After the photoreaction, the film was immersed in acetonitrile for over 24 hours to remove the unreacted reactants.

The absorbtion spectra of the modified PHEMA films are shown in Fig. 1 together with that of **1.** In Fig. 1, absorption by a quartz plate and PHEMA itself is subtracted from the observed spectra, so that the absorption is responsible for the chromophore introduced into the film by the photoreaction. Although the spectra of the films are broader than that of **1,** the characteristic absorption around 240, 270, and 350 nm could be ascribed to the pyrenyl chromophore. The corresponding fluorescence spectra in Fig. 2 exhibit the bands around 400 nm and 530 nm. The spectrum of the film showed the vibrational structure around 377 nm and slightly shifted to the higher energy as compared with that of **1**. The results suggest that the double bond in **1** reacts with a -OH group of the film as shown in Eq. 1. Analogous results were obtained when DMTP was replaced by 1-cyanonaphthalene. Furthermore, addition of a strong electron donor (triethylamine, 8 x 10^{-3} mol dm^{-3}) completely inhibited the reaction. As a controlled experiment, fluorescence of **1** was efficiently quenched by DMTP in acetonitrile. All these results strongly indicate that the radical cation of **1** generated by photoinduced electron transfer between the excited state of **1** and DMTP is an intermediate of the

Fig. 3. High-resolution XPS spectra of C_{1s} for the PHEMA films a) with and b) without photochemical surface modification. The film was irradiated at 313 nm for 30 min with an acetonitrile solution of [**1**] = 3 x 10^{-3} mol dm^{-3} and [DMTP] = 5 x 10^{-3} mol dm^{-3}.



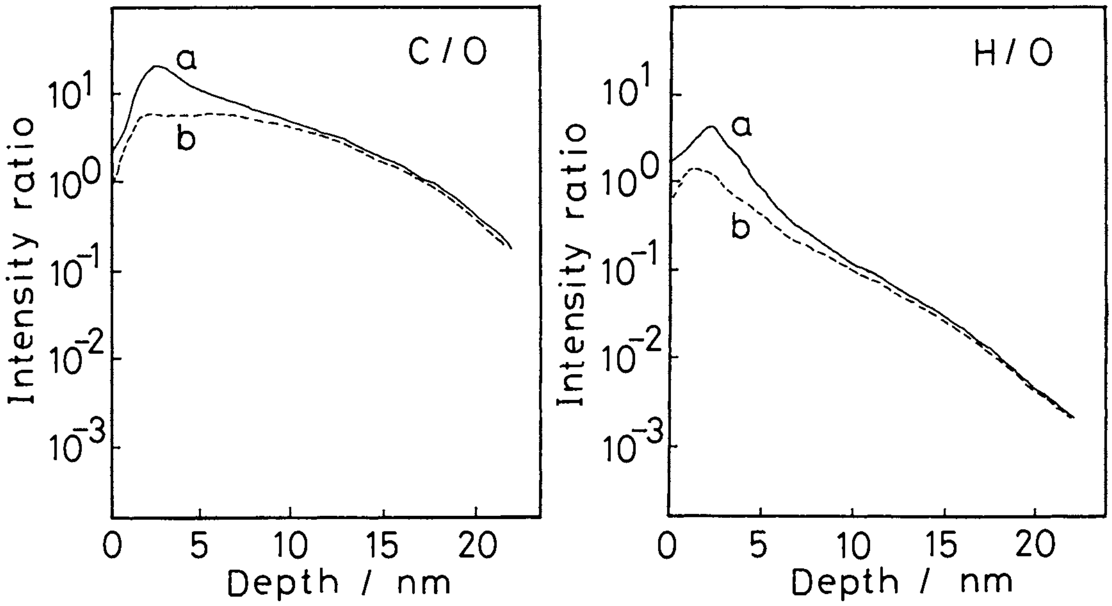


Fig. 4. SIMS depth profiles of C/O and H/O intensity ratios for the PHEMA films. The samples a) and b) correspond to those in Fig. 3.

reaction and, the pyrenyl group could be introduced to the PHEMA film. As a characteristic feature of the present surface functionalization method, the amount of S introduced to the film can be controlled by the concentration of **1** as demonstrated in Fig. 1. The absorption intensity increased with the concentration of **1** and the fluorescence spectrum exhibited larger contribution of excimer-like fluorescence around 530 nm. Similarly, the amount of S introduced to the film was controlled by the irradiation time at constant [**1**].

Characterization of the pyrene-modified PHEMA film was performed by means of both X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). XPS spectra in Fig. 3 demonstrate that the intensity of the C-H band at 288 eV increases upon the photoreaction while those of the C-O (290 eV) and C=0 (297 eV) bands remain almost constant before and after the surface modification. The increase in the C-H band intensity manifests the introduction of pyrenyl groups to the film surface. SIMS spectra in Fig. 4 also support our conclusion. Although the carbon/oxygen (C/O) or hydrogen/oxygen (H/O) intensity ratio varies in the surface layer (0-3 nm) of the film due to the artifacts of the present experimental conditions,$^{4)}$ the values of the C/O and H/O of the modified film in the surface layer of 0-7 nm are always larger than those of the unmodified film. Clearly, pyrenyl groups are introduced to the film surface (up to 7 nm). On the basis of the absorbtion spectrum (Fig. 1) and the depth profile of the pyrene-modified film (Fig. 4), we estimated the concentration of the pyrenyl chromophore in the film to be ≈ 0.3 mol dm^{-3}.

As a preliminary experiment, the present technique was applied to spatially-resolved surface functionalization of the film by S. Although the resolution is not satisfactory at present (≈ 70 μm), contact exposure of a film with a photomask will improve the spatial resolution. We believe that the present method will be fruitful to prepare a series of micrometer-order photofunctional sites on various materials and, photochemical/physical processes occuring at the modified surface could be elucidated by the currently developed technique of 3-dimensional space- and time resolved fluorescence spectroscopy.$^{5)}$ The study along the strategy is now in progress and will be reported in the forthcoming papers in detail.

The authors are greatly indebted to Dr. M. Kawai and Mr. Y. Shichi at Nissan Motor Co. Ltd. for their kind courtesy to measure XPS and SIMS spectra.

References

1) T. Sugawara and T. Matsuda, *Polym. Preprints Japan*, **39**(3), 597(1990); T. Sugawara, K. Inoue, and T. Matsuda, *ibid.*, **39**(3), 598(1990).
2) S. Tazuke, *Polym. -Plast. Technol. Eng.*, **14**(2), 107(1980), and references cited therin.
3) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080(1973).
4) The C intensity up to 3 nm was underestimated due to the initial unequilibrium in sputtering processes. On the other hand, since the film was very thin, the O intensity was overestimated owing to the effect of oxygen of a quartz substrate.
5) K. Sasaki, M. Koshioka, and H. Masuhara, XVII International Quantum Electronics Conference, Anaheim, U.S.A., Technical Digest, p.170, 1990.

(Received July 20, 1990)