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U.v.-irradiation of thin films of polystyrene derivatives: formation of carboxylic group and crosslinking from 4-trimethylsilylmethyl substituent

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Photoirradiation of thin films of poly(4-trimethylsilylmethylstyrene) (PTMSMS), poly(4-methylstyrene) (P4MS), and polystyrene (PS) at 254 nm with a low-pressure Hg lamp in air made the surfaces hydrophilic through oxygenation. The hydrophilicity estimated from the contact angle with water was in the order of PTMSMS $\approx$ P4MS $>$ PS. Formation of carboxylic acid group on the surface and crosslinking in the bulk were demonstrated for PTMSMS, whereas the photoirradiation of PS and P4MS was accompanied by degradation of the polymer main chain. The chemical behaviour of the polymers reflected selectivities in the cleavage of the benzylic C–Si or C–H bond of the 4-substituents toward that of the benzylic C–H bond on the main chain. Copyright © 1996 Elsevier Science Ltd.

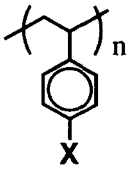
(Keywords: photooxygenation; polystyrene derivatives; organosilicon polymer)

Introduction

Photooxygenation of polymer surfaces is a subject to elucidate degradation processes of polymers and is also a useful tool to control the surface properties. Formation of polar functionalities such as carboxylic acid group through the photooxygenation has been utilized for the pretreatment of polymer surfaces for adhesion or staining. Furthermore, its control in a minute space is of current interest for some potential applications to micro-electronics or biotechnology[1–4]. Polystyrene derivatives, whose excited states are characterized as substituted benzenes, are typical polymers readily prepared by radical polymerization in laboratories. However, their photochemical properties are strongly dependent on the nature of the substituents. We have studied photochemical properties of some polystyrene derivatives in films in the presence of oxygen to elucidate the reactivity of the benzylic C–H bond on the main chain as compared to those of the 4-substituents, in particular, trimethylsilylmethyl group whose C–Si bond is expected to have high reactivity owing to hyper conjugation with the aromatic ring.

Experimental

Poly(4-trimethylsilylmethylstyrene) (PTMSMS, $M_w = 7.7 \times 10^4$)[5–7], poly(4-methylstyrene) (P4MS, $M_w = 7.2 \times 10^4$, Aldrich), and polystyrene (PS, $M_w = 4.3 \times 10^4$, Aldrich) thin films (1–1.5-μm thickness) were prepared by spin-coating on quartz plates (29 mm diameter, 1 mm thickness) from their toluene solutions (80 g l^{-1}). The polymer films were irradiated at 254 nm with a 60-W low-pressure Hg lamp through a water filter (3 cm thickness) in air. Contact angle of the film with water droplet was measured to estimate the surface wettability before and after the irradiation. The contact angle was also measured with standard buffer solutions of pH 1.68, 4.01, 6.86, 9.18, and 10.02 (Nacalai Tesque) to detect surface acidic functionality in a qualitative manner[8]. Surface composition of the polymer films was analysed by measuring atomic ratios and C_{1s} X-ray photoelectron spectra with a Shimadzu ESCA-850S



PTMSMS : **X** = $CH_2Si(CH_3)_3$
P4MS : **X** = CH_3
PS : **X** = H

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spectrometer. X-ray photoelectrons were collected at a take off angle of 90° with respect to the sample surface. ATR-*FT*i.r. spectra were taken on a Perkin-Elmer 1720 i.r. spectrometer with a KRS-5 crystal (incidental angle of 45°). The polymer films were also irradiated in contact with a photomask by use of an excimer laser (Lumonics PM-884) operated with a KrF gas mixture (248 nm) at 10 Hz through a beam homogenizer (Leonix EWO-FI-60-248, beam size 12 × 12 mm^2).

Results and discussion

Thin films of PTMSMS, P4MS, and PS were irradiated with a low-pressure Hg lamp in air. The contact angle of each film with water droplet (*ca.* 90° before irradiation for each film) decreased gradually with the irradiation time to indicate that the surfaces became hydrophilic. After 30 min irradiation, contact angles were PS(56°) > P4MS (32°) ≈ PTMSMS (30°). The hydrophilicity of the surface of PTMSMS was attributed mainly to formation of carboxylic acid group. Contact angles of the irradiated PTMSMS (θ) with buffer solutions of various pHs showed a sigmoidal curve in the plot of θ vs. pH, which is characteristic of surfaces bearing acidic functionality[8], where the surface showed a good wettability (small contact angle) to alkaline buffers, whereas that of PS showed little change with pH. By the treatment with an aqueous solution of dyes, Rhodamine

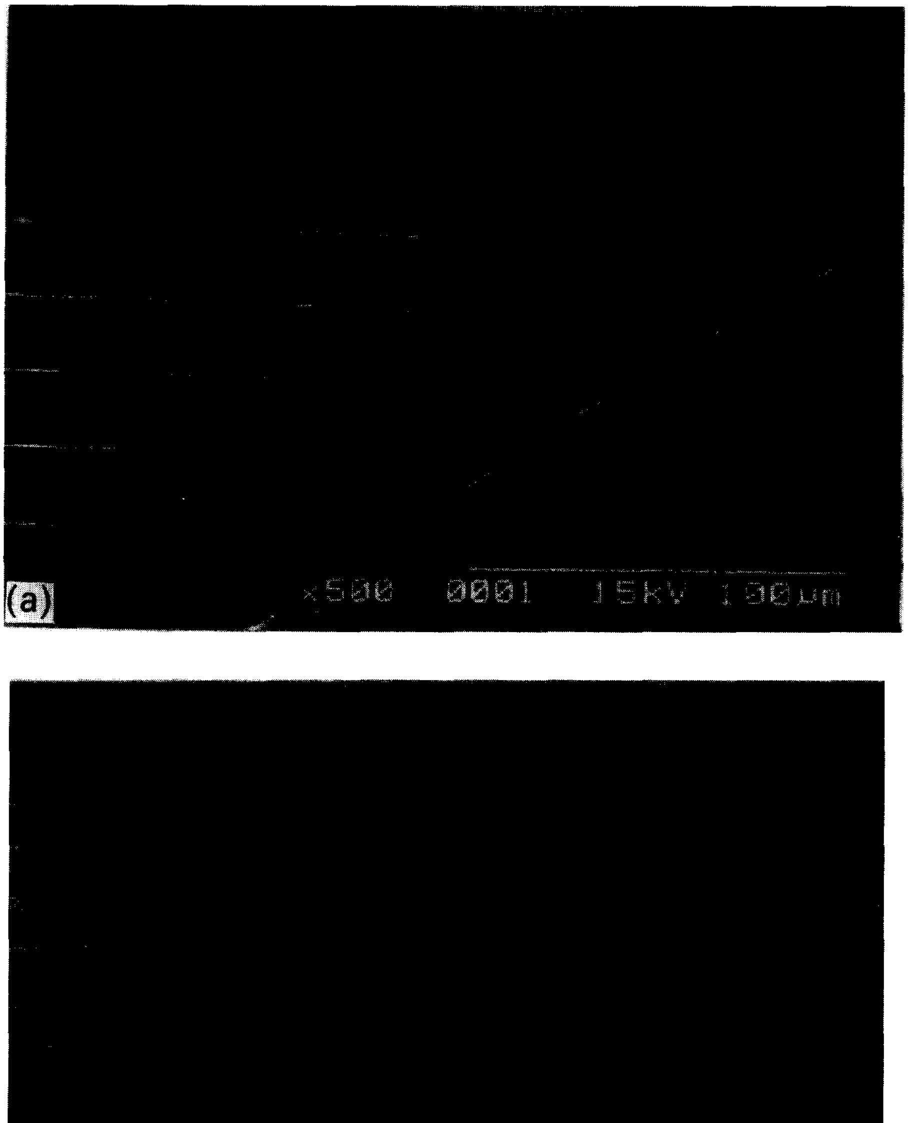


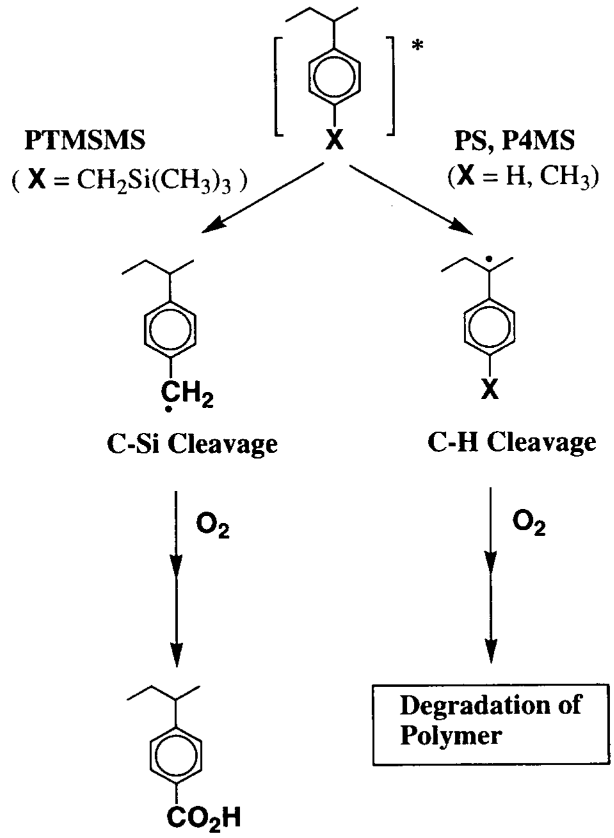
Figure 1 An SEM of the polymer films irradiated with KrF laser through a photomask. (a) Negative image for PTMSMS obtained by the development with xylene. (b) Positive image for P4MS obtained by the development with ethanol–benzene (6 : 1)

6G (Rh6G), a basic dye was adsorbed selectively onto the irradiated surfaces of PTMSMS, whereas anionic or acidic dyes such as sulforhodamine were not adsorbed. Elemental analysis of the surfaces of the polymers by X-ray photoelectron spectroscopy (X.p.s.) indicated that both of PTMSMS and P4MS were oxygenated by the irradiation. The O/C atomic ratio for P4MS increased from 0.012 to 0.448 by the irradiation for 30 min. For PTMSMS, the increase of the O/C atomic ratio from 0.046 to 0.533 was accompanied by the decrease of the Si/C atomic ratio from 0.113 to 0.065, which suggests that the oxygenation of PTMSMS occurs via the elimination of trimethylsilyl group. ATR–*FT*i.r. measurement of the irradiated films showed a broad peak at 1720 cm^{-1} indicating the formation of various carbonyl groups on the film surface. A broad band at 3000–3300 cm^{-1}, which was assigned to O–H stretching vibration, was also observed for PTMSMS, whereas only trace intensities of the band were observed for P4MS and PS.

The inside of irradiated PTMSMS film became completely insoluble in toluene or xylene, which is a good solvent for the polymers (the outer layer of the irradiated surface was soluble toward the solvents). Similar irradiation scarcely made P4MS and PS films insoluble in xylene. On the other hand, the irradiation made P4MS and PS films soluble in an ethanol–benzene mixture (6 : 1, v/v), which is a poor solvent for the polymers. These results can be attributed to the formation of a crosslinked structure for PTMSMS and the reduction of molecular weights by the oxidative degradation for P4MS and PS[9–13].

Irradiation of the PTMSMS films with the Hg-lamp through a photomask for 15–30 min, followed by the treatment with an aqueous solution of the dye Rh6G, gave the negative photo-images derived from the dye adsorbed onto the irradiated area (see Appendix). Similar irradiation of PTMSMS film, followed by development with xylene, gave the insolubilized negative images, whereas irradiated P4MS film developed with ethanol–benzene mixture (6 : 1) gave the positive images left by the solubilization. Similar photoirradiation with KrF laser (15 mJ cm^2 pulse^{-1}) produced the photo-images with a higher resolution in a short time than those obtained with the Hg-lamp (*Figure 1*). This must be due to the high photon density and the high directivity of the laser beam.

Alkylbenzenes and benzyltrimethylsilane (trimethylsilylmethylbenzene) undergo photochemical cleavage of benzylic C–H or C–Si bond to give benzyl-type radicals via their excited states[14–18]. The photooxygenation of PTMSMS will possibly proceed via the C–Si bond cleavage as a major pathway (*Scheme 1*). Generation of the benzyl-type radical near the polymer surface, followed by an attack of molecular oxygen in air, will lead to the formation of carboxylic acid. For P4MS and PS, the cleavage of benzylic C–H bond of main chain will occur to result in the degradation of the polymers. Reactivity of the polymers with oxygen must reflect the efficiencies of three processes: (1) radical generation; (2) radical recombination; and (3) attack of oxygen toward radical. The selective C–Si bond cleavage for PTMSMS could be explained by: (i) the excited state where the C–Si bond will be preferable for process 1[19]; (ii) the large size of trimethylsilyl group will be sterically unfavourable for process 2 but will be favourable for diffusion of oxygen molecules for process 3; and (iii) the glass transition temperature for PTMSMS (T_g; 89.5°C) was almost the same as those for P4MS and PS (85°C for P4MS, and 87°C for PS) so that segmental motion will have no effect on the difference in the reactivity. In contrast, the radical species inside the polymer will undergo alternative processes such as radical recombination or crosslinking because of low concentration of oxygen.



Scheme 1

The present work has demonstrated the formation of the carboxylic acid group on the surface of PTMSMS film by selective photooxygenation and crosslinking inside the film, in contrast to those of P4MS and PS. The reactivity of PTMSMS will be inherent to the benzylic trimethylsilylmethyl group. The spatial control of the photoreaction of PTMSMS also shown here will be a potential tool for integration of chemical functionalities such as solid state synthesis in combination with the reactivities of the remaining benzyltrimethylsilyl group as a radical or cation precursor[5,20].

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Appendix

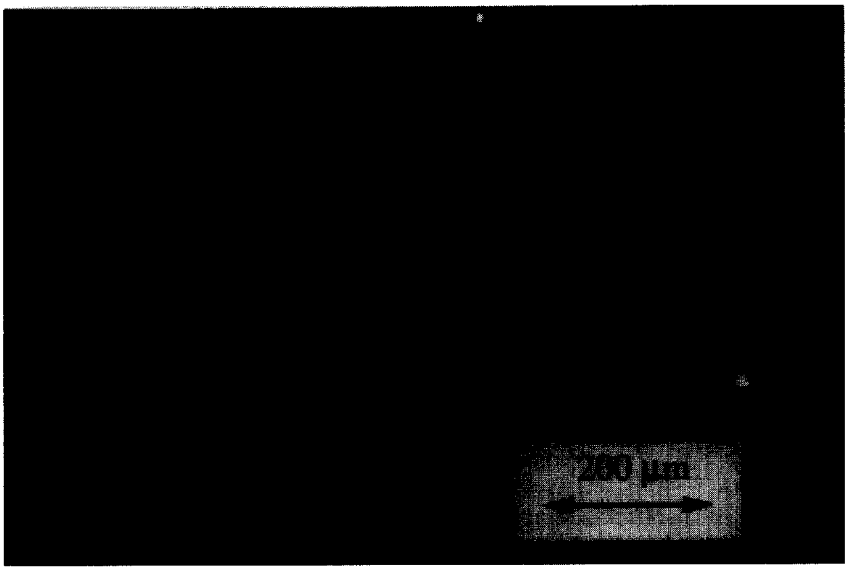

Figure A1 A fluorescence micrograph of a PTMSMS film which was irradiated with KrF laser through a photomask and was immersed in an aqueous solution of Rh6G