Photo-triggered Surface Relief of Polystyrene Films—Highly Photo-sensitive Formation by the Addition of a Benzophenone Derivative

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1. Introduction

Surface relief (SR) formation due to mass transfer by spatially patterned photoirradiation has attracted significant attention from both viewpoints of academic scientific interest and potential technological applications because it involves only a facile, entirely optical, and single step with no wet chemistry.[1-7] Since the first two reports,[8, 9] various types of azobenzene-containing materials, including polymers,[1-7, 10] sol–gel matrices,[11] molecular glasses,[12] and crystal surfaces,[13] have been extensively explored. However, an SR structure using azobenzene-containing materials is not suitable for use with optical elements in the visible region since azobenzene compounds have strong absorption bands in that region.[1]

Recently, it has been reported that colorless large SR structures due to mass transfer can be fabricated using materials that do not contain azobenzene compounds.[14-33] It is considered that SR formation is concerned with photoreaction-induced internal diffusion processes. Recently, we have reported that the SR structure is fabricated by spatially patterned ultra-violet (UV) light, even in a general-purpose polystyrene (PS) film.[34] However, PS films must be irradiated with deep UV light with wavelengths shorter than 300 nm. Moreover, significant amount of irradiation energy ($2.4 \times 10^5 \text{ J cm}^{-2}$, $0.05 \text{ W cm}^{-2}$, 80 min) is needed to construct SR structures with amplitudes greater than 200 nm.

Here we report the highly photosensitive SR formation of a PS film using additives. As additives, we selected benzophenones (BPs), which are known to be initiators for the photodegradation of PS.[35-38] When PS films doped with BPs are irradiated with UV light, excited triplet BPs would abstract hydrogen from PS to give polystyryl radicals. Thus, it is anticipated that the rate and efficiency of photodegradation of PS are increased, which accelerates the speed of SR formation.

2. Experimental

Monodisperse PS was purchased from Alfa Aesar ($M_w = 3.35 \times 10^3$, $M_w/M_n = 1.10$) and used without further purification. 4,4′-Dimethylbenzophenone (DMBP) was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. Spectroscopic-grade chloroform was used for film preparation (Wako Pure Chemical Industries, Ltd.).

A thin PS film doped with DMBP was prepared by spin-coating from a chloroform solution on a clean glass substrate. A spin coater (Mikasa 1H-D7) was used with two program steps (step 1: 1000 rpm, 50 s; step 2: 3000 rpm, 2 s). The film thickness was calculated by curve fitting the reflection fringe obtained from a UV–visible–near-infrared spectrometer (Jasco V-670) equipped with an absolute reflectance measurement unit (ARSN-733). The film thickness was set to 150 nm.

A UV LED (Keyence, UV-400) was used as the UV light (365 nm) source. The UV light...
intensity was measured using a power meter (Newport 1830-C) equipped with a detector (818-UV) over the entire exposed area. Patterned UV light irradiation (stripes with a period of 8 \( \mu \text{m} \)) was performed using the light source through a custom-made photomask (Toppan Printing Co., Ltd.) attached to the film. During irradiation, the film was set on a hot plate (Corning PC-420D), and the film temperature was measured using an infrared thermometer (Horiba IT-550). After irradiation, the film was immediately quenched to room temperature. Surface relief structures were observed by an atomic force microscope (AFM; Shimadzu Co., 9500 equipped with an Olympus Co., OMCL-TR800PSA-1 cantilever) in the contact mode.

3. Result and discussion

Figure 1 shows AFM images of the SR structures of PS films doped with 15 wt% of DMBP after UV light irradiation through various photomask patterns. Irradiation through a grating photomask produces a regular sinusoidal surface modulation (Figure 1a). Its spatial period, 8 \( \mu \text{m} \), is similar to that of the photomask, and the observed modulation depth is approximately 250 nm, which is greater than the initial film thickness of 150 nm. The result clearly demonstrates that SR formation is due to lateral mass transfer. The photomodulated structure remains stable and unchanged at room temperature.

To investigate the direction of material transfer, we performed an additional experiment, irradiation through a single-slit photomask (Figure 1b; slit width 4.0 \( \mu \text{m} \)). The cross-sectional topography shows the top of the convex irradiated area to be higher and the base of the depression to be lower than the initial surface level. Thus, lateral material transfer clearly occurs from the shaded areas to the irradiated areas, enabling the formation of variable surface structures (Figures 1c and 1d).

The efficiency of mass transfer strongly depends on the film temperature during spatially patterned UV light irradiation. Figure 2 shows plots of relief height as a function of the film temperature for PS films doped with 10 wt% of DMBP. The height of the relief produced on the DMBP-doped PS films showed a gradual increase at \( T = 79 \, ^\circ\text{C} \) (2 \( ^\circ\text{C} \) higher than the \( T_g \) of bulk PS), the maximum around 98 \( ^\circ\text{C} \) (21 \( ^\circ\text{C} \) higher than the \( T_g \) of bulk PS), and a gradual decrease with increasing temperature. The various relief heights follow an approximately Gaussian distribution centered at this maximum temperature. This temperature dependence on relief height is similar to that of the pure PS film, which is probably due to competition between increasing molecular mobility and the smoothing effect of surface tension with increasing temperature.

To investigate the sensitivity of relief formation, we examined SR height produced with different irradiation times using different irradiation

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**Fig. 1.** AFM images of the surface relief structures in PS films doped with 15 wt% of DMBP after UV light irradiation (365 nm, 100 mW cm\(^{-2}\)) for 10 min at 98 \( ^\circ\text{C} \) through various photomask patterns: (a) pattern of stripes with a period of 8 \( \mu \text{m} \); (b) pattern with a single 4.0-\( \mu \text{m} \)-wide slit; (c) pattern of squares with dimensions of 4 \( \times \) 4 \( \mu \text{m}\)\(^2\) separated by 4 \( \mu \text{m} \); (d) inverted pattern of (c).

**Fig. 2.** Plots of relief height as a function of film temperature for PS films doped with 10 wt% of DMBP. The films were measured after UV light irradiation (365 nm, 100 mW cm\(^{-2}\)) through a photomask (stripes with a period of 8 \( \mu \text{m} \)) for 10 min.
Fig. 3. Plots of relief height as a function of irradiation time for PS films doped with 10 wt% of DMBP. The films were measured after UV light irradiation with different intensities (12, 23, 37, 48, and 100 mW cm\(^{-2}\)) through a photomask (stripes with a period of 8 \(\mu\)m) for 10 min.

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**References**


**Conclusion**

In summary, it is found that an SR was constructed on the PS film by spatially patterned UV light of 365 nm with a relatively short irradiation time, and thus relatively low irradiation energy, when DMBP was added to the PS film.

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