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Selective Dyeing of Organopolysilane Films Patterned by Ultra-violet Light Irradiation

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Utilizing the swelling effect induced by UV light irradiation in organopolysilane films, the patterned dyeing with water-soluble dyes was successfully demonstrated. Only basic dyes gave the dyeing effect, suggesting the existence of a specific interaction between basic dyes and Si-OH moieties formed by UV photodecomposition. The narrow line pattern of 40 μm width was completely reproduced with dyeing.

Recently, organopolysilanes consisting of Si backbone with two organic side groups (alkyl and/or aryl groups) on each Si atom have attracted considerable attention as a new class of solvent-soluble and film-forming amorphous polymeric materials in view of their unique chemical and physical properties different from the carbon-based polymers widely in use heretofore.1) In their physical properties, for example, organopolysilanes are characterized with their high hole drift mobility as much as 10^{-4} $cm^2V^{-1}s^{-1}$,2-4) which has stimulated many investigations on their application as charge carrier transporting polymeric materials for photoreceptors of electrophotography,5-8) and the σ-conjugation in the Si backbone has prompted to explore the possible utilization as a film material for the third-order non-linear optics.9,10) In their chemical properties, on the other hand, it is known that organopolysilanes exposed to ultra-violet (UV) light in air easily undergo the photodecomposition, which forms Si-O-Si and Si-OH bonds as a result of Si-Si bond scission of the backbone. The most characteristic feature of the photodecomposition in organopolysilanes is that the photodegradation by UV light (300-400 nm) proceeds as patterned from surface to bulk of the film due to the well-known spectral self-bleaching effect.11) It can readily be imagined that the formation of Si-O-Si or Si-OH only in the UV-exposed area of the film causes various changes in physical and chemical properties from the unexposed area, e.g., in the mechanical properties due to incorporation of much flexible Si-O-Si bonds, in the wettability or swelling for water due to the hydrophilic Si-O-Si or Si-OH formation, and in the refractive index due to the shortening of σ-conjugation length in the Si backbone by incorporating different O atom and so on.

In the present letter, we have concentrated on the swelling effect induced by UV irradiation among those, and have tried to examine the patterned dyeing of organopolysilane films with water-soluble dyes. As a result, it has been successfully demonstrated that organopolysilane films patterned by UV light is selectively dyed as patterned only in the UV-exposed area, and more interestingly, the specific interaction between Si-OH moieties formed by UV irradiation and basic dyes has been found.

Poly(phenylmethylsilane), $(PhMeSi)_x$, was selected as a typical organopolysilane, which surpasses others in film-forming ability and has a σ-σ^* absorption band in the relatively longer wavelength UV region of near 340 nm, which is suitable to the light source for photodecomposition. The polymer was prepared by the Wultz-coupling of phenylmethyldichlorosilane monomers with sodium metal in toluene according to the literature.12) The molecular weight of $(PhMeSi)_x$ used in this work was >5000 as measured by GPC using polystyrene for calibration. The about 20 μm-thick films were prepared on glass or quartz plates by spinning coat and dried at 60 ℃. The films were exposed to the UV light (300 – 400 nm, $24 mW/cm^2$) from a Xe lamp through a color filter (UV-D35, Toshiba) and when desired, through a photomask for the pattern exposure. The dyeing was carried out by soaking the UV-exposed films in aqueous solutions containing various kinds of water-soluble dyes for an appropriate duration, usually for about an hour. In order to enhance the homogeneous swelling in the UV-exposed area, 10% of acetonitrile (CH_3CN), to which UV exposed $(PhMeSi)_x$ is partially soluble, was added. Water-soluble dyes used here involve Rhodamine B (CI: 45170), cyanine (1,1'-di-isopropyl-2,2'-quinocyanine iodide), Brilliant Green (CI: 42040), Malachite Green (CI: 42000), Acridine Yellow (CI: 46025) for basic dyes, and Rose Bengal (CI: 45440), Eosin Y (CI: 45380), Tartrazin (CI: 19140), Uranine (CI: 45350), Methyl Orange (CI: 13025) for acidic dyes, respectively. Most of the experiments were performed using red colored Rhodamine B.

In order to confirm UV-induced swelling effect of organopolysilane films, contact angles for the CH_3CN (10%)-containing water droplet were measured for the UV-exposed and unexposed $(PhMeSi)_x$ films using a Model CA-Z contact angle measurement system (Kyowa Kaimenkagaku Co. Ltd.). Figure 1 shows the variation of contact angles with the elapse of time after putting a droplet on these $(PhMeSi)_x$ films, respectively. The contact angle of the unexposed film kept a constant value with the time passage, while that of the UV-exposed film decreased, apparently indicating that UV-decomposition induced the hydrophilicity owing to the formation of Si-OH and Si-O-Si bonds, which were also confirmed by appearance of the IR absorption bands attributed to Si-OH and Si-O-Si bonds near 3400 and 1100 cm^{-1}, respectively. The result is shown for the water droplet containing 10% CH_3CN, but the similar behavior was obtained even for the pure water droplet, although the contact

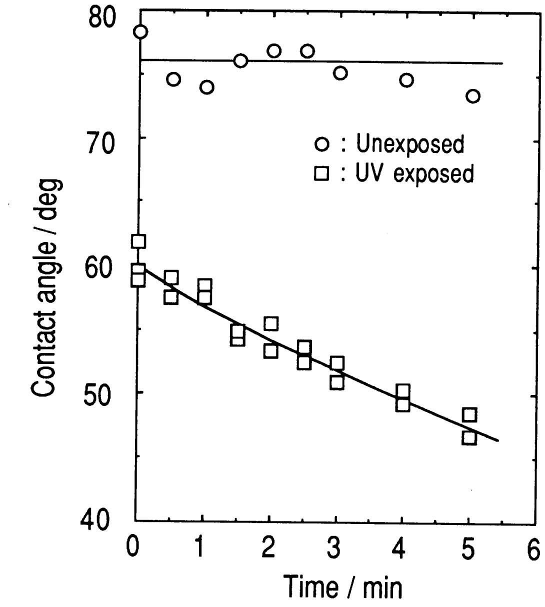

Fig. 1. Contact angles with the elapse of time after putting a droplet on UV unexposed (○) and exposed (□) $(PhMeSi)_x$ films.

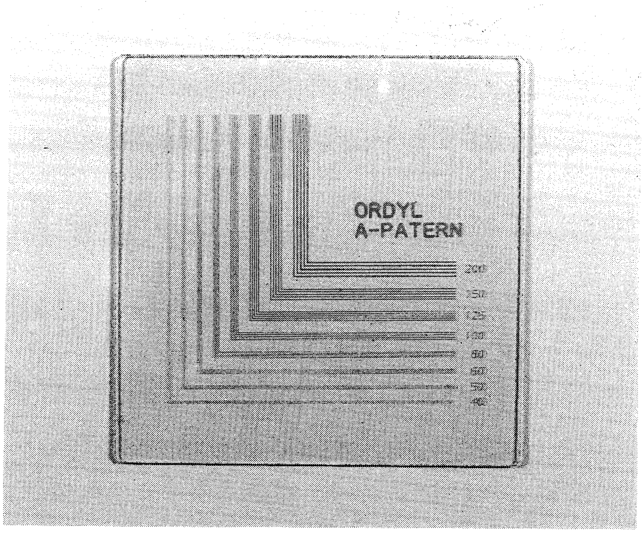

Fig. 2. Patterned dyeing of $(PhMeSi)_x$ film imaged by UV irradiation with water-soluble Rhodamine B dye. The dark line pattern indicates the red colored dyeing pattern in the photograph.

angles immediately after dropped were 93 and 70° for UV-unexposed and exposed films, respectively. Actually, by soaking into just water the UV-exposed area of the film exhibited cloudiness due to swelling, and the addition of CH_3CN accelerated swelling and improved homogeneity.

Figure 2 shows a typical example of patterned dyeing of the organopolysilane film imaged by UV irradiation through a photomask, which was obtained by soaking in Rhodamine B aqueous solution added with 10% CH_3CN for about 30 min after UV exposure and drying under vacuum. Optical microscopic observation revealed that the narrow line pattern of 40 μm width was completely reproduced at least. Different colored patterns can be obtained by choosing different water-soluble dyes.

In Fig. 3 is shown the coloration density traced by an absorption of the dye (Rhodamine B, λ_{max} = 556 nm) as a function of the UV exposure time when soaked in dye solutions of various concentration. Coloration density depended linearly on the UV exposure time until about 30 min irrespective of the dye concentrations of the solution, whereas beyond it the coloration showed saturations, depending on the dye concentrations.

The UV exposure time at that dyeing exhibited a saturation indicated the exposure necessarily to decompose the whole thickness of the 20 μm $(PhMeSi)_x$ films, from which the energy required for the effective photodecomposition of 1 μm thick $(PhMeSi)_x$ can be.estimated to be about 0.5 J/cm^2 taking the effective absorption of $(PhMeSi)_x$ in the 300 – 400 nm region and spectral light intensity irradiated into account. The fact that the saturated color density of the dyed film depended on the dye concentration of the solutions, indicates that the dyes in the swollen films seems to be in some equilibrium with dyes in the solution, and actually the colored films suffered the decoloration by being soaked into water without dyes, although the complete bleaching took much longer time than the coloration. The coloration and decoloration processes were found to be diffusion-controlled since both process rates showed the $t^{1/2}$ – time dependence at relatively initial stage of the respective process, and the diffusion constant of Rhodamine B dye in the swollen films was evaluated to be the order of 10^{-10} cm^2/s.

Although the dyeing process was thus found to be diffusion-controlled, very interestingly, only basic dyes among the various dyes listed above resulted in the successful dyeing of $(PhMeSi)_x$ films, but no acidic dyes did. This is so distinct that a dyed $(PhMeSi)_x$ films showed only an absorption of Rhodamine B when soaked in a mixture of Tartrazin (acidic) and Rhodamine B (basic) with a mole ratio of 10:1, still more at 100:1. Other combinations of acidic and basic dyes gave the similar results. These results indicate

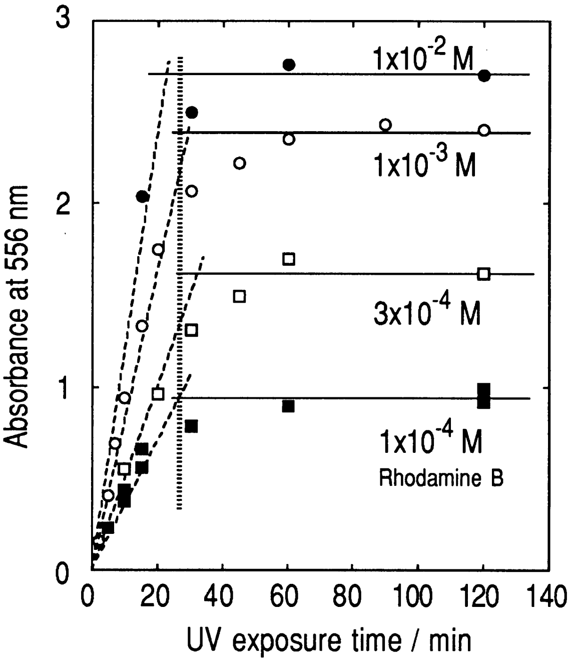

Fig. 3. Coloration density of the $(PhMeSi)_x$ films (thickness : 20 μm) traced by an absorption of Rhodamine B, λ_{max} = 556 nm as a function of UV exposure (300–400 nm, 24 mW/cm^2). Dyeing : 1 hr soaking in 10% CH_3CN-containing aqueous dye solution with various dye concentrations as indicated.

that the dyeing of UV exposed $(PhMeSi)_x$ is very selective to the nature of dyes.

Figure 4 shows the FT-IR spectra of UV-exposed films before and after dyeing with Rhodamine B. The characteristic bands to be attributable to Si-OH at 3400 and 900 cm^{-1} in the UV-exposed film completely disappeared in the dyed film. Taking the basic dye selectivity mentioned above into account, this result strongly suggests that the acidic atmosphere in UV-decomposed organopolysilane film which possesses many $Si\text{-}O^{-}H^{+}$ moieties, plays an important role for coloration of the $(PhMeSi)_x$ films. From the saturated density of Rhodamine B dye the number of Si-OH groups in the UV-exposed film was estimated assuming that all of the Si-OH sites were replaced with $Si\text{-}O^{-}$ Dye^{+} by ion exchange and that the absorption coefficient of the dye in the film is the same to that in the solution. In this estimation the Si-OH sites are found to be produced with the frequency of one Si-OH per about 500 repeating units of $(PhMeSi)_x$.

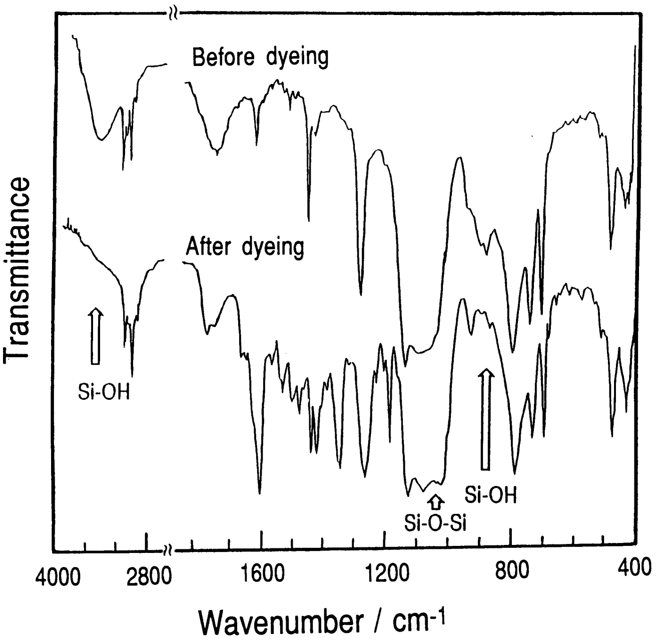

Fig. 4. FT-IR spectra of UV-exposed $(PhMeSi)_x$ films before and after dyeing with Rhodamine B.

In conclusion, we have successfully demonstrated the patterned dyeing of organopolysilane films with water-soluble dyes using the swelling effect induced by their unique UV-photodecomposition. The well-defined narrow line patterns were reproducible to the extent sufficient for micro-patterned color filter fabrications in TFT(Thin Film Transitor)–driven liquid crystal display. Moreover, the basic dye selectivity discovered during the present study may open us many avenues of applications taking skillful utilization of Si-OH moieties formed selectively as patterned by UV irradiation.

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