Novel Offset Printing without a Developing Process Utilizing the UV-Photodecomposition of Polysilane

Norio Nagayama, Yasuhiro Tachibana, and Masaaki Yokoyama*

Material and Life Science, Graduate School of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871

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Utilizing a surface modification of polysilane film due to photodecomposition by patterned UV-light irradiation, we have confirmed that polysilanes have a potential application as a material for novel offset printing, which will enable us to skip the alkaline development process required in current offset printing. This has been achieved by a wettability change of photodecomposable polysilane and a modified fountain solution. It has been found that the hydrophilicity in the UV-exposed area is sufficiently maintained by a treatment with tris(2-hydroxyethyl)methylammonium iodide added to the fountain water, which rejects an oil ink in the printing process.

Polysilanes are linear polymers having a Si sequence in their backbone and organic substituents in the side groups. These polymers have recently attracted considerable attention as a new class of functional polymers from the viewpoint of their unique physical and chemical properties, which are different from conventional carbon-based polymers.[1—9]

The photodecomposition of polysilanes by UV-light, one of their unique chemical properties, has been extensively studied concerning the photoresist in lithography. Polysilanes easily undergo a Si–Si bond scission of the backbone chain to form Si–O–Si and Si–OH bonds when exposed to UV-light corresponding to the σ–σ^* transition of the Si backbone in air. These Si–O–Si and Si–OH bond formations are expected to cause various changes in their properties. A deterioration in the charge-transporting ability[10] and a decrease in the refraction index[11] are examples of a physical property change; also, chemical ones are an enhancement of the wettability and swelling for water and some chemical reaction triggered by UV-decomposed species.[12] Another interesting things is that the σ–σ^* absorption decreases with UV-exposure due to bond scission of the backbone; that is, polysilanes show the so-called self-bleaching behavior.[9] Therefore, UV-exposure through a photomask gives rise to a decomposition of the polysilane film from the surface to bulk as patterned. As a result, UV image exposure can introduce different natured patterns in polysilane film. Utilizing the deterioration in the charge-transport ability by UV-photodecomposition, we successfully demonstrated several applications, such as a multi-duplication xerographic printing system based on persistent memory photoreceptor imaged by UV-light.[10,13] Utilizing the swelling effect for water, the patterned coloration[12,14—16] and conducting pattern formation due to the electrochemical polymerization of thiophenes[17] in polysilane films were also successfully demonstrated.

The present work is focusing on the water wettability change of a polysilane film surface induced by UV-exposure. The difference between UV-exposed hydrophilic and unexposed hydrophobic surfaces reminds us of attempting to apply polysilanes as a material for a novel offset printing master, by which the alkaline solution development process necessary in the current offset printing master plates based on the conventional photopolymer[18] would be omitted.

Experimental

Materials. Poly[methyl(phenyl)silane] (PMPS, Fig. 1(a)) was prepared by the Wurtz-type coupling reaction of dichloro(methyl)(phenyl)silane with highly dispersed molten sodium powder in dry toluene at 110 °C. The fluorine-containing polysilane of poly[methyl(phenyl)silane-*co*-methyl(3,3,3-trifluoropropyl)silane] (CF_3PMPS, Fig. 1(b)) was prepared by similar procedures using a mixture of dichloro(methyl)(phenyl)silane and dichloro(methyl)(3,3,3-trifluoropropyl)silane monomers with a molar fraction of 10 : 1. The elementary analysis confirmed that the resulting polymer has an identical composition to that of monomer feed (10 : 1). The molecular weights of PMPS and CF_3PMPS were determined to be 34000 and 45000 by gel-permeation chromatography using polystyrene as the standard, respectively. Tris(2-hydroxyethyl)methylammonium iodide used as additives was a light-yellow oily solution.

Measurements. The contact angles for the water were determined by a droplet-monitoring system (FACE CA-Z, Kyowa interface science Co. Ltd.).

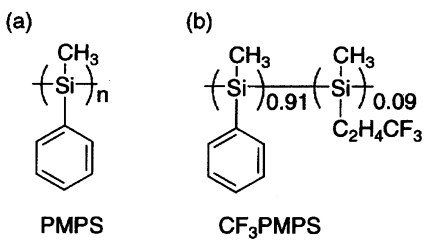

Fig. 1. Chemical structures of polysilanes used in this study: (a) poly[methyl(phenyl)silane] (PMPS) and (b) poly[methyl(phenyl)silane-*co*-methyl(3,3,3,-trifluoropropyl)silane] (CF_3PMPS).

The sample stamp plates, consisting of PMPS or CF_3PMPS film of typically 1 μm thickness laminated on a commonly used aluminium plate, were prepared by spin coating from toluene or a *p*-xylene solution of PMPS or CF_3PMPS, respectively. The printing test was accomplished in the following process (Fig. 2). Image exposure was carried out by UV light (10 mW cm^{-2} for 310—400 nm) from a Hg lamp (TOSCURE, Toshiba) through a photomask, usually for 5 min dose. Omitting development and a hydrophilic treatment by Arabic gum, the fountain solution and oil-ink (offset-ink, blue color) were sequentially supplied on the surface of the plate by transposition from rubber rollers, respectively. Subsequently, the ink-image formed on the plate was directly transferred to art paper with a press roller.

To estimate how long the fountain water remains on the UV-exposed hydrophilic surface, the covered length of water film on a 6.5 mm × 1.0 mm rectangular UV-exposed area was measured after providing fountain water on it.

The state of the art for the present offset printing was examined by testing tone image reproduction. Standard testing dot patterns (150/line) of UGRA-Offset-Testkeil version 1982 were used for the photomask, by which the UV-exposure intensity changed continuously and linearly from 0% to 100% in 10% steps. Thus, the ink density of the point image was measured with a reflectance density meter (Macbes RD514).

Results and Discussion

Print Plates Using PMPS Films. PMPS films were first examined as plates in order to obtain a print image because of the good film-forming ability and the large absorption in the UV region suitable to UV-exposure from a Hg lamp. If the plate was processed with the usual fountain water and oil-ink, the print image on a paper was rather poor after a few cycled processes because of the spreading of oil-ink to a hydrophilic wet area covered with fountain water. This may have been caused by the low hydrophilic nature of the UV-exposed surface. Oppositely, in the picture area, oil-ink was not sufficiently supplied on the unexposed PMPS surface due to residual fountain water, i.e., the PMPS surface seemed to not be sufficiently hydrophobic for rejecting the fountain water. Indeed, PMPS films showed a relatively large change of contact angle for fountain water from about 80° to 45° only by UV-exposure, although such a degree of wettability change seems to be insufficient for our purpose.

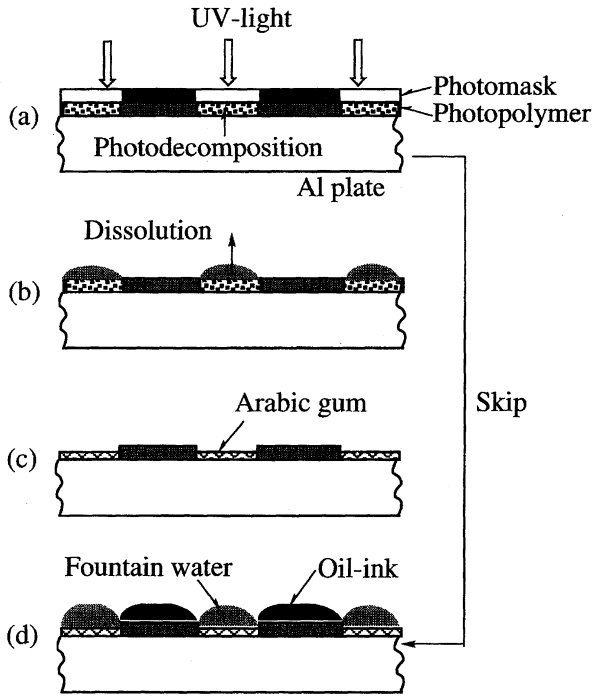

Fig. 2. The comparison of the present "developer-less offset printing" and the conventional offset printing process, in which the latter consists of (a) UV-image exposure, (b) development, (c) hydrophilic treatment by Arabic gum, and (d) print processes, and the former can skip both (b) development and (c) hydrophilic treatment processes.

Enhancement of Wettability Difference. In order to enhance the wettability difference induced by UV-exposure, the following material modification and process improvement were made. Firstly, instead of PMPS, fluorine-containing polysilane (CF_3PMPS) was used in order to increase water rejection in the unexposed surface. The synthesized CF_3PMPS exhibited a larger contact angle of 108° for water, and showed almost the same absorption spectra and a similar UV photodecomposition behavior to that of PMPS, as shown in Fig. 3.

Another approach was performed by adding tris(2-hydroxyethyl)methylammonium salt to fountain water in order to introduce a larger amount of hydrophilic OH groups to the UV-exposed area by the following ion-exchange:

$$\cdots SiO^- H^+ + N^+CH_3(CH_2CH_2OH)_3 \rightarrow \cdots SiO^- N^+CH_3(CH_2CH_2OH)_3 + H^+ \quad (1)$$

Owing to the SiOH formed by UV-exposure, the polysilane surface has a weak acidic nature. A similar ion-exchange mechanism was encountered in the case of dye coloration of the UV-exposed PMPS film, as reported previously,[13] where the PMPS film was colored only by cationic dyes. Tris(2-hydroxyethyl)methylammonium cation ($[THEMA]^+$) incorporated in the fountain water, therefore, may exchange with a hydrogen ion, and thereby enhance the hydrophilicity due to an increase in hydroxy groups.

The wettability difference was evaluated based on contact-angle measurements for the fountain water, as summarized in Table 1. CF_3PMPS film showed a rather larger contact angle for both water and commonly used fountain water by about 20° than that of PMPS. Furthermore, CF_3PMPS still maintained a large contact angle for the fountain water including $[THEMA]^+$, although it decreased in the case of a UV-light unexposed PMPS film. In the case of PMPS film, the $[THEMA]^+$ effectively interacts with a small amount of hydroxy groups, which would be formed on the surface of PMPS film during handling under the room light. The incorporated fluorine groups, in contrast, may effectively weaken the interaction between the hydroxy groups formed on the surface and $[THEMA]^+$. The CF_3PMPS, however, showed almost the same degree of contact angle difference of contact angle between UV-light unexposed and exposed films for the $[THEMA]^+$ containing fountain water as compared

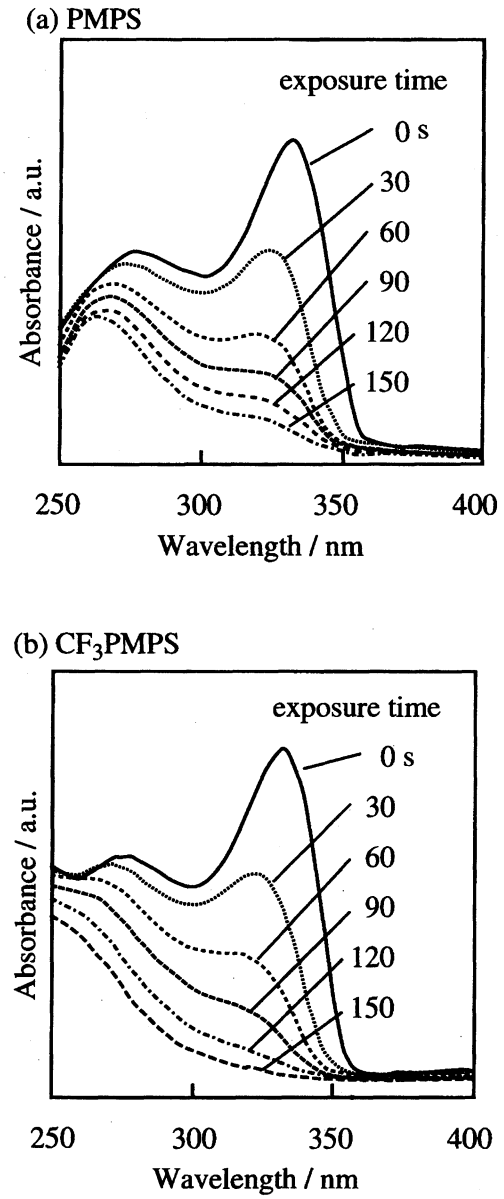

Fig. 3. The changes in absorption spectra of (a) PMPS and (b) CF_3PMPS upon the UV-irradiation. Film thickness of both samples was about 0.5 μm. UV light (10 mW cm^{-2} for 310—400 nm) from a Hg lamp was used for exposure.

with that of PMPS.

To evaluate the effect of $[THEMA]^+$ additives, we also measured the retention time of fountain water covered on the UV-exposed hydrophilic surface. Changes in the length of retaining water film on the UV-exposed surface with the passage of time are shown in Fig. 4. The length of fountain water

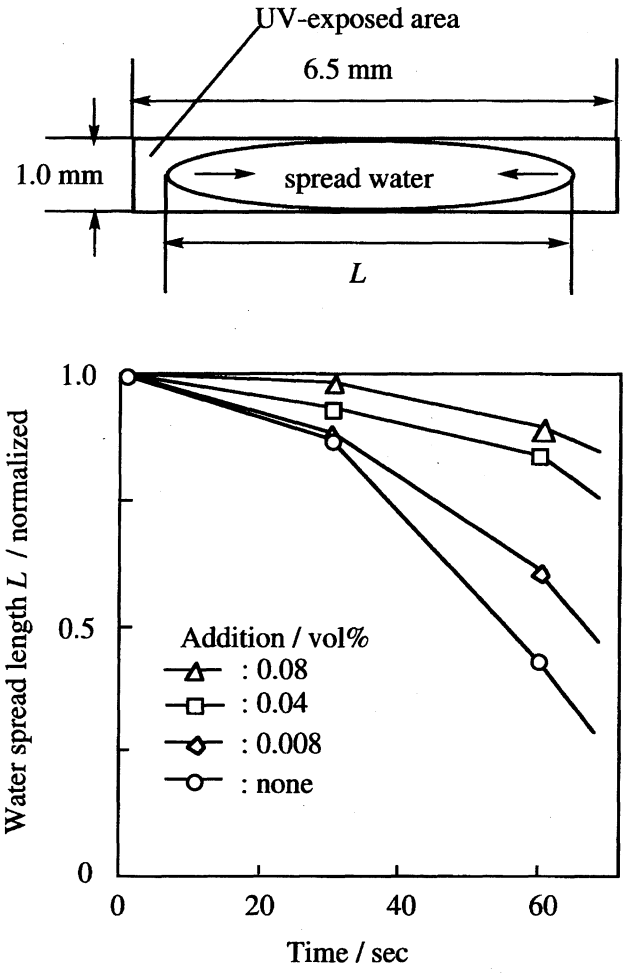

Fig. 4. The changes in the fountain water spread length L on UV-exposed hydrophilic surface of a CF_3PMPS base plate. Fountain waters consist of usual components and tris(2-hydroxyethyl)methylammonium salt with various concentration. The upper illustration represents the model of our measuring method.

Table 1. Contact Angles of the Sample Film Surfaces for Fountain Waters

Sample	Solution	Contact angle (°)		
		Unexposed	UV-exposed	Differece
PMPS	Deionized water	88.1	64.2	23.9
	Commonly used FW[a)]	77.9	44.8	33.1
	FW including $[FHEMA]^+I^-$ [b)]	62.3	23.6	38.7
CF_3PMPS	Deionized water	108.3	96.2	12.1
	Commonly used FW[a)]	100.7	69.1	31.6
	FW including $[THEMA]^+I^-$ [b)]	97.3	58.4	38.9

a) Fountain water. b) Tris(2-hydroxyethyl)methylammonium iodide; Concentration: 0.04 vol% in the fountain water.

film without $[THEMA]^+$ on the UV-exposed hydrophilic surface of a CF_3PMPS base plate was rapidly reduced, and after 60 s; it became 50% of the initial length. By adding tris(2-hydroxyethyl)methylammonium iodide ($[THEMA]^+I^-$) of 0.04 vol % to fountain water, however, a pronounced retardation in the drying time was observed on the UV-exposed surface, the length being maintained at about 85% of the initial value, even after 60 s. Thus, the effect of adding $[THEMA]^+$ was confirmed to be effective for retaining sufficient water on the UV-exposed area. The composition of the fountain solution used in this study is summarized in Table 2. By using fountain water which included $[THEMA]^+$ and the Arabic gum usually used, the hydrophilic treatment step, which is needed in the conventional offset printing process, may become unnecessary.

Offset Printing Test. Using a CF_3PMPS-coated plate and fountain water including $[THEMA]^+$ we have succeeded in obtaining well-reproduced print images of morning glories, as shown in Fig. 5. The image was 5-by-5 centimeters in size. Sufficient adhesion of blue-colored oil-ink on the UV-unexposed area and less contamination on the UV-exposed area were performed. These results clearly indicate that the enhancement of wettability difference between UV-exposed and unexposed surfaces was accomplished both by employing CF_3PMPS to assure water repulsion and by adding $[THEMA]^+$ to fountain water to enhance the hydrophilicity in the UV-exposed surface.

Table 2. Constitution of the Modified Fountain Water by Addition of Tris(2-hydroxyethyl)methylammonium Salt

Components	Quantities
Deionized water	750 g
2-Propanol	250 g
10 vol% $[THEMA]^+I^-$ [a]	4 ml
14° Bé[b] Arabic gum solution	4 ml
0.1 mol dm^{-3} Disodium carbonate solution[c]	4 ml

a) Tris(2-hydroxyethyl)methylammonium iodide; Concentration: 0.04 vol% in the fountain water. b) °Bé is correlated with density, d by expression of $d=144.3/(144.3-°Bé)$. c) pH control agent (pH=10.5) to accelerate the dissociation of –SiOH to SiO^- and H^+ under alkaline solution.

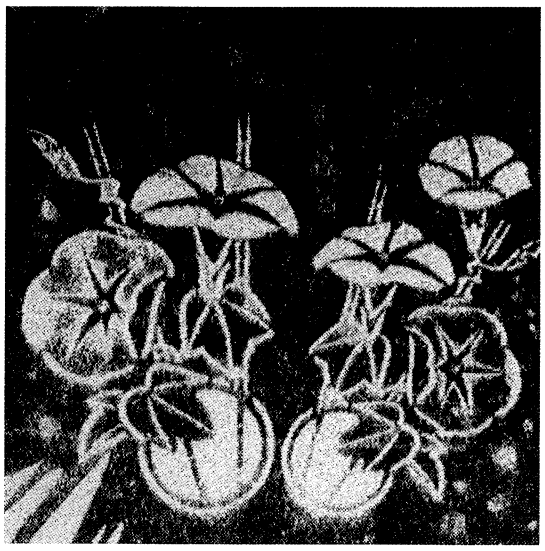

Fig. 5. A print image sample on a paper after several printings. The image was 5 by 5 centimeters in size.

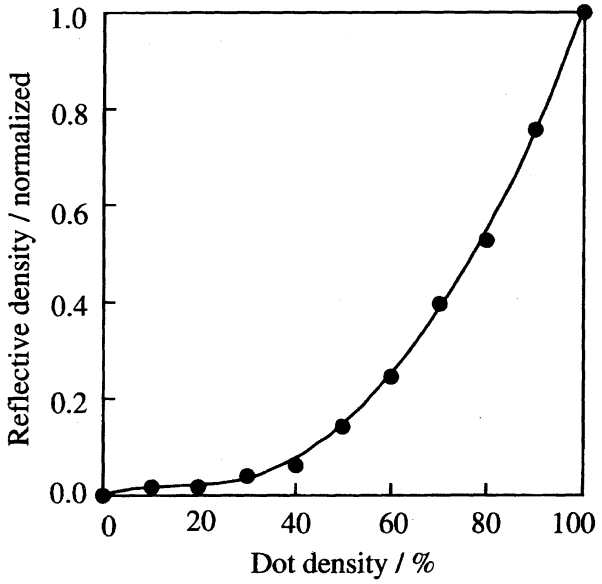

Fig. 6. Tone reproduction curve of the print image using a CF_3PMPS plate and the modified fountain water added with 0.04 vol% tris(2-hydroxyethyl)methylammonium iodide.

The tone-image reproduction characteristics, which represent the state of the art for the present printing process, are shown in Fig. 6. The ink density of the ordinate was normalized by a value at 100% in the abscissa, which means that the whole area was covered with ink. The curve rises rapidly at a dot density of 50% and above. However, the ink densities were found to be almost zero for a dot density of less than 50%. Since the gray scale based on the dot density is composed of a continuous change in the size of the square patterns, but not in the number of dots of a constant size, these results indicate that oil-ink was still supplied insufficiently to reproduce a small dot pattern. For example, the case for 50% of dots density is composed of about a 67 μm square pattern. The poor tone reproduction below 50%, therefore, seems to resulted because the small-sized picture area was almost covered with fountain water because of low adhesion between CF_3PMPS and the oil-ink used in this study. This problem, however, can be improved by optimizing the oil-ink viscosity and the amount of fluorine groups to be introduced in the copolymer.

Conclusion

In summary, we successfully developed a novel offset printing process, which can skip the developing step necessary in the conventional offset routine, as shown in Fig. 2. The present novel offset printing process may therefore be named "developer-less offset printing". This was achieved by utilizing wettability enhancement induced by UV-exposure in polysilane. Further spectral sensitization of the photodecomposition of polysilanes would provide a possible ap-

plication of this plate a direct marking-plate by a laser.

References

1) R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).

2) R. G. Kepler, J. M. Zeigler, L. A. Harrah, and S. R. Kurtz, *Phys. Rev. B*, **35**, 2818 (1987).

3) M. A. Abkowitz, M. J. Rice, and M. Stolka, *Philos. Mag., Part B*, **61**, 25 (1990).

4) K. Yokoyama and M. Yokoyama, *Philos. Mag., Part B*, **61**, 59 (1990).

5) M. Stolka, H.-J. Yuh, and D. M. Pai, *J. Polym. Chem. Ed.*, **25**, 823 (1987).

6) K. Yokoyama and M. Yokoyama, *Chem. Lett.*, **1989**, 1055.

7) K. Yokoyama and M. Yokoyama, *J. Appl. Phys.*, **67**, 2974 (1990).

8) T. Enokida, R. Hirohashi, and R. Kurata, *Nippon Kagaku Kaishi*, **1990**, 575.

9) R. D. Miller, D. Hoffer, D. R. Mckean, C. G. Willson, R. West, and P. Trefonas, III, "Materials for Microlithography," ed by L. F. Thompson, C. G. Willson, and J. M. J. Frechet, American Chemical Society, Symposium Series, New York (1984), pp. 293—310.

10) K. Yokoyama and M. Yokoyama, *Appl. Phys. Lett.*, **55**, 2141 (1989).

11) Y. Sakata, M. Hiramoto, and M. Yokoyama, "Japan Sciety of Applied Physics and Related Societies, 41st Spring Meet. 1994," Ext. Abstr. No. 28p-N15.

12) M. Kakui, K. Yokoyama, and M. Yokoyama, *Chem. Lett.*, **1991**, 867.

13) K. Yokoyama and M. Yokoyama, *J. Imaging Technol.*, **16**, 219 (1990).

14) M. Yokoyama, T. Koura, Y. Hiroshige, and S. Notsu, *Chem. Lett.*, **1991**, 1563.

15) M. Yokoyama, M. Kakui, and Y. Yamaguchi, *J. Imaging Sci. Technol.*, **38**, 350 (1994).

16) H. Tsushima, M. Kawabata, I. Sumiyoshi, and M. Yokoyama, "Proc. Int. Symp. of the Society for Information Display (SID)," San Jose, CA, Society for Information Display, Santa Ana, CA, Vol. 25, 936 (1994), ed by J. Morreale Palisades.

17) Y. Tachibana, Y. Sakurai, and M. Yokoyama, *Chem. Lett.*, **1994**, 1119.

18) J. A. Perry, *Tappi*, **55**, 722 (1972).