

# Designed Surface Modification by Photo-induced Vapor Phase Assisted Surface Polymerization of Vinyl Monomers

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The photo-induced vapor phase assisted surface polymerization (photo-VASP) technique was developed to achieve designed fine 2D and 3D patterns on solid surfaces. When used with pre-patterned photo-masks, photo-VASP, via polymer accumulations, reproduced pre-patterns on glass plate, Si-wafer, and Au-plate surfaces. Patterns from covalently bonded polymer were achieved with immobilized photo initiators. Moreover, a multi-layered 3D pattern was also made of block copolymer chains grafted from the surfaces.

**Keywords:** photo-induced polymerization, patterning, surface design, graft polymerization

## 1. Introduction

Many researchers are now becoming interested in the fine surface design of solid materials as a subject of study because there are a growing number of fields where fine surface work is becoming increasingly important and even crucial, such as in printing, coating, and applications using fibers, membranes, and biomedical material [1]. In these fields, the ability to produce fine surface architecture, as found in continuous micro arrays or complex patterns is a key point. Such fine work has been achieved through various advanced techniques, examples being 1) surface initiated polymerization (SIP) with free radicals, atom-transfer radical (ATRP), anion, iniferter polymerization methods [2]; 2) micro-contact printing with free radical polymerization, ATRP, ring-opening metathesis polymerization (ROMP) methods, and “grafting on” the surface [3]; and 3) photo lithography with free radical, iniferter, ATRP methods [4], and “grafting on” the surface [5]. These technologies have allowed the design of fine patterns to be easily reproduced on solid surfaces.

Recently, there has been a development in the study of the construction of these fine surface architectures from 2D-patterning to 3D-construction. To construct these 3D designed

surface architectures with fine structures, well-controlled liquid processes such as micro stereo lithography have been developed [6]. However, there are still some problems associated with the liquid process, such as the high viscosity of the monomer solution; the swelling of products in solution; volume shrinkage in the subsequent drying process, and the difficulty of achieving monomer change. A more simple and precise constructing process may be achievable by a vapor-phase assisted polymerization (VASP) technique, which is able to construct the fine structures on the surface without the above problems. This was demonstrated by Fu *et al.* [7] and Chang *et al.* [8] who reported on the 3D-constructing by ROMP of norbornenes and ring opening condensation of *N*-carboxyanhydrides on Au-plate and silicon oxide surfaces.

To give a durable surface modification, it is necessary to covalently bond the coating materials to surfaces. Of the two reliable grafting procedures: “grafting from” and “grafting on” surfaces, the former is preferred because its high grafting density allows living polymerization methods to be used to make permanent modifications of surfaces. Some reports have dealt with the SIP that uses controlled polymerization

methods, such as anionic, iniferter, nitroxide-mediated, ROMP, and ring-opening condensation methods [2c-d,4c,8,9], to make polymer chains propagate from substrate surfaces. A more robust and convenient technique, however, is the free-radical polymerization method, because the reaction is independent of moisture levels and tolerates a large variety of organic functional groups. Huang *et al.* successfully synthesized the covalently bonded graft-chains on Au surfaces using an azo-type free radical initiator immobilized on the surface in a solution [2a]. They showed that the polymer layer accumulated on the surface with a thickness that increased linearly with reaction time, but they gave no details characterizing the obtained polymers..

There are some reports that deal with VASP of vinyl monomers by free radical initiators; for example, Chan *et al.* [10] investigated the chemical vapor deposition of 2-hydroxyethyl methacrylate and glycidyl methacrylate by azo- and peroxide-type free radical initiators on Si substrate, in which the molecular weight of deposited polymer chains was controlled through the monomer to initiator ratio. Our own work has focused on the combination of physically controlled VASP [11] with a photo-induced polymerization technique [12], producing block copolymers on surfaces by using the free radical initiators. The earlier reported results encouraged us to develop the designed fine structures by covalently bonding on substrate surfaces. This article describes our efforts to produce some two- and three-dimensional architectures by combining the VASP technique and a surface patterning technique with a photo-induced polymerization method [13]. The result was a formation of finely patterned architectures, in particular, those created by covalently bonding block copolymers on solid surfaces.

## 2. Method

### 2.1. Materials

Monomers, methyl methacrylate (MMA, >99.0%) and styrene (St, >99.5%) from Kishida Chemical Inc. were purified by distillation just before use. 2,2'-Azobis(isobutyronitrile) (AIBN, >99%) was purchased from Otsuka Chemical Inc. and recrystallized from methanol. Other materials used as received were: tetramethylthiuram disulfide (97%) purchased from Aldrich Chemical Company Inc.; sodium *N,N*-diethyldithiocarbamate purchased from Wako Pure Chemical Industries,

Ltd; *p*-chloromethyl phenyltrimethoxysilane obtained from Azmax Co., Ltd., and inhibitor, 4-tert-butylprocatechol purchased from Tokyo Kasei Kogyo Co. Ltd. (TCI). Substrates, glass plate (14 mm $\phi$ ), Si-wafer (20  $\times$  20 mm<sup>2</sup>) and aluminum pan (Al pan, 5 mm $\phi$ ) were used after surface cleaning and treatments. All other reagents were commercially obtained and purified by distillation.

### 2.2. Characterization methods

Fourier transform infrared (FTIR) spectroscopy was performed using a JASCO FTIR 460 plus spectrometer. Reflection spectra of as-polymerized samples were measured on a Nicolet Thunderdome swap-top module with a germanium crystal, by the single-reflection ATR method. Transmission spectra were measured by coating the polymer solution on a KBr plate and evaporating the chloroform.

Scanning electron microscopy (SEM) was performed with a HITACHI S3000N scanning electron microscope at an accelerating voltage of 15 kV with a backscattered electron (BSE) detector. The microscope operated with specimen chamber pressure of 80 Pa without an electron conductive layer of gold or carbon. The compositional image was formed from BSE.

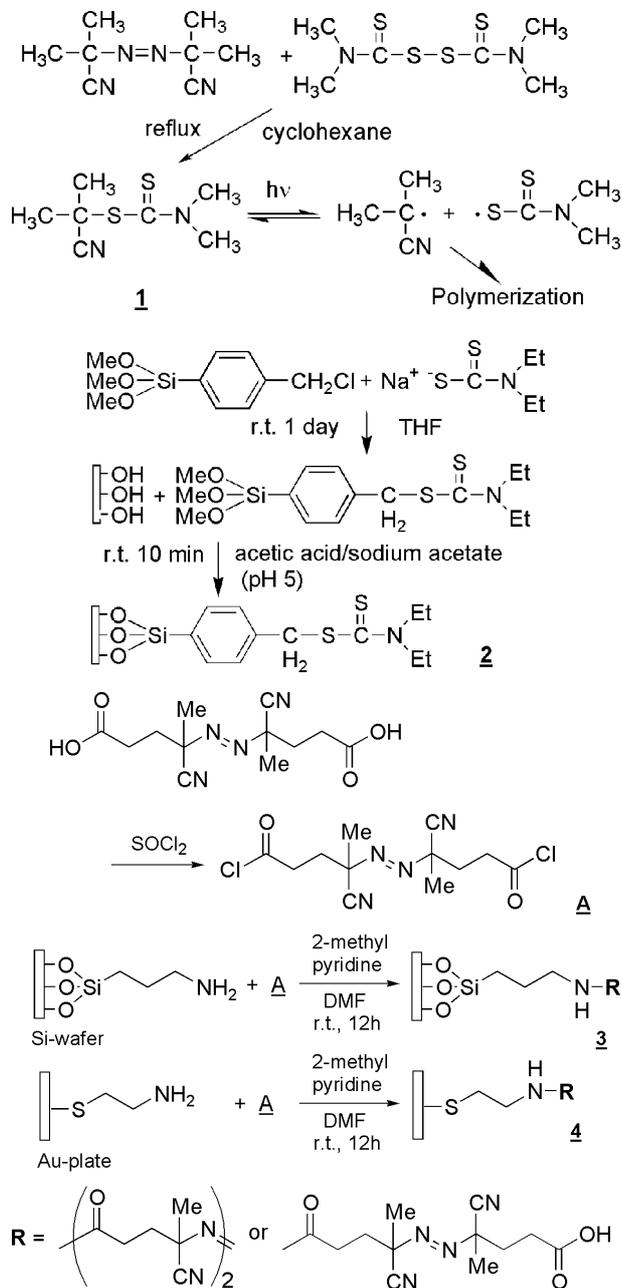
Atomic force microscopy (AFM) was performed on a SII Nanopics 2100 in a tapping mode.

### 2.3. Synthesis of photoinitiators

Four kinds of photoinitiators were synthesized. 2-Cyanoprop-2-yl *N,N*-dimethyldithiocarbamate (CPDTC, **1**) was a free initiator, *N,N*-(diethylamino)dithiocarbamoyl-benzyl (trimethoxy silane) (SBDC, **2**) was immobilized on glass plate, and the other two azo-type initiators **3** and **4** were immobilized on Si-wafer and Au-plate, respectively. The photoinitiator **1** and precursor **A** were prepared according to our previous reports [12,13] and confirmed by <sup>1</sup>H NMR and FTIR analyses.

Photoinitiator **2** was synthesized according to a report of Boer *et al* [2d]. In a typical procedure, *p*-(chloromethyl)phenyl-trimethoxysilane (22.3 mmol) and sodium *N,N*-dimethyldithiocarbamate (22.3mmol) were dissolved separately in 50 mL of dry tetrahydrofuran (THF). The solutions were mixed slowly via a syringe and stirred for 5 h at room temperature. The solution changed to a yellow color and a white salt precipitated. After removing the precipitate by filtration, THF was

evaporated to obtain a yellow viscous liquid. The liquid was distilled in a Kugelrohr (180 °C, 0.6 kPa) to isolate a precursor (*p*-trimethoxysilyl) benzyl *N,N*-dimethyldithiocarbamate (21.2 mmol) in a 95.6% yield.



**Scheme 1.** Synthesis of photoinitiators.

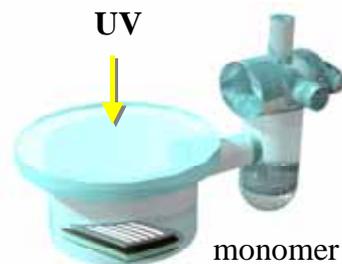
Glass plates were sonicated and washed by acetone, MeOH, and distilled water to remove organic residues on the surface. Then, the glass plates were treated by “piranha” solution: a mixture of 70% concentrated sulfuric acid and 30% hydrogen peroxide, followed by rinsing with distilled water. A solution of the precursor (1

vol%) in acetic acid/sodium acetate buffer (pH 5) was stirred for 30 min to allow the precursor to hydrolyze. The glass plates were immersed in the precursor solution and after 10 min taken out before being heated in an oven thermostated at 60 °C for a further 10 min. Then, after washing away physically adsorbed precursor molecules with distilled water, the surface-modified glass plates **2** were dried *in vacuo*.

Si-wafer (20 × 20 mm<sup>2</sup>) surface was modified with a solution of (3-aminopropyl)trimethoxysilane (5 wt% in toluene) [14], whereas the Au-plate (10 × 25 mm<sup>2</sup>) was modified by a solution of 2-aminoethanethiol hydrochloride (1.0 mM in THF) [15]. Both the modified substrates were then functionalized by a reaction with precursor **1** according to the method reported by Schmidt *et al.* [15] to prepare immobilized photoinitiators **3** and **4** as shown in Scheme 1.

#### 2.4. Line patterning by photo-VASP on glass plate

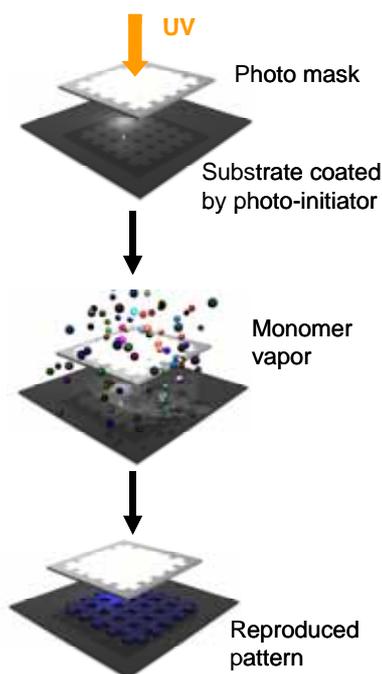
Photo-VASP was carried out in an H-shaped glass reactor with a vacuum cock, a quartz cap, and a glass filter separator (pore size 20-30 μm) at the bridge part (Fig. 1). The photo-VASP process is illustrated in Scheme 2. UV irradiation was performed with a 500W high-pressure mercury-xenon lamp in Universal Arc Lamp Housing Model 66901 from Oriel Instrument. The illuminance on the substrate surface was measured with an AS ONE LM-332 light meter.



**Fig. 1.** H-shaped glass reactor for photo-VASP

The photoinitiator **1** was dissolved in acetone (**1**) = 4.02 × 10<sup>-2</sup> mol L<sup>-1</sup>) and a 1.50 mL aliquot of the solution (CPDTC 60 μmol) was spread on a glass plate surface (154 mm<sup>2</sup>). The glass plate was dried at ambient temperature for 2 h and set in the bottom of one leg of the reactor. MMA (0.5 mL) and 4-tert-butylprocatechol (20 mg) were added into the bottom of the other leg. The MMA in the reactor was subjected to a freeze-pump-thaw cycle

repeated three times and then sealed *in vacuo*. The photo-VASP was carried out in an oven at 40 °C for 2 h in a saturated vapor pressure of MMA (23.7 kPa) under UV irradiation through a quartz cover and pre-patterned photo mask with slit widths of 50-500 μm at a distance of 8 cm from the surface of the glass plate. The space between the substrate surface and photo mask was set at 1 mm. The illuminance on the substrate surface was changed in a range of  $1.84 \times 10^3$  to  $1.64 \times 10^3$  lx depending on the vapor concentration of MMA. After the VASP, the treated glass plate surface was observed with SEM.



Scheme 2. Photo-VASP on the substrate surface.

### 2.5. 2D patterning by photo-VASP with photo iniferter 2 on glass plate

Photo-VASP of MMA was carried out on glass surfaces with immobilized photoinitiator 2 and photo masks, with circular (400 μm in diameter) and striped (300 μm in width) pre-patterns, under the same UV-irradiation conditions as for the above line patterning. After the VASP, physisorbed monomers and polymer chains on the surface were completely removed by immersing the surfaces in THF 4 times for 5 min at room temperature under irradiation with the supersonic wave and rinsing with THF. Then, the treated glass plate surface was observed with SEM.

### 2.6. 2D and 3D patterning by photo-VASP with azo initiators 3 and 4 on Si-wafer and Au-plate

To fabricate the designed square and lattice

patterns on a surface, the photo-VASP of MMA was carried out at 40 °C for 24 h in a saturated vapor-phase of MMA under UV-irradiation through the patterned photo-masks with a slit width of 100 μm. The patterns were irradiated with a point source of UV light using a 320 W high-pressure mercury lamp (MORITEX Co., MUV-202-U) at an intensity of  $49 \text{ mW}\cdot\text{cm}^{-2}$  ( $\lambda=280\text{-}320 \text{ nm}$ ) and a distance of 10 cm from the substrate surface. After the VASP, physisorbed monomers and polymer chains on the surface were completely removed in the same manner as above-mentioned. The grafting polymer chains on the surface were determined with SEM using the BSE detector, FTIR in a reflection absorption mode and AFM.

## 3. Results and Discussion

### 3.1. Accumulated line patterning

Dithiocarbamates 1 and 2 are well known as the photo-iniferter and the reversible addition fragmentation chain transfer reagent that are used to generate radical species under UV irradiation, initiate the radical polymerization, and recombine reversibly according to Scheme 1 [16].

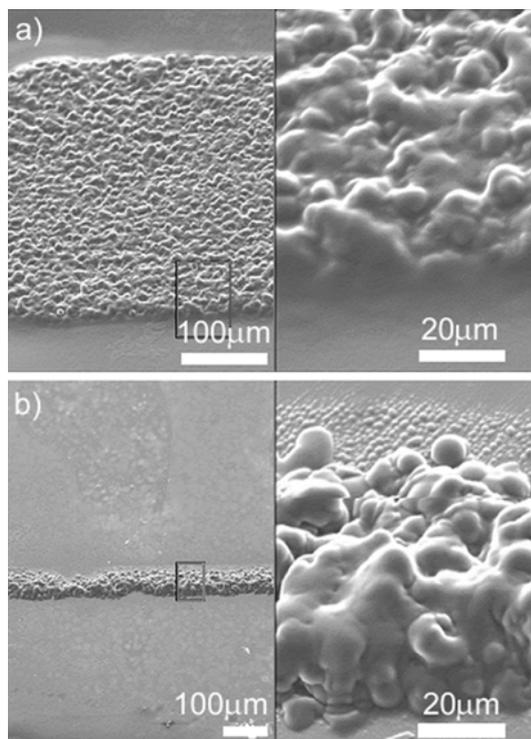


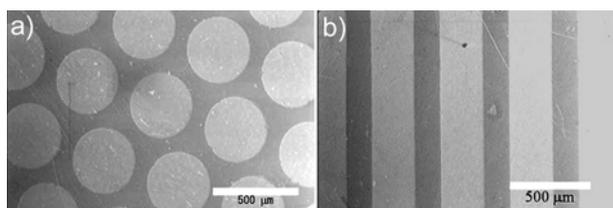
Fig. 2. Line patterns by polymer accumulation on glass plate surface after photo-VASP at 40 °C for 2 h. Line width: a) 300 μm and b) 50 μm.

The photo-VASP of MMA was carried out on a glass plate coated with 1 under UV-irradiation through a pre-patterned photo mask, on which line

patterns of 50-500  $\mu\text{m}$  in width were formed. The photo-VASP gave a line-patterned polymer deposition on the glass plate surface, which was determined by the SEM observation. As shown in Fig. 2, the formed line patterns reflected the original pre-patterns replicating the 50 and 300  $\mu\text{m}$  line widths of the original photo-mask. The height of the deposition layer was about 10  $\mu\text{m}$ . Though the top surfaces of the line patterns were markedly uneven, the edge was relatively sharp. The SEM images indicate that the PMMA had accumulated within the UV irradiation area without diffusing, as illustrated in Scheme 2. The unevenness may be lessened by control of the deposition rate, itself a function of other parameters, such as initiator concentration, choice of monomer, temperature, monomer vapor pressure, and UV intensity.

### 3.2. Covalently bonded 2D patterning

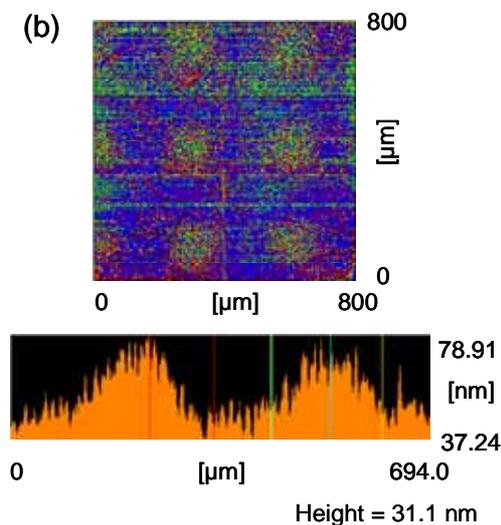
To prepare covalently bonded 2D patterning on solid surfaces, immobilized photoinitiator **2** was employed for the photo-VASP of MMA. After irradiation through photo-masks with circular and striped patterns, free polymer deposits were removed by dissolving and washing with good solvent. Covalently grafted polymer chains were observed by compositional SEM analysis with a BSE detector. SEM images are depicted in Fig. 3. As shown in the figures, the photo-VASP successfully gave 2D patterns comprised of PMMA grafted from the glass surface. These patterns precisely replicated the pre-patterns of the photo-masks.



**Fig. 3.** Circular and striped patterns of polymer accumulation grafted from glass plate surface by photo-VASP at 40 °C for 2 h. Bar=500  $\mu\text{m}$ .

To evaluate the thickness of the polymer layer grafted from the surface, Si-wafer surface bonded azo initiator group **3** was used for photo-VASP of MMA. The polymerization of MMA was initiated by free radicals generated *via* the photochemical decomposition of the azo-initiators, resulting in the accumulation of polymer chains in the patterned areas irradiated. Fig. 4 depicts an AFM image of the accumulated square pattern on the Si-wafer surface. This pattern must be made up of the

polymer chains grafted from the surface, because the reflection absorption FTIR spectrum of the accumulated area exhibited a typical characteristic absorption band of PMMA at 1725  $\text{cm}^{-1}$ . The thickness of the resulting accumulation ranged from 20 to 30 nm as shown in Fig. 4. The thickness profile was broad in shape, because of the process of washing by THF.



**Fig. 4.** Square pattern of polymer accumulation grafted from Si-wafer surface by photo-VASP at 40 °C for 24 h.

### 3.3. Multi-layered 3D patterning

To make the best use of the living nature of the VASP method [11a], construction of multi-layered patterns by block copolymerization was tried by consecutive application of photo-VASP; in other words the monomer vapors of MMA and styrene (St) were consecutively fed onto the azo-functionalized Au-plate surface. In the first step, VASP of MMA was carried out in a saturated vapor-phase of MMA under UV-irradiation through a stripe-patterned photo-mask at 40 °C for 24 h. After the first reaction, remaining MMA vapor was thoroughly removed *in vacuo*, followed by the introduction of St vapor (2.2 kPa at 40 °C), rotation of the photo-mask through 90°, and irradiation with UV light to start the second-step reaction. VASP of St was carried out at 40 °C for 24 h. After the second reaction, any remaining St vapor was removed *in vacuo*. Physisorbed monomers and polymer chains were completely removed with THF. Previously, in a similar procedure it was determined that the block copolymer: poly(MMA-*block*-St) was formed on the surface with a high block-structure ratio of 81.4 % [12]. Thus, the block copolymer chains must be grafted from the Au-plate surface in a similar way.

After the consecutive VASP and the following treatment, the accumulated polymer pattern on the Au-plate surface was observed by SEM. Fig. 5 shows the compositional SEM image formed from BSE at a crossing point, where use of block copolymerization has caused the overlapping vertically and horizontally striped patterns to over-accumulate. In Fig. 5, bright vertical and dark horizontal stripes indicate PMMA and PSt accumulations, respectively. It is clear that the PMMA-block segment was overlaid with the PSt-block segment. This observation was confirmed from the microscopic FTIR absorption mapping images [13]. In the areas that were not exposed to UV-light, no accumulation of polymer chain was detected. This means that the graft-polymerization from the surface occurred *via* photo-induced reactions, not *via* a thermal reaction. This accumulation of the block copolymer demonstrates the building up of the designed pattern structures.



**Fig. 5.** SEM image with BSE detector of accumulated polymer chains by consecutive photo-VASP of MMA and St on Au-plate surface. Bar=100  $\mu\text{m}$ .

#### 4. Conclusion

To build up finely designed polymer patterns on solid surfaces, photo-VASP technique with pre-patterned photo-masks was investigated on glass plate, Si-wafer, and Au-plate surfaces, resulting in the patterned polymer accumulation and reproduction of the pre-patterns. This ultimately led to the building up of multi-layered 3D patterns made of block copolymer chains grafted from the surfaces.

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