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Auto-Drawing and Functionalization by Vapor-Phase Assisted Polymerization on Solid Surface

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Formation of two- and three-dimensional micro architectures with chemical functions was verified by photo-vapor phase assisted surface polymerization (VASP) of functional monomer vapors combined with an auto-drawing system manipulated by prescribed programs. The surface modification by the photo-VASP of styrene vapor progressed rapidly, and a fine lines-pattern of photo-mask was transcribed as the corresponding polymer accumulations on poly(methyl methacrylate) (PMMA) substrate surfaces. Substrate surface modified by photo-VASP of acrylic acid showed reversible changes in hydrophilic/hydrophobic properties according to repeating external chemical stimuli. The successive auto-drawing by photo-VASP of three kinds of monomer vapors was examined under spot illumination from a fine optical fiber on an X-Y stage manipulated by a prescribed program, resulting in the production of a pre-designed functional structure by successful accumulations of corresponding polymers on the substrate surface.

Keywords: vapor-phase surface-assisted polymerization, photopolymerization, surface accumulation, auto-drawing, functionalization

1. Introduction

Fine surface design of solid materials has been attracting interest of many researchers, because there are a growing number of applicable fields, where fine surface creation methods are becoming increasingly important and even crucial, such as in printing [1], coating [2], and other applications using fibers [3], membranes [4], and biomedical materials [5,6]. In these fields, effective methodology to produce fine surface architectures as found in continuous micro arrays and complex 2D-patterns is a key point. Such fine work has been achieved through various advanced techniques, for example, 1) surface-initiated polymerization with free radicals, atom-transfer radical polymerization (ATRP), anionic polymerization, and iniferter polymerization methods [7], and 2) micro-contact printing with free radical polymerization, ATRP, ring-opening metathesis polymerization (ROMP) methods, and "grafting on" the surface [8]; and 3) photo-lithography with free radical polymerization, iniferter polymerization, ATRP methods [9], and "grafting on" the surface [10]. These methodologies have allowed the design of fine patterns to easily reproduce on solid surfaces.

A simple and precise constructing process of the surface architectures may be achievable by the vapor-phase assisted polymerization (VASP) technique [11], which is able to construct the fine structures on the surface without various problems associated with the liquid process, such as high viscosity of the monomer solution; swelling of polymer in the monomer solution; volume shrinkage in the subsequent drying process, and difficulty of monomer exchange. VASP technique has been demonstrated by Fu *et al.* [12], Chang *et al.* [13], Gleason *et al.* [14], and Nishida *et al.* [15-17]. Fu *et al.* reported on the 3D-constructing by ROMP of norbornenes and Chang *et al.* performed by a ring opening condensation method of *N*-carboxyanhydrides on Au-plate and silicon

oxide surfaces. Chan and Gleason investigated the chemical vapor deposition of 2-hydroxyethyl methacrylate and glycidyl methacrylate by azo- and peroxide-types free radical initiators on Si substrate, in which the molecular weight of deposited polymer chains was controlled by the ratio of monomer to initiator. Nishida *et al.* [11] has been focusing on the combination of physically controlled VASP with a photo-induced polymerization technique, producing block copolymers on surfaces by using the free radical initiators. The previous results made us notice great potentiality of fine auto-drawing with various functions on substrate surfaces by combination of VASP and photo-drawing.

In this article, the potentiality of two- and three-dimensional micro architectures formation is demonstrated by the combined photo-induced VASP technique (photo-VASP) with an auto-drawing system consisting of an optical fiber-irradiation apparatus and a programed manipulator. As results, the reproduction of fine patterns designed beforehand was confirmed on solid substrates, on which corresponding polymer chains were accumulated by photo-VASP of plural monomers having different chemical properties, accompanying of covalently bonding on the solid surfaces.

2. Experimental

2.1. Materials

Monomers: styrene (St, >99.0%), acrylic acid (AA, >98.0%), and N-isopropylacrylamide (NIPAAm, >98.0%); photo-initiator: 2.2-dimethoxy-2-phenylacetophenone (DMPAP, >98.0%); and inhibitor: 4-tert-butylpyrocatechol were purchased from Tokyo Chemical Industry Co., Ltd. (Japan) and Wako Pure Chemical Industries, Ltd. (Japan). Substrate: poly(methyl methacrylate) plate was obtained from ACRYSUNDAY Co., Ltd. (Japan).

2.2. Photo-VASP combined with auto-drawing method

Photo-VASP of the monomers was carried out on a PMMA plate ($3 \times 3 \times 0.1$ cm^3) using the photo-initiator (DMPAP) in an H-shaped glass reactor with a vacuum stopcock and a quartz plate cap (Figure 1). The H-shaped glass reactor was set on an X-Y stage (SIGMAKOKI Co., Ltd., Japan) manipulated by a prescribed computer program. Irradiation was performed via an optical fiber (0.5 or 5 mmφ) from a light source of an ozone-less

mercury-xenon lamp MUV-202-U (MORITEX Co., Tokyo, Japan) (»=200-600 nm).

In a typical procedure, the PMMA plate was coated with 64.7 mg (0.252 mmol) of a DMPAP initiator solution (0.1 M in ethanol) and followed by drying in an air flow at room temperature under dark. The coated PMMA plate was set on a table at one bottom of large leg of the H-shaped glass reactor to keep a clearance of 0.5 mm from an inner surface of the quartz plate cap. Monomer St (0.5 ml) and inhibitor 4-tert-butylpyrocatechol (20 mg) were introduced into another small leg bottom. The St/inhibitor solution in the leg was subjected to three freeze–pump–thaw cycles and then the reactor was sealed *in vacuo*. Photopolymerization was carried out in a saturated St-vapor atmosphere (815 Pa) at 25ºC under the photo-irradiation at a distance of 0.8-0.9 cm from an end of optical fiber through the quartz plate cap for prescribed time. Illumination intensity on the PMMA plate surface was 120 mW·cm^{-2}. After the photopolymerization, residual monomers were evacuated and a product accumulated on the plate was analyzed using various methods described in the characterization part.
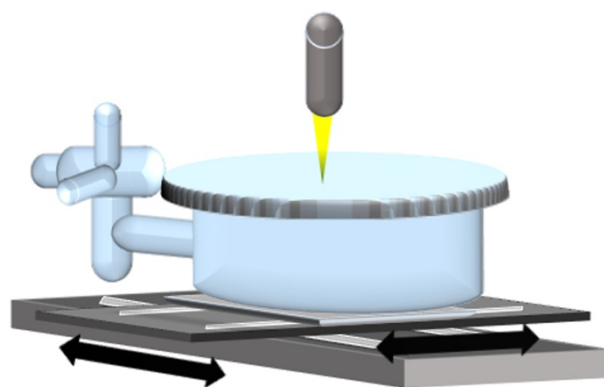

Fig. 1. H-shaped glass reactor set on X-Y stage for auto-drawing photo-VASP

2.3. Characterization

Accumulated materials on the PMMA plate surface were directly detected by fluorescence observation under UV-irradiation with a handy UV-lamp SLUV-4 (»=365 nm) (AS ONE, Osaka, Japan).

Surface morphology of accumulations on the surface was observed with a 3D Laser Scanning Confocal Microscope Model VK-X 100/105 (KEYENCE, Japan) under prescribed conditions of laser: red semiconductor laser, » = 658 nm, 0.95 mW, and pulse width 1 ns.

Chemical structure of the accumulations was

analyzed by Fourier transform infrared (FTIR) spectroscopy, which was recorded on a Nicolet iZ10 attached SMART iTR (Thermo Fisher SCIENTIFIC, Japan) in a wavenumber range of 650–4000 cm^{-1} at a resolution of 4 cm^{-1}. Reflection spectra of samples were measured on an attenuated total reflectance (ATR) module with a Zinc selenide crystal, by the single-reflection ATR method. Moreover, microscopic FTIR mapping of the accumulated substrate surface was achieved on a microscopic FTIR equipped with an image-mapping system Nicolet iN10 MX (Thermo Fisher SCIENTIFIC, Japan): in a reflection absorption mode and a wavenumber range of 675-4000 cm^{-1}.

Static contact angle value of the accumulated surface against a water droplet was measured with a contact angle equipment model DMs-401 (KYOWA, Japan). The reported values are averaged from ten determinations conducted at random locations.

Finally, the accumulated materials were dissolved in chloroform by Soxhlet extraction method for 8 h. Molecular weights of the dissolved materials were measured on a TOSOH HLC-8120 size exclusion chromatograph (SEC) with refractive index (RI) and ultraviolet (UV, » = 254 nm) detectors under the following conditions: TSKgel Super HM-H linear column (linearity range, 1×10^3 - 8×10^6; molecular weight exclusion limit, 4×10^8), CHCl$_3$ (HPLC grade) eluent at a flow rate of 0.6 mL·min^{-1}, and column temperature of 40 ℃. Calibration curves for SEC analysis were obtained using polystyrene standards with lower polydispersity values than 1.10 (weight average molecular weight = 7.70×10^2, 2.43×10^3, 3.68×10^3, 1.32×10^4, 1.87×10^4, 2.93×10^4, 4.40×10^4, 1.14×10^5, 2.12×10^5, 3.82×10^5, 5.61×10^5, 2.00×10^6, Aldrich). The sample (10 mg) was dissolved in chloroform (2 mL) and the solution was filtered through a membrane filter with a 0.45 μm pore size.

3. Results and Discussion

3.1. Macroscopic changes in substrate surfaces after photo-VASP of St

Photo-VASP of St was carried out under photo-irradiation from the mercury-xenon lamp under prescribed conditions. Photopolymerization and thereby chemical modification of the surface were detected by change in fluorescence emission property, 3D morphology, FTIR spectrum, and contact angle value.

Figure 2 shows the change in fluorescence emission property of PMMA plate surface before and after the photo-VASP of St at illumination intensity of 120 mW·cm^{-2} at 25 ℃ for 30 min. Distinguishable boundary was observed between the half areas with and without the UV exposure for VASP. Clear fluorescence emission from photo-VASP area was observed. It is considered to occur due to excimers of polystyrene [18]. This suggests the coverage by polystyrene of the irradiated half area of surface.
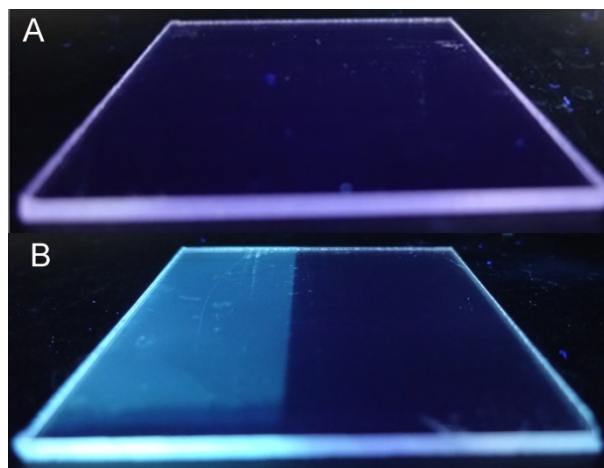

Fig. 2. Fluorescence images before and after VASP of St under illumination intensity of 120 mW·cm^{-2} at 25 ℃ for 30 min. a) before and b) after VASP with half coverage of surface area.
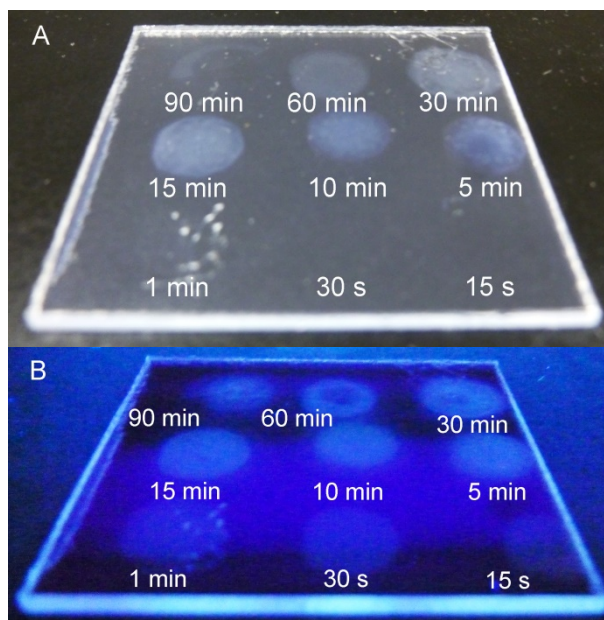

Fig. 3. Visual (A) and fluorescent images (B) after photo-VASP of St under spot (5 mmϕ) illumination intensity of 120 mW·cm^{-2} on PMMA plate surface at 25 ℃ for various periods.

In order to confirm the modification time of

PMMA plate surface, photo-VASP of St was carried out by spot (5 mmϕ) UV-irradiation under intensity of 120 mW·cm^{-2} for various periods of 15 s to 90 min. Visual fluorescence images are shown in Figure 3. Over the time of 5 min of photo-VASP, observable macroscopic changes in transparency of the substrate were confirmed even by eyesight on the surface (Figure 3A). On the other hand, the fluorescence images after photo-VASP (Figure 3B) revealed that the surface modification by photo-VASP was achieved even after 30 s.

3.2. Characterization of surfaces after photo-VASP

Three kinds of monomers: St, AA, NIPAAm were used for the photo-VASP to modify the PMMA plate surface with hydrophobic, hydrophilic, and reversibly variable polymers, respectively. The surfaces after the photo-VASP of monomers at intensity of 20 mW·cm^{-2} and 25 ℃ for 10 min were analyzed by FTIR-ATR spectroscopy as shown in Figure 4. The treated surfaces showed corresponding characteristic absorption peaks and shoulders of polystyrene at 1601/1493 ($\nu_{aromatic\ CC}$), 1451 cm^{-1} (ν_{CH2}), and 756/697 cm^{-1} ($\nu_{aromatic\ C-H}$); poly(acrylic acid) at 1703 cm^{-1} ($\nu_{C=O}$) and 2500-3300 cm^{-1} (ν_{O-H}); and polyNIPAAm at 1646/1546 cm^{-1} (amide I/II) and 3200-3600 cm^{-1} (ν_{N-H}), respectively, on a base spectrum of PMMA substrate. These characteristic absorptions indicate that corresponding polymeric materials were formed on the PMMA plate surfaces by photo-VASP of the monomers.
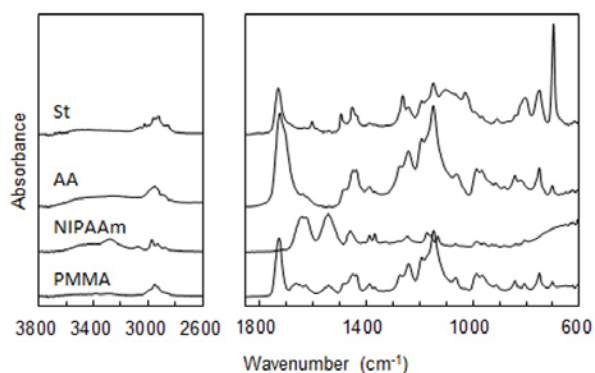

Fig. 4. FTIR-ATR spectra of PMMA substrate surfaces after photo-VASP of St, AA, and NIPAAm under 20 mW·cm^{-2} at 25 ℃ for 120 min.

Molecular weight of the accumulated product on PMMA substrate surface after the photo-VASP of St under 20 mW·cm^{-2} at 25 ℃ for 4 h was measured with SEC. As shown in Figure 5, St-oligomer production (M_n 370, PDI 1.14) was

confirmed as a main product and some higher molecular weight polymers in a range of 10^3-$10^{5.5}$ were also detected as minor components. This means that the product has totally a large PDI value. In a previous report [16], similar photo-VASP of St was carried out on a PMMA substrate pre-coated by a photo-iniferter: 2-cyanoprop-2-yl N,N'-dimethyldithiocarbamate at 40 ℃ for 12 h, resulting in polystyrene production having M_n 5230 and PDI 6.67. In this study, the obtained St-oligomer is considered to be due to the different conditions: photo-initiator, temperature, and polymerization time in comparison with the previous result.
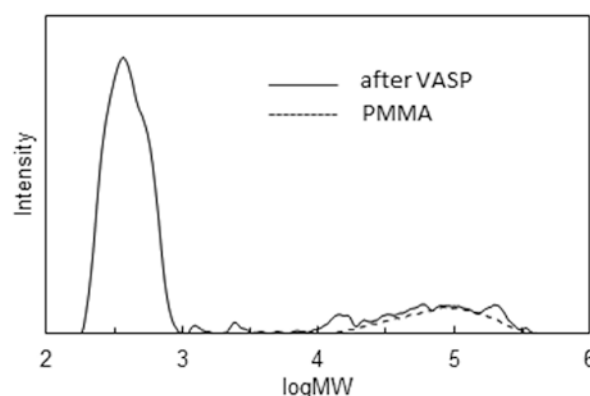

Fig. 5. SEC profile of extracted material from PMMA substrate surface after photo-VASP of St. Polymerization conditions: initiator: 2,2-dimethoxy-2-phenylacetophenone under irradiation intensity of 20 mW·cm^{-2} at 25 ℃ for 4 h.

3.3. Reversible changes in hydrophilicity of surface modified by photo-VASP of acrylic acid

A PMMA substrate surface was modified by photo-VASP of AA under 20 mW·cm^{-2} at 25 ℃ for 240 min. The modified substrate surface was measured changes in the static contact angle value associated with external stimuli, i.e., NaOH and HCl treatments: immersion in each 1M solution at 25 ℃ for 1 min, resulting in reversible changes in hydrophilic/hydrophobic properties according to repeating each external stimulus as shown in Figure 6. The reversible static contact angle values between 50-55 ° and 85-90 ° reflect the reversible changes in chemical structure of side group: –COOH and –COO$^-$ Na$^+$ of poly(acrylic acid) (polyAA), respectively. The result clearly indicates that the polyAA accumulated on the PMMA plate surface and the polyAA was not washed away during the NaOH and HCl treatments, suggesting the grafting on/from the substrate surface.
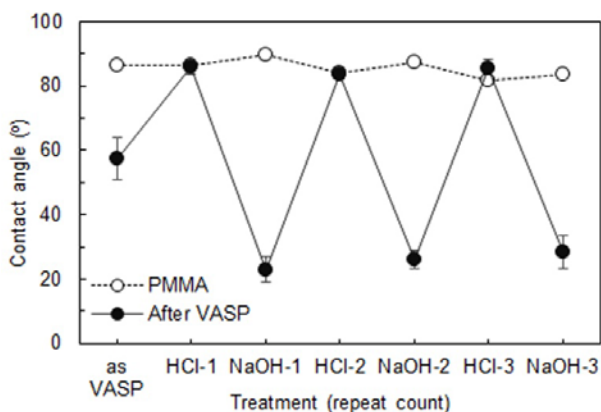
Fig. 6. Reversible changes in static contact angle value against water droplets of PMMA substrate surface modified by photo-VASP of AA with repeating external chemical stimuli. VASP: under 20 mW·cm^{-2} irradiation intensity at 25 °C for 4 h, external chemical stimuli: immersion in NaOH (1M) and HCl (1M) solutions at 25 °C for 1 min. Bar: standard deviation.

3.4. Image transcription by photo-VASP of styrene

A line pattern image, which was designed beforehand, was transcribed on a PMMA plate surface by photo-VASP of St through a photo-mask. The photo-mask had a multi-lines pattern of various aperture widths in a range of 10-100 μm.
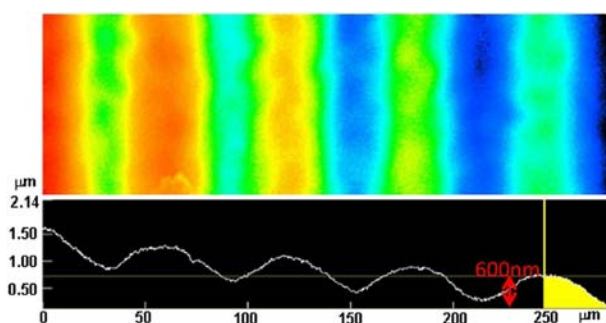

Fig. 7. 3D laser digital microscopic altitude image in color (a) and height profile (b) transcribed from a photo-mask having multi-lines pattern on PMMA plate surface by photo-VASP of St. VASP: under irradiation intensity of 20 mW·cm^{-2} at 25 °C for 2 h.

In Figure 7, a 3D laser digital microscopic image, which was transcribed from the multi-lines pattern on the PMMA substrate surface after the photo-VASP of St under UV-irradiation intensity of 20 mW·cm^{-2} at 25 °C for 2 h, is shown as an altitude image in color and a height profile in bottom. From the image and height profile, the multi-lines pattern of photo-mask was transcribed by the polystyrene accumulation on the plate surface as it is. The height profile indicates that the polystyrene accumulation was found to be at least 600 nm in height after the photo-VASP. The accumulation height increased with widening in

aperture width of the lines pattern, showing gentle curved peaks, which were owing to the diffusion of UV-light irradiated. Considering the accumulation height, the results indicate that the polymerization continued as to be piling up on formerly accumulated surface [19].

3.5. Auto-drawing by photo-VASP of styrene on X-Y stage

Auto-drawing of a designed character was carried out under the spot illumination (5 mmϕ) from a thick optical fiber under irradiation intensity of 140 mW·cm^{-2} at 25 °C on the PMMA substrate surface, which was set on an X-Y stage manipulated by a computer program. Based on the fast modification rate by the photo-VASP of St as shown in Figure 3, the manipulation rate of X-Y stage was set at 50 μm·s^{-1}. In Figure 8, the designed character was automatically drawn and clearly appeared on the PMMA surface as a fluorescence image under UV irradiation.
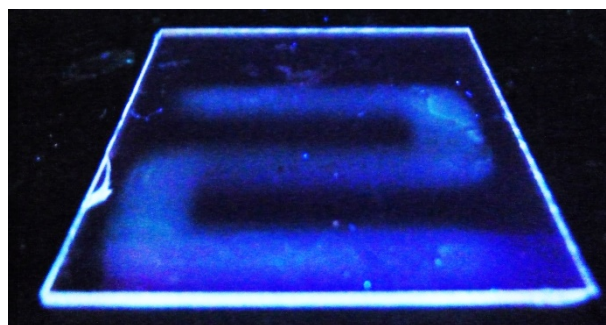

Fig. 8. Auto-drawing of a character by photo-VASP of St at PMMA substrate surface and spot illumination (5 mmϕ) under irradiation intensity of 140 mW·cm^{-2} at 25 °C on an X-Y stage. Manipulating rate of X-Y stage: 50 μm·s^{-1}.

3.6. Successive auto-drawing by photo-VASP of different monomers

Successive auto-drawing by photo-VASP was carried out using three kinds of monomers: NIPAAm, St, and AA under spot illumination (0.5 mmϕ) from a fine optical fiber under UV-irradiation intensity of 17 mW·cm^{-2} at 25 °C on PMMA substrate surface set on the X-Y stage manipulated according to a computer program. When the monomer vapor was exchanged, the former vapor in a reactor was removed by a suction method, and the reactor was fulfilled by introduction of next monomer vapor. The auto-drawing was achieved by manipulating the X-Y stage according to a prescribed program to re-produce a pre-designed functional image on the substrate surface.

Microscopic FTIR mapping image at 1730cm^{-1} ($\nu_{C=O}$) of the substrate surface after the auto-drawing by the successive photo-VASP was shown in Figure 9. Large round-shaped accumulation at an upper side was formed by photo-VASP of NIPAAm. Curved line part, which was connected to the round-shaped NIPAAm accumulation, showed weak absorption intensity due to photo-iniferter bound to PolySt accumulation, and following linear part having high absorption intensity at a bottom side was due to accumulation of polyAA. When the mapping was achieved at 1740cm^{-1}, the PMMA substrate showed high absorption intensity as a background.
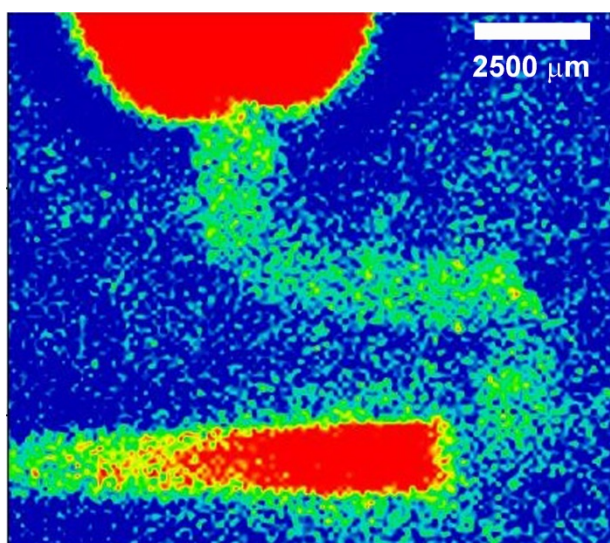

Fig. 9. Microscopic FTIR mapping image at 1730cm^{-1} of PMMA substrate surface drawn by photo-VASP under a spot (0.5 mmϕ) illumination of 17 mW·cm^{-2} UV-irradiation intensity at 25 °C of 3 kinds of monomers: NIPAAm, St, and AA, successively.

4. Conclusion

The potentiality of two- and three-dimensional micro architectures formation by combining the photo-VASP of monomer vapors with the auto-drawing method using the programed manipulation system was verified. The surface modification by photo-VASP was rapidly achieved even after 30 s. The fine lines pattern of photo-mask was transcribed by the photo-VASP of St as the corresponding polymer structure on the solid substrate surface. PMMA substrate surface modified by photo-VASP of AA showed the reversible changes in hydrophilic/hydrophobic properties according to repeating external chemical stimuli.

The successive auto-drawing by photo-VASP was achieved using contrastive three kinds of monomers: NIPAAm, St, and AA, on the X-Y stage manipulated by a computer program, resulting in the production of a pre-designed functional structure by successful accumulations of corresponding polymers on the substrate surface. The successive photo-VASP technique with the auto-drawing system will be applied to preparation of many micro-devices such as micro-reactors with various chemical functions.

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