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Monitoring Chemical Transformations at Buried Organic Interfaces by Electric Force Microscopy

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Reactions at buried interfaces play critical roles in areas ranging from corrosion control[1] to cellular signaling.[2] Toward this end, we recently reported that electric force microscopy (EFM),[3] has the remarkable ability to detect terminal group differences in alternating, micrometer-sized domains of alkanethiol-derived monolayers (i.e., $HO(CH_2)_{16}SH$ and $CH_3(CH_2)_{16}SH$) that were buried under a 430 nm coating of polystyrene (PS).[4] The preliminary results described herein show that EFM can map chemical transformations at buried organic interfaces. This capability is demonstrated by imaging the transformation of the interface formed between an azide-terminated monolayer and a PS overlayer as the azide group is photolytically coupled to the PS overlayer.

Figure 1 details the structure of the composite sample and the transformation induced by UV photolysis through a photomask. The composite consisted of a gold substrate, an azide-terminated monolayer, and a PS coating and was constructed in two steps. Step 1 formed the gold-bound thiolate monolayer by immersion of a substrate into a 100 μM ethanolic solution of bis-[β-(4-azidosalycylamido)ethyl] disulfide (BASED; Pierce Chemical) for ~12 h in the dark.[5] Each substrate was then rinsed with ethanol and dried with a stream of nitrogen. Step 2 cast a PS overlayer (400 ± 50 nm via profilometry) onto the modified substrate by spin coating a 5 wt % toluene solution. The transformation of the monolayer was induced by the UV conversion of the azide groups to nitrenes, which then coupled to the aromatic groups of PS via an insertion process to form a secondary amine.[6]

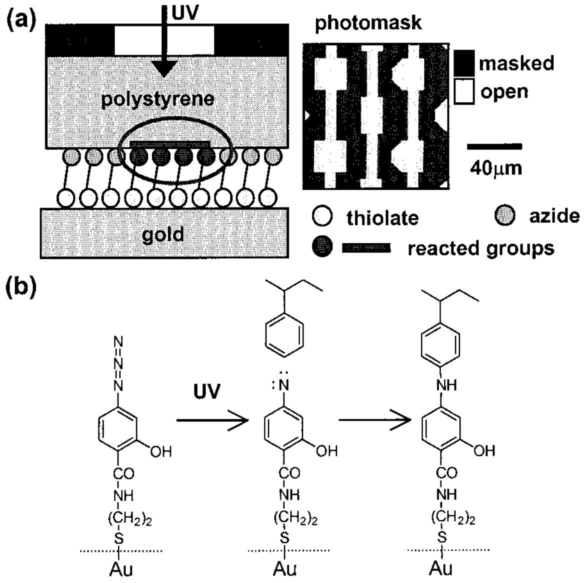

Figure 1. (**a**) Idealized schematic of the polystyrene/BASED/gold composite after the patterned transformation by UV irradiation through a photomask. (**b**) Photochemical conversion of the azide terminus of BASED to a nitrene, which then binds to the aromatic groups of PS.

As a starting point, experiments using infrared reflection spectroscopy (IRS)[7] were conducted to determine the progression of the composite transformation under our photolysis conditions.[8] These experiments used five identically prepared composites, which were irradiated for 0, 2, 5, 15, or 30 min. After photolysis, each sample was rinsed extensively with toluene to remove unreacted PS. Figure 2 presents the results, and includes the spectrum for a thin PS film coated directly on a gold substrate. With the use of the $N{=}N{=}N$ stretching modes (out-of-phase at ~2120 cm^{-1} or in-phase at 1280 cm^{-1}) as a diagnostic of the azide group and the C−H bending mode for the aromatic ring (700 cm^{-1}) as an indicator for PS, three important conclusions can be drawn from these data. First, there is no evidence of PS in the spectrum of the nonphotolyzed composite. This finding indicates that there is no detectable residue of PS after rinsing. Second, the magnitude of the $N{=}N{=}N$ stretch decreases as photolysis time increases to an undetectable level in ~30 min. This dependence is in accordance with the exhaustive loss of the azide moiety upon continued irradiation. Third, the strength of the aromatic C−H bend increases with photolysis time. This increase confirms that the amount of PS coupled to the gold substrate via the thiolate monolayer increases in a manner consistent with the process shown in Figure 1b.

Having established the general details for the transformation of the composite under our photolysis conditions, we carried out a series of experiments in which five identically prepared composites were irradiated through a photomask for 0, 2, 5, 10, and 20 min and imaged by EFM at a bias voltage of +5 V.[9] The phase shift ($\Delta\phi$) of the oscillating cantilever was used as a diagnostic for the changes in the attractive force between the tip

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(1) Maege, I.; Jaehne, E.; Henke, A.; Adler, H.-J. P.; Bram, C.; Jung, C.; Stratmann, M. *Prog. Org. Coat.* **1998**, *34*, 1−12.

(2) Haydon, P. G. *Nat. Rev. Neurosci.* **2001**, *2*, 185−193.

(3) (a) Martin, Y.; Abraham, D. W.; Wickramasinghe, H. K. *Appl. Phys. Lett.* **1988**, *52*, 1103−1105. (b) Stern, J. E.; Terris, B. D.; Mamin, H. J.; Ruger, D. *Appl. Phy. Lett.* **1988**, *53*, 2717−2719. (c) Nonnenmacher, M.; O'Boyle, M. P.; Wickramasinghe, H. K. *Appl. Phys. Lett.* **1991**, *58*, 2921−2923. (d) Weaver, J. M. R.; Abraham, D. W. *J. Vac. Sci. Technol.* **1991**, *B9*, 1559−1561. (e) Sarid, D. *Scanning Force Microscopy: With Applications to Electric, Magnetic and Atomic Forces*; Oxford Univ Press: London, 1994. (f) For a recent review of EFM applications, see: Takano, H.; Kenseth, J. R.; Wong, S.-S.; O'Brien, J. C.; Porter, M. D. *Chem. Rev.* **1999**, *99*, 2845−2890 and references therein.

(4) Takano, H.; Wong, S.-S.; Harnisch, J. A.; Porter, M. D. *Langmuir* **2000**, *16*, 5231−5233.

(5) For reactions of disulfides with gold, see Ishida, T.; Yamamoto, S. I.; Mizutani, W.; Motomatsu, M.; Tokumoto, H.; Hokari, H.; Azehara, H.; Fujihira, M. *Langmuir* **1997**, *13*, 3261−3265 and references therein.

(6) (a) Reactions of azides with polystyrene were reported by Wybourne, M. N.; Wu, J. C.; Yan, M.; Cai, S. X.; Keana, J. F. W. *J. Vac. Sci. Technol., B* **1993**, *11*, 2210−2213. (b) Reactions of azides with aromatic compounds in solution are detailed by Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054−5067. (c) For a review, see: *Azides and Nitrenes: Reactivity and Utility;* Scriven, E. F. V., Ed.; Academic Press: Orlando, 1984.

(7) These spectra were acquired with a Nicolet MAGNA 750 FT-IRS using *p*-polarized light incident at 82° with respect to the surface normal. The *y*-axis is given as reflectance absorbance ($-\log(R/R_o)$), where R is the reflectance of the sample and R_o is the reflectance of a gold film coated with $CD_3(CD_2)_{17}SH$). See Zhong, C.-J., Brush, R. C., Anderegg, J., and Porter, M. D. *Langmuir* **1999**, *15*, 518−525 for more details.

(8) Photolysis experiments used light from a 200-W medium-pressure mercury lamp that was reflected off a dichroic mirror (reflectivity range: 260−400 nm) and focused on samples housed in a sealed plastic casing. The power incident on the sample was estimated at ~25 mW/cm^2. The photomask (Figure 1a) was used only in the EFM experiments.

(9) All EFM experiments were conducted with Nanoscope IIIa controller and MultiMode SPM, (Digital Instruments) which was equipped with a 130-μm tube scanner and Extender module box. Silicon cantilevers (Nanosensors, 224-μm length and 36-μm width), coated with chromium (3 nm) and then with gold (22 nm), were used as tips. An oscillation frequency near the resonant frequency of 58 kHz was used for both topography and electric force measurements. The EFM images were obtained at a lift-height of 50 nm. Further details are given in ref 4.

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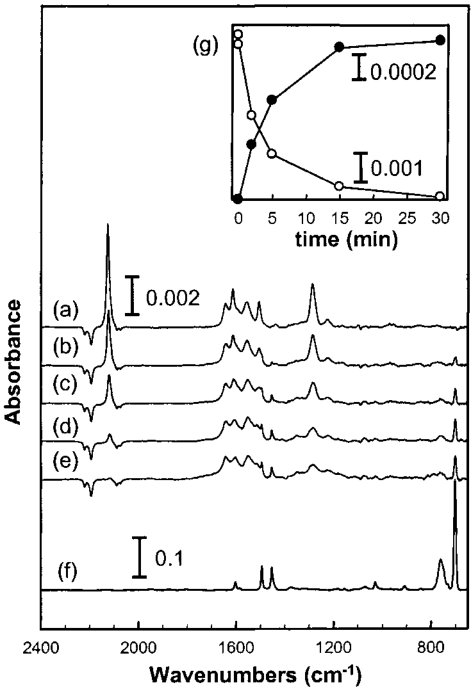

Figure 2. (a−e) IRS spectra of polystyrene/BASED/gold composites as a function of UV irradiation time after washing extensively with toluene.[7] Exposure times are **(**a**)** 0 min (no UV exposure), **(**b**)** 2 min, **(**c**)** 5 min, **(**d**)** 15 min, and **(**e**)** 30 min. **(**f**)** IRS spectrum of polystyrene on gold. **(**g**)** Plot of reflectance absorbance for the N═N═N stretch of the BASED monolayer (~2120 cm^{-1}) (○), and aromatic C−H bend of polystyrene (~700 cm^{-1}) (●) as a function of UV exposure time.

and grounded substrate. Note that a darker image contrast is indicative of a stronger attractive force. The images, which are shown in Figure 3, a−e, undergo a marked change with increasing irradiation time. The image of the as-prepared composite is devoid of any recognizable pattern. After irradiation, however, a pattern consistent with that expected for the photomask appears in all of the images. Moreover, the change in the phase shift (i.e., $\Delta(\Delta\phi)$) between the irradiated and masked regions of the samples increases with irradiation time, as plotted in Figure 3f. The evolution of these images is consistent with the photolytically induced conversion that is depicted in Figure 1b and confirmed by the data in Figure 2. These results therefore demonstrate the ability of EFM to function as a technique for mapping chemical transformations at buried interfaces.[10]

We next briefly discuss the molecular origins of the contrast mechanism. The images in Figure 3 show that the attractive force between the tip and sample at the masked domains are always greater than that at the irradiated domains. This difference reflects how the dipole moment of the chemical groups at the monolayer−polymer interface couples with the applied bias voltage.[11] The aromatic azide moiety has a large dipole moment and is oriented with its negative end closer to the tip than its positive end.[12] The dipole moment for the secondary amine linkage, however, is intuitively much lower and is likely to be oriented more along the surface parallel. Thus, the dipole moment of the azide moiety couples more effectively with the +5 V bias voltage and enhances the attractive force between the tip and substrate. We note that images of a photolyzed composite at a bias voltage of −5 V exhibit a reversal in image contrast (i.e., the attractive force at the irradiated domains is greater that that at the masked domains), which supports our qualitative mechanistic interpretation.

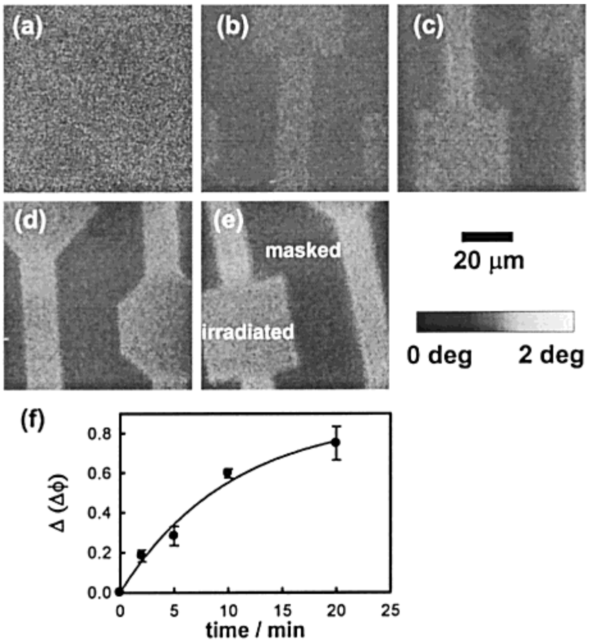

Figure 3. **(**a−e**)** EFM images (50 μm × 50 μm) of a polystyrene/BASED/gold composite as a function of UV irradiation time through a photomask. Exposure times are **(**a**)** 0 min (no UV exposure), **(**b**)** 2 min, **(**c**)** 5 min, **(**d**)** 10 min, and **(**e**)** 20 min. EFM images were collected at a lift height of 50 nm and bias voltage (grounded sample) of +5 V. The thickness of the PS film was 400 ± 50 nm. **(**f**)** Plot of the changes in the phase shift (i.e., $\Delta(\Delta\phi)$) between the irradiated and masked regions of the samples as a function of exposure time.

In summary, we have shown that EFM can be applied as a tool for mapping the chemical transformation of functional groups buried under comparatively thick organic polymer films. Ongoing work is beginning to address factors that contribute to the contrast mechanism as well as those of importance to the vertical and lateral resolution.

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(10) Control experiments have shown that PS also undergoes a light-induced transformation under our experimental conditions. We ascribe this observation to the photogeneration of radicals in PS (Kuzina, S.; Mikhailov, A. I. *Eur. Polym. J.* **1998**, 34, 291−299). Contrast changes when imaging a PS coating that was photolyzed for 20 min were ~40% of that for the composite after an equivalent exposure period. Contrast changes found when imaging a composite that had been photopatterned prior to coating with PS were, in fact, ~60% of that for the composite in Figure 3e.

(11) The contribution of terminal group dipole moments in monolayers to surface potentials is discussed in refs 3f and 4; see also: Thomas, R. C.; Tangyunyong, P.; Houston, J. E.; Michalske, T. A.; Crooks, R. M. *J. Phys. Chem.* **1994**, *98*, 4493−4494.

(12) Minkin, V. I.; Osipov, O. A.; Zhdanov, Y. A. *Dipole Moments in Organic Chemistry*; Plenum Press: 1970.