LETTERS

Lithography by Simultaneous Chemical and Photochemical Polymerization of Aniline at the Air−Water Interface

Devasish Chowdhury, Anumita Paul, and Arun Chattopadhyay*

Department of Chemistry, Indian Institute of Technology, Guwahati, North Guwahati 781 039 India

Received: September 20, 2001; In Final Form: February 11, 2002

We report here a new technique of lithography in thin polyaniline film formed at the air−water interface, by simultaneous chemical and photochemical polymerization of aniline. A solution of aniline in acidic $KBrO_3$/KBr polymerized to form thin film at the air−water interface. When the polymerization was carried out in the presence of light at the interface, a macroscopic pattern could be seen formed on the film in the shape and size of the incident light beam. A desirable shape of the pattern could be achieved by using appropriate optical mask. The lithographic pattern could be imprinted using incident light of wavelength in the range of 320−650 nm. Observation under optical microscope revealed that nucleation pattern of polymer growth was absent in the area of the polymer film grown in the presence of light that otherwise was present in the film formed in dark. FTIR spectra of polymer films grown in light and dark were the same.

Introduction

Photochemical pattern generation is ubiquitous in modern technology including lithography, microelectronics, and micro-fluidics.[1−4] Even though soft lithographic[5] techniques have made considerably progress to increase the resolution of patterns, use of light is still very important. For example, the master for soft lithography is generally made with the help of photolithographic techniques. In general, photochemical pattern formation at a solid surface is achieved by either polymerization of the surface attached molecules or chemical reaction between the molecule and the surface material. Optical masks are used for appropriate pattern formation. Self-assembled monolayer of thiols on gold is one of the extensively used materials for photopatterning.[6,7] Also, micropatterned polymer lipid bilayers on solid support, with potentially important biomedical applications,[8] have been created. On the other hand, oriented growth of polymer at the air−water interface, in the presence of light or by reaction coupled to bulk reactants, has assumed significance owing to

improved material properties over their conventionally grown counterparts.[9] In addition, Langmuir−Blodgett film transfer technique has been utilized to generate extended patterned surfaces with controlled wetting properties.[10] Greater control in the synthesis of patterned polymers at an interface can be achieved if patterns could be "imprinted" from the top on to a growing polymer film at the interface. One of the ways of achieving this is to carry out polymerization at an interface, simultaneously in the presence of light from above and chemical reactions from below. A polymer generated by light catalysis might have or might not have the same properties as that generated by chemical catalysis. This control can be achieved by selecting appropriate monomer, wavelength of incident light or chemical reagents that catalyze polymerization. The polymer film thus generated could possibly have variations in optical, electronic and chemical properties and even mechanical properties characterized by thickness variations or otherwise across the film. This has the unique advantage over other methods as one could have a better control over size, shape, and nature of patterns formed onto the films by controlling parameters, from

* To whom correspondence should be addressed. E-mail: arun@iitg.ernet.in. Fax: +91-361-690762.

above the surface for light catalyzed polymerization, and from the bulk below for chemical polymerization. Potential applications include designed polymer surfaces with controlled wettability or porosity, incorporation of catalysts inside a polymer surface, arrays of sensors in polymer films, lithographic pattern formation, generation of patterned polymers for electronic display systems, and oriented film generation using appropriately polarized light. As we know, the above method of patterned polymer film formation at an interface has not been reported in the literature.

Here we introduce a new method of generation of patterned polymer thin films, at air−water interface, which attempts to address a major part of the above idea. Our choice of synthesis of polyaniline films, at the air−water interface, was guided by application potential owing to its electrical conductivity. That the synthesis of polyaniline can be catalyzed by oxidizing chemical reagents is well established.[11−15] We have recently found that polymerization of aniline in aqueous acidic $KBrO_3$/KBr solution occurred with thin film formation at the air−water interface, in addition to bulk polymerization. The films consisted of mesoscopic nucleation patterns that were characteristic of the catalysts used. For example, when the reaction was carried out in the presence of acidic $KBrO_3$/KBr, the nucleation patterns were polygonal, whereas circular patterns formed when $FeSO_4$ was used as catalysts in addition to the above reagents. We have reported these results separately.[16] Here we report air−water interface polymerization of aniline coupled to reaction with acidic $KBrO_3$/KBr in the bulk and in the presence of UV or visible light impinging from above on a selected part of the interface. The polymer film formed at the interface in the presence of light consisted of a macroscopic imprint of the shape and size of the light beam plus the usual film formed in the remaining part of the interface as generally observed in absence of light. In other words, a polymer film was formed with an imprint in a part of the film in the shape and size of the light beam. Observation under optical microscope revealed that the characteristic nucleation pattern of growth was absent in that part of the film where light was impinged. The imprinted patterns could be observed over a wide range of UV and visible incident light wavelength. Our observations suggest that the absence of patterns may be due to simultaneous polymerization of aniline at the interface in the presence of Br^- radicals generated by photodissociation of Br_2 in addition to polymerization catalyzed by $BrO_2^\bullet$ that is generated by chemical reaction in the bulk.

Experimental Section

We have used the output of the excitation beam of a fluorescence spectrophotometer as the light source. The beam was impinged on top of the reaction mixture after reflection from a plane mirror. To induce pattern formation at various incident wavelengths, the excitation monochromator was tuned to the desired wavelength. A schematic view of the experimental set up is shown in Figure 1.

Stock solutions of reagents in Milli-Q water were prepared from which appropriate amounts were withdrawn and mixed in a test tube. The final concentrations of various reagents were as follows: 0.12 M $KBrO_3$; 1×10^{-4} M KBr; 0.3 M H_2SO_4 and 0.15 M of aniline. The mixture was then poured into a watch glass that was kept inside the sample compartment of a Shimadzu RF-5301PC spectrofluorophotometer. The exit beam of the excitation source, with 20 nm slit width, was reflected by a plane mirror onto the surface of the solution. The film was allowed to grow for about 1 h. Afterward, the film was
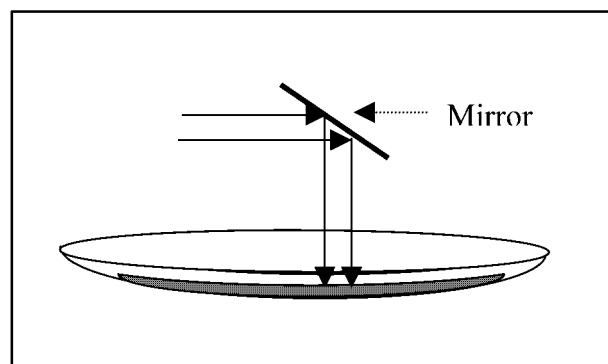

Figure 1. A schematic view of the experimental setup. The output beam from the excitation monochromator was reflected from a plane mirror and impinged onto the reaction mixture kept in a watch glass.

made to float above the watch glass by pouring water carefully into a Petridish where the watch glass was placed. After a few cycles of water draining and refilling, the film was carefully transferred to a microscope slide. The film thickness was measured with the help of an optical microscope by focusing at the top surface of the film and the top surface of the slide. The difference in height was taken to represent the approximate film thickness. The macroscopic patterns were recorded by using a HP5200C or HP5370 optical scanner. The optical micrographs were recorded by a Carl Zeiss (Axiotech) microscope. The colors in the micrographs are not due to any color of the film material but are due to interference of light in the thin polymer layers. Room temperature was between 20 and 25 °C. Typical film thickness varied between 30 and 200 μm.

UV−vis spectra of films in slides and polymer forming solution were recorded by a Hitachi U-2001 UV−vis spectrophotometer. To record FTIR spectra of polymers, photo illuminated and nonilluminated parts of films were scraped off from the slide and transferred separately for making KBr pellets with them. A Nicolet IMPACT 410 FTIR spectrophotometer was used for recording IR spectra.

Results and Discussions

Photographs of three such films, generated at the air−water interface in the presence of 320 nm light followed by transferring to microscope slides, are shown in Figure 2A−C. The horizontal dimension of each slide is about 25 mm. The illuminated parts appeared as "I I T" (we refer to the rectangular impressions as "I" and the T-letter-shaped ones as "T") and are clearly visible with other parts, where the polymer had grown in absence of light, as the background film. The ratio of optical density between the illuminated part and the nonilluminated part was about 2 measured at the absorption maxima of 320 nm. Investigation under optical microscope revealed that characteristic polygonal nucleation sites of growth of polymer film were present in the film that formed in absence of light. These are shown in Figure 2D,E. These patterns could easily be identified from the occasional presence of spots of dried up films that appear to have been formed at some parts of the films. That the spots are above the nucleation growth layers resulted in the observation of the patterns in Figure 2D being slightly defocused. On the other hand these characteristic nucleation patterns of growth of film were absent in the illuminated part of the film. This is shown in Figure 2F.

It may be noted here that the imprint of light beam on the film had the same size as the original beam. This suggests that the initial film structure formed did not get altered due to diffusion of films after formation. The initial film template
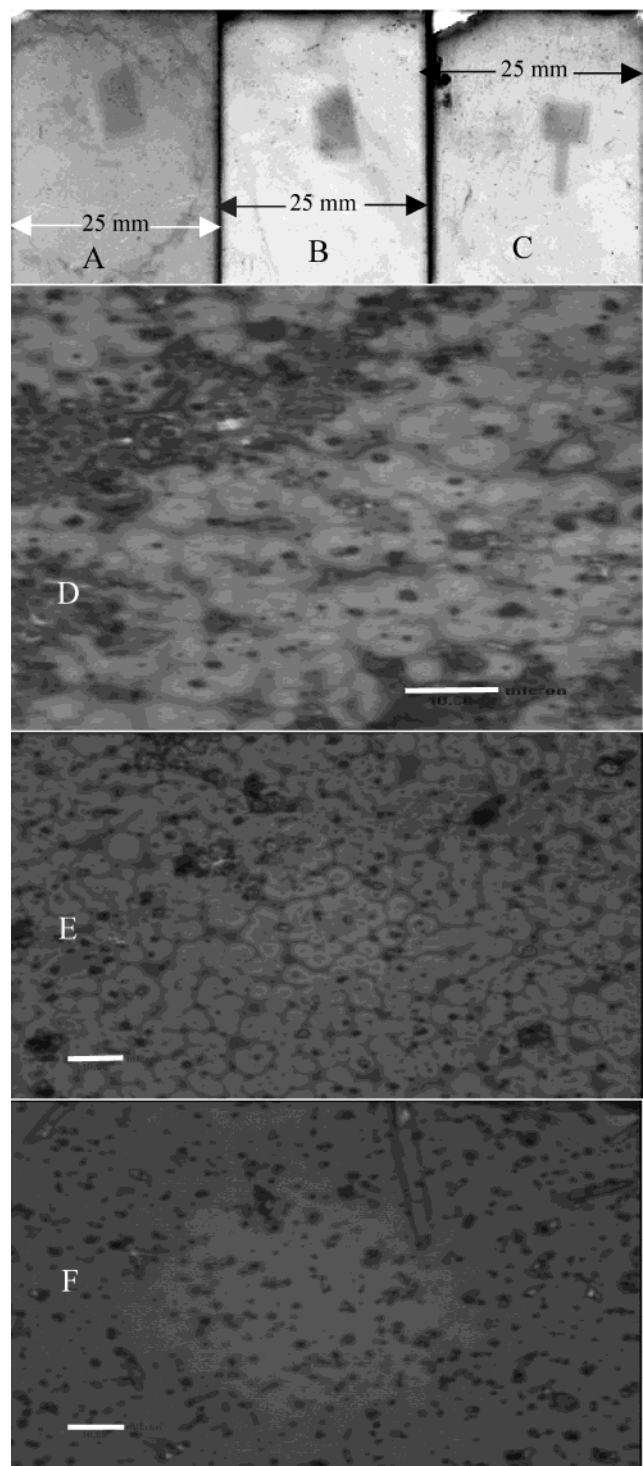
Letters

J. Phys. Chem. B, Vol. 106, No. 17, 2002 **4345**

Figure 2. Photographs and optical micrographs of polymer films taken after transferring to microscope slides. The top three images (I I T) on three separate 25 mm slides (A, B, C) were recorded by HP5200C Scanner. Here the rectangular impressions, referred to as "I" and the T-letter-shaped impression referred to as "T", are 320 nm light illuminated parts of films with nonilluminated parts of the films as backgrounds. The bottom three micrographs were recorded by Carl Zeiss (Axiotech) microscope. D and E are micrographs of nonillumi-nated parts of A and C with characteristic polygonal nucleation pattern. F is the 320 nm light illuminated part of the first "I" part (A) of the top films. Bar is 10 μm.

formed at the interface remained the same all through the reaction that lead to thicker film formation as the mesoscopic patterns would not have been observed otherwise. We also note a negative result here. When a film was grown in absence of
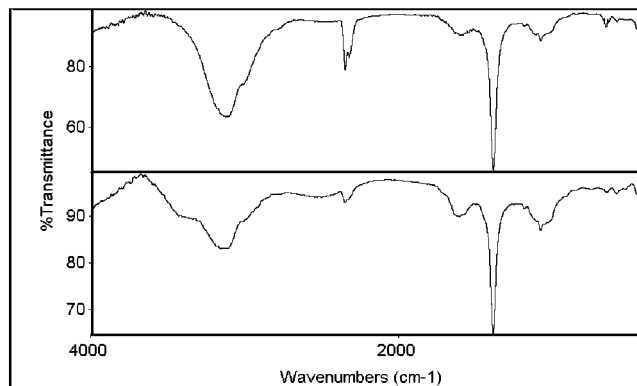

Figure 3. FTIR spectra of 320 nm illuminated (top) and nonilluminated (bottom) parts of a film recorded in KBr pellet.
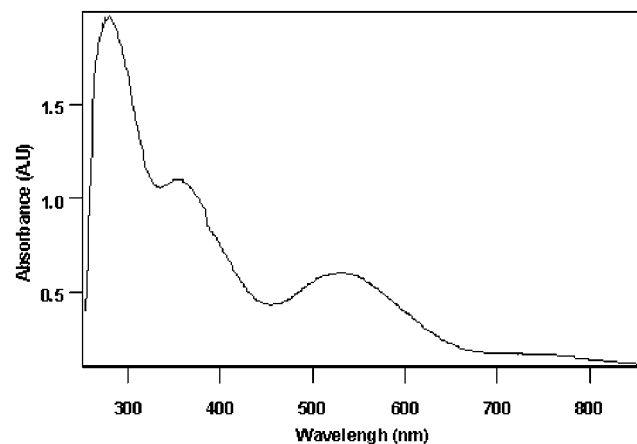

Figure 4. UV−vis absorption spectrum of a mixture (diluted from the original mixture) of $KBrO_3$, KBr, and aniline in aqueous H_2SO_4 recorded about 7 min after mixing.

light and subsequently illuminated with 320 nm light, after transferring to a microscope slide for about $^3/_2$ h no imprint was observed. This result indicates that the imprint on the film resulted due to polymerization reaction in the presence of light and not due to degradation of a film upon UV radiation. Also, when aniline dissolved in H_2SO_4 and dried up on a slide followed by placing the slide under UV irradiation for about $^3/_2$ h, no observable film formation took place.

FTIR spectra of illuminated and nonilluminated parts of a film grown in the presence of 320 nm light indicated that the nature of the polymers in both the parts was identical. This is shown in Figure 3. It is possible that even though the mechanism of polymerization in the presence and absence of light are different the polyaniline formed in both cases are same. Characteristic UV−vis spectra of the pernigraniline form of polyaniline in both the cases were also observed.

As shown in Figure 4, a solution of aniline in acidic $KBrO_3$/ KBr absorbs strongly in the region of 200−600 nm. We have taken advantage of this absorption and obtained imprints with incident light wavelength ranging between 320 and 650 nm. We did not observe any significant imprint when the incident light wavelength was beyond 650 nm.

Figure 5 shows the images of polymer films generated at the interface in the presence of incident light at various wavelengths. The illuminated part in each film appeared as rectangular in shape surrounded by the polymer film grown in absence of light. As evident from the figure, the clarity of the rectangular mark went down with increasing wavelength with nearly vanishing mark at 650 nm. Even then, the marks could easily be identified up until an incident wavelength of 500 nm.
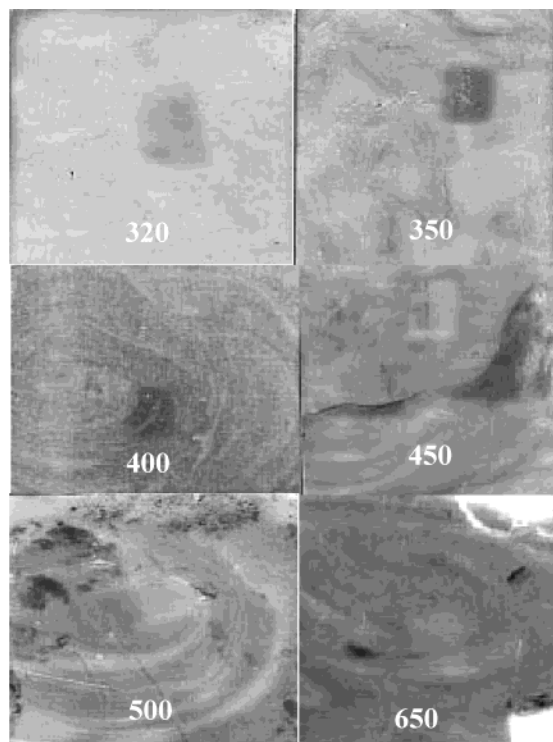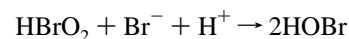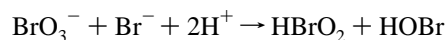
Figure 5. Figure 5. Images of polymer films generated under illumination of incident light at various wavelengths. [The impressions appeared in the form of rectangles.] Films transferred to microscope slides were scanned using a HP5370C scanners. The contrasts of the images were changed (equally for all) for more clear views. The number written on each plate corresponds to the wavelength of light (nm) used for imprints. The horizontal dimension of each plate is 25 mm, and the same scale length is applicable to vertical dimension.

We have described here a method for generating lithographic patterns, on thin polyaniline films grown at the air–water interface, in the presence of light over a wide incident wavelength range and chemical reagents in the bulk. The method takes advantage of the simultaneous chemical and photochemical reaction leading to polymerization of aniline. Our observation suggests that the polymer formed in the illuminated and nonilluminated parts of the films are chemically same. Radicals or other species generated by the chemical reaction might play a key role in the product formation in the presence of light. That may be the reason for obtaining mark even beyond the wavelength where aniline typically absorbs. When light of an appropriate wavelength is illuminated on a part of the interface where the film is grown, the mesoscopic nucleation patterns are not formed in that part where the light beam is present. On the other hand, the rest of the film grows with characteristic nucleation pattern. This results in light induced imprints with a darker appearance in the film.

Based on our observation and previous related studies we propose the following as a possible mechanism for the formation of pattern in the film. There are two competing catalytic polymerization reactions that are responsible for the polymerization of aniline in the present system. One is due to chemical reaction in the presence of light and the other is due to chemical reaction only. At lower wavelengths of incident light, the photochemical reaction dominates over chemical reaction where light is impinged and the imprint is clearer as the nucleation patterns are destroyed. On the other hand, with increasing wavelength of the incident light beam, the photochemical reaction becomes less and less important while the chemical catalyzed polymerization becomes predominant and as a result

the imprint becomes increasingly nebulous. This is evident from the continuous macroscopic patterns observed in both the illuminated and nonilluminated parts of the film, when the wavelengths of light were longer (Figure 5).

From the study of the Belousov–Zhabotinskii reaction[17] it is known that $KBrO_3$ and KBr in acidic medium produces $BrO_2^\bullet$ radical and Br_2

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$$

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2^\bullet + H_2O$$

In absence of light, $BrO_2^\bullet$ may play the key role as a radical initiator necessary for polymerization of aniline (ANI)

$$ANI + BrO_2^\bullet + H^+ \rightarrow PANI^\bullet + HBrO_2$$

$$PANI^\bullet + PANI^\bullet \rightarrow PANI$$
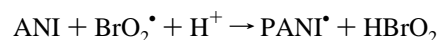
$PANI^\bullet$ is the polyaniline polymer radical.

In presence of light, Br_2 might dissociate into $Br^\bullet$ atoms[18] that probably initiate the polymerization in addition to $BrO_2^\bullet$ initiator.

$$Br_2 + h\nu \rightarrow 2Br^\bullet$$

$$Br^\bullet + ANI \rightarrow PANI^\bullet + HBr$$

$$PANI^\bullet + PANI^\bullet \rightarrow PANI$$
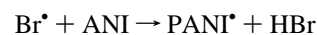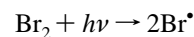
This reaction would be wavelength dependent depending on the dissociation of Br_2 upon absorption of light at various wavelengths. In the absence of light, a nucleation pattern in the polymer formation at the interface formed is characteristic of the polymerization initiator. In presence of light, $Br^\bullet$ radicals act as initiators in addition to $BrO_2^\bullet$ This probably destroys the nucleation pattern that occurs in absence of light.

The new technique of photolithography reported here in thin polymer films formed at the air–water interface may have certain advantage over other methods as the imprint is embedded in the film of the same material and a wide range of wavelengths of incident light can be used. Even though the resolution of the imprints is low in our case, in principle the resolution can be made much higher with appropriate light source and optical masks. In addition, the contrast in optical density of the films could be tuned with appropriate choice of polymer forming materials. Also, one can envision the generation of polymer doped with chemical sensors whose chemical nature could be altered by light. Thus an array of molecules with different chemical structures can be imprinted in the polymer thin film.

References and Notes

(1) Fodor, S. P.; Reid, J. L.; Pirrung, M. C.; Stryer, L.; Lu, A. T.; Solas, D. *Science* **1991**, *251*, 767.

(2) Zhao, B.; Moore, J. S.; Beebe, D. J. *Science* **2001**, *291*, 1023.

(3) Doshi, D. A.; Huesing, N. K.; Lu, M.; Fan, H.; Lu, Y.; Simmons-Potter, K.; Potter, B. G., Jr.; Hurd, A. J.; Brinker, J. *Science* **2000**, *290*, 107.

Letters

J. Phys. Chem. B, Vol. 106, No. 17, 2002 **4347**

(4) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431.

(5) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550.

(6) Huang, J.; Hemminger, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 3342.

(7) Tarlov, M. J.; Burgess, D. R. F., Jr.; Gillen, G. *J. Am. Chem. Soc.* **1993**, *115*, 5305.

(8) Morigaki, K.; Baumgart, T.; Offenhauser, A.; Knoll, W. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 172.

(9) Bruno, F. F.; Akkara, J. A.; Samuelson, L. A.; Kaplan, D. L.; Mandal, B. N.; Marx, K. A.; Kumar, J.; Tripathy, S. K. *Langmuir* **1995**, *11*, 889.

(10) Gleiche, M.; Chi, L. F.; Fuchs, H. *Nature* **2000**, *403*, 173.

(11) MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27.

(12) Sun, Y.; MacDiarmid, A. G.; Epstein, A. *J. Chem. Soc., Chem. Commun.* **1990**, 529.

(13) Wei, Y.; Sun, Y.; Tang, X. *J. Phys. Chem.* **1989**, 93, 4878.

(14) Kim, B. J.; Oh, S. G.; Han, M. G.; Im, S. S. *Langmuir* **2000**, *16*, 5841.

(15) Moon, D. K.; Osakada, K.; Maruyama, T.; Yamamoto, T. *Makromol. Chem.* **1992**, *193*, 1723.

(16) Chowdhury, D.; Paul, A.; Chattopadhyay, A. *Chem. Mater.* In press.

(17) Washington, R. P.; West, W. W.; Misra, G. P.; Pojman, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 7373.

(18) Oldman, R. J.; Sander, R. K., Wilson, K. R. *J. Chem. Phys.* **1975**, *63*, 425.