

Spectroscopic and Microscopic Analysis of Photo-cross-linked Vinylbenzylthymine Copolymers for Photoresist Applications

Sofia Trakhtenberg,[†] John C. Warner,^{*,†} Ramaswamy Nagarajan,[‡] Ferdinando F. Bruno,[§] Lynne A. Samuelson,[§] and Jayant Kumar[‡]

Center for Green Chemistry, Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01854, Departments of Chemistry and Physics, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts 01854, and U.S. Army Natick Soldier Center, Natick, Massachusetts 01760

Received July 14, 2005. Revised Manuscript Received March 28, 2006

The success of semiconductor technology over the last few decades has clearly established the importance of photoresists in manufacture of these devices. While the fundamental focus of the development in the photoresists area has often been in obtaining smaller feature size(s) at reduced cost, the toxicity and the environmental impact of these photoresists are not always factored into the design of these resists. Here we report a new family of water-soluble photopolymers that can potentially be useful as environmentally benign “negative working” photoresists. This water-soluble polystyrene copolymer, vinylbenzylthymine–vinylphenylsulfonate (VBT–VPS) can be easily coated on a variety of substrates including flexible plastics such as polyethylterephthalate (PET). The chemistry of the cross-linking and immobilization of these “bio-inspired” photoresists has been derived from a simple photochemical transformation that occurs in nature ($2\pi + 2\pi$ photodimerization of thymine). In this study we report the irradiation-dose dependence of cross-linking/immobilization of VBT–VPS films on PET substrates. Noncontact atomic force microscopy has been used to measure the thickness of films formed at various exposure times. In addition, attenuated total reflectance Fourier transform infrared spectroscopy has been used to estimate the dose-dependent progression of film thickness and qualitatively observe the change in composition of the films upon irradiation. It has been demonstrated that these techniques can provide complementary information on photoinduced immobilization of VBT–VPS films that are crucial for developing this new class of environmentally benign materials for photoresist applications.

Introduction

The selective degradation or immobilization of polymers by photo-cross-linking on various nonreactive substrates to create thin three-dimensional relief images provides the technological basis for the electronics industry. Photoresists are currently being extensively used for a wide variety of applications that include fabrication of electronic components and circuits, printed illustrations, and printing plates and for photoengraving and screen printing.¹ The substrates may include inorganic semiconductors, fabric, glass, and metal depending on the desired applications. The resolution achievable depends on the fundamental chemical composition of the photoresist and the nature of the transformation that occurs during exposure of the resist. While a variety of “negative” resists based on diazo salts and oxides, diazo-formaldehyde resins, cinnamate polyesters, and chalcone polymers have been used extensively, these resists are not inherently benign and often contain toxic starting materials,

intermediates, and products. On the other hand, the performance requirements of microelectronic components are becoming increasingly challenging as the industry struggles to keep up with society’s demand for increased speed and capacity while insisting on reduced costs and size. While improving resolution will continue to drive the majority of technological advances, there is a growing realization that significant manufacturing costs lie hidden within a corporation’s materials management infrastructure. Specifically, the use of environmentally hazardous or toxic materials is being found to have tangible impact on profits. These costs come from the added expenses of dealing with the transportation, storage, treatment, and disposal of hazardous materials. Green chemistry is a philosophical approach to research, development, and manufacturing that seeks to put pollution prevention and hazardous materials avoidances as far “upstream” as possible.² Photoresist materials which can be cast from and developed in pure water would prevent pollution by reducing the use of organic solvents typically used for casting photoresist films and of strong bases typically used for photoresist development. It would improve the environmental footprint of microelectronics manufacturing as well as decrease the cost of the final product. Although water-soluble and developable photoresists entered com-

* To whom correspondence should be addressed. E-mail: John_Warner@uml.edu.

[†] Center for Green Chemistry, Department of Plastics Engineering, University of Massachusetts Lowell.

[‡] Departments of Chemistry and Physics, Center for Advanced Materials, University of Massachusetts Lowell.

[§] U.S. Army Natick Soldier Center.

(1) Roffey C. G. *Photopolymerization of Surface Coatings*; John Wiley and Sons: New York, 1982.

(2) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: London, 1998.

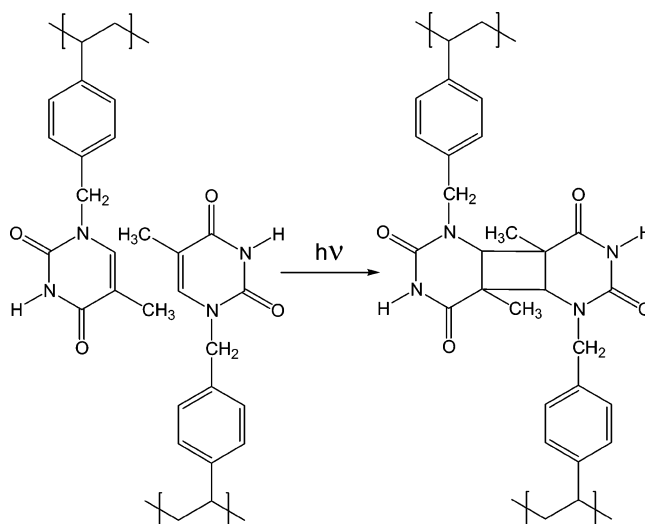
mercial use in electronics applications a few decades ago, such as in the use of fish-glue-based photoresists in the production of color picture tubes,³ they did not achieve wide popularity. Moreover, traditionally aqueous solubility was considered not an advantage but an undesirable quality in photoresists.⁴ The drawbacks of using water for both casting and developing result from the swelling behavior of the developed photoresist films, responsible for typically low resolution of aqueous photoresists. Nevertheless, aqueous-processable photoresists with resolution as high as 0.2 μm have been reported recently.⁵

An example of a water-castable and water-developable photoresist system includes a photoacid generator, cross-linker, and a polymer, all three of which are water-soluble.⁶ Upon irradiation the acid generated serves as a catalyst for the cross-linking, rendering the polymer water-insoluble. In a later work the three-component system was replaced by a two-component system, where the need for a separate photo-cross-linker was eliminated by using a polymer with cross-linkable pendant groups.^{5,7} Use of photoacid generators allows for high sensitivity, chemically amplified photoresist systems, which provide excellent resolution and have been used in manufacturing since the 1980s.⁸ Nevertheless, water-castable and water-developable one-component photoresist systems deserve investigation since they may be more environmentally benign than the chemically amplified photoresists. Photoacid generators are low molecular weight, possibly toxic compounds, which even though used in small amounts, of about 5 wt %, might eventually pollute the environment. One-component systems, where the photoactive groups are attached to a polymer backbone, provide the environmental benefit of avoiding the use of low molecular weight compounds.

We have been working with a family of water-soluble photopolymers that can potentially be useful as environmentally benign “negative working” photoresists for applications in the electronics industry. The chemistry that we have developed derives its inspiration from a simple photochemical transformation that occurs in nature.

The specific process is that of the $2\pi + 2\pi$ photodimerization of thymine base units within DNA.^{9,10} This process involves the formation of a cyclobutane ring junction between the 5 and 6 carbon positions on two adjacent thymine units in response to the short-wave ultra violet component of sunlight. In the spirit of bio-inspiration, we

Scheme 1. UV-induced VBT-Polymer Photo-cross-linking via $2\pi + 2\pi$ Photodimerization of Thymine Pendant Groups

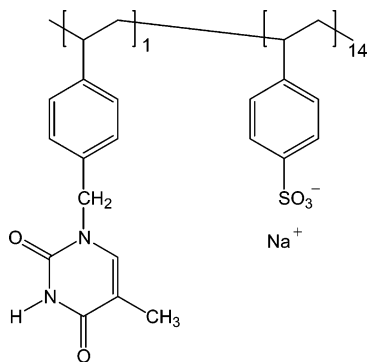


have incorporated thymine units into water-soluble polystyrene copolymers.^{11–23} The synthetic monomer 1-(4-vinylbenzyl)thymine (VBT) can be used to form copolymers that undergo the same $2\pi + 2\pi$ reaction as in DNA as presented in Scheme 1.

A homopolymer of VBT, however, due to its strong intermolecular interactions (mostly hydrogen bonding), is insoluble in water. When it is copolymerized with a minimum of 50% loading of charged monomer, water-soluble copolymers can be prepared. This approach also provides considerable versatility because either cationic or anionic monomers can be incorporated into the polymer backbone, thus providing the desired functionality. These polymers have already been demonstrated to have potential

- (3) Holahan, J. F. *Electron. World* **1965**, *74*, 30–32, 56.
- (4) Bowden, M. J. In “*Materials for Microlithography. Radiation-Sensitive Polymers*”; Thompson, L. F., Willson, C. G., Frechet J. M. J., Eds.; American Chemical Society: Washington DC, 1984; p 43.
- (5) Havard, J. M.; Vladimirov, N.; Frechet, J. M. J.; Yamada, S.; Willson, C. G.; Byers, J. D. *Macromolecules* **1999**, *32*, 86–94.
- (6) Lin, Q.; Steinhäuser, T.; Simpson, L.; Wilder, M.; Medeiros, D. R.; Willson, C. G.; Havard, J. M.; Frechet, J. M. J. *Chem. Mater.* **1997**, *9*, 1725–1730.
- (7) Havard, J. M.; Shim, S.-Y.; Frechet, J. M. J.; Lin, Q.; Medeiros, D. R.; Willson, C. G.; Byers, J. D. *Chem. Mater.* **1999**, *11*, 719–725.
- (8) Frechet, J. M. J.; Matuszczak, S.; Stover, H. D. H.; Willson, C. G.; Reck, B. In *Polymers in Microlithography. Materials and Processes*; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington DC, 1989; p 74.
- (9) Blackburn, G. M.; Davies, R. J. H. *J. Chem. Soc. C* **1966**, *23*, 2239–2244.
- (10) Lamola, A. A.; Mittal, J. P. *Science* **1966**, *154*, 1560–1561.

- (11) Cheng, C. M.; Egbe, M. I.; Grasshoff, J. M.; Guarrera, D. J.; Pai, R. P.; Taylor, L. D.; Warner, J. C. *Proceedings of IS&T's 47th Annual Conference. The Physics and Chemistry of Imaging Systems*, 1994; p 810.
- (12) Cheng, C. M.; Egbe, M. I.; Grasshoff, J. M.; Guarrera, D. J.; Pai, R. P.; Warner, J. C.; Taylor, L. D. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2515–2519.
- (13) Grasshoff, J. M.; Taylor, L. D.; Warner, J. C. Copolymeric mordants and photographic products and processes containing same. U.S. Patent 5,395,731, March 7, 1995;
- (14) Grasshoff, J. M.; Taylor, L. D.; Warner, J. C. Vinylbenzyl thymine monomers. U.S. Patent 5,455,349, Oct 3, 1995;
- (15) Grasshoff, J. M.; Taylor, L. D.; Warner, J. C. Method of imaging using a polymeric photoresist having pendant vinylbenzyl thymine groups. U.S. Patent 5,616,451, April 1, 1997.
- (16) Grasshoff, J. M.; Taylor, L. D.; Warner, J. C. Copolymers having pendant functional thymine groups. U.S. Patent 5,708,106, Jan 13, 1998.
- (17) Lloyd-Kindstrand, L.; Warner, J. C. In *Biopolymers*; Matsumura, S., Steinbüchel, A., Eds.; Wiley: Weinheim, Germany, 2003; Vol. 9, pp 165–174.
- (18) Warner, J. C.; Morelli, A.; Ku, M.-C. Methods of solubilizing and recycling biodegradable polymers containing photoreactive moieties using irradiation. U.S. Patent Appl. Publ. 2003, 4 pp US 2003224497.
- (19) Cannon, A. S.; Raudys J.; Undurtti, A.; Warner, J. C. Photoreactive Polymers and Devices for use in Hair Treatments. PCT Int. Appl. 2004, 23 pp WO 2004058187.
- (20) El-Hayek, R.; Warner, J. C. *J. Biomed. Mater. Res.: Part A*, in press.
- (21) Trakhtenberg, S.; Hangun-Balkir, Y.; Warner, J. C.; Bruno, F. F.; Kumar, J.; Nagarajan, R.; Samuelson, L. A. *J. Am. Chem. Soc.* **2005**, *127*, 9100–9104.
- (22) Whitfield, J.; Morelli, A.; Warner, J. C. *J. Macromol. Sci., Pure Appl. Chem.* **2005**, *42*, 1541–1546.
- (23) Kiarie, C.; Bianchini, J.; Trakhtenberg, S.; Warner, J. C. *J. Macromol. Sci., Pure Appl. Chem.* **2005**, *42*, 1489–1496.

Scheme 2. (VBT)₁(VPS)₁₄ Photo-cross-linkable Water-Soluble Anionic Copolymer

applications in electrically conductive coatings,²¹ antibacterial coatings,²⁰ hair-styling products,¹⁹ removable large area photolithographic coatings,^{13–16,18,22,23} and recyclable plastics.^{18,22} For the present study, vinylphenylsulfonate sodium salt (VPS) was used as the solubilizing monomer and the copolymer synthesized was (VBT)₁(VPS)₁₄. This copolymer presented in Scheme 2 was recently demonstrated to be a viable template for the enzymatic surface synthesis of electrically conducting polyaniline.²¹

Here we report the study of irradiation dose-dependent VBT–VPS film formation on PET substrates using atomic force microscopy [AFM] and attenuated total reflectance Fourier transform infrared spectroscopy [ATR FTIR]. Non-contact AFM [NC-AFM] was used to measure the dose-dependent progression of film thickness, while ATR FTIR was used to obtain complementary information on film thickness as well as the change in chemical composition of the films.

Experimental Section

Materials and Methods. Vinylphenyl sulfonate (VPS) and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich in its purest available form and used as received. Vinylbenzyl thymine (VBT) was synthesized from thymine and vinylbenzyl chloride as described previously.¹² NMR spectroscopy was performed on a Bruker 250 MHz spectrometer. Elemental analysis was performed on an Exeter Analytical 240 analyzer. The hydrophilic treated side of PET-X4C1 film base (Dupont) was used without preparation. Wire-wound milled coating rods were obtained from R. D. Specialties Inc., Webster, NY. UV irradiations at $\lambda \sim 254$ nm were performed with a FisherBiotech Electrophoresis UV Hand Lamp, FBUVLS-80 (Spectronics). The intensity of UV light at a distance of 15 cm is 0.5 mW/cm². UV-opaque mask (US Airforce 1951 resolution test target) was obtained from Applied Image, Inc. FTIR measurements were performed on a Nicolet Avatar FTIR spectrometer. For measurements in attenuated total reflection (ATR) mode a single-bounce Ge crystal was used and the incidence angle was 45°. Atomic force microscopy imaging was performed on the Autoprobe CP Atomic Force Microscope (Veeco) in noncontact mode with a silicon ultralever cantilever (spring constant 3.2 N/m). The typical image size was 60 $\mu\text{m} \times 60 \mu\text{m}$, imaged at 1 line/s across the PET–VBT photoresist interface.

Synthesis of VBT–VPS Copolymer. VBT (1.0 g, 4.13 mmol) and VPS (13.6 g, 66.9 mmol) were added to 165 mL of a 20% (v/v) aqueous solution of 2-propanol. The solution was heated while stirring to 65 °C, and then AIBN (0.3 g, 1.8 mmol) was added.

Stirring was continued for 15 h while the temperature was maintained at 65 °C. The reaction mixture was cooled to room temperature and concentrated to 50 mL *in vacuo*. The polymer was precipitated by adding the aqueous solution to 400 mL of acetone while stirring. The supernatant was decanted and the solid residue was redissolved in 30 mL of water. Precipitation into 400 mL of acetone, followed by filtration, provided 11.7 g (80% yield) of polymer. ¹H NMR spectroscopy confirmed the absence of unreacted monomer. Elemental analysis revealed a C/N mass ratio of 54.6 and S/N mass ratio of 16, which are consistent with a VBT:VPS ratio of 1:14. [C, 40.39%; N, 0.74%; S, 11.89%]. SEC/MALLS analysis compared against polystyrene sulfonate standards was consistent with an average molecular weight of 260 kDa.

Preparation of VBT–VPS Films. A 6.8 μm thick layer of 10% aqueous solution of VBT–VPS was coated onto either PET film or silicon wafer using a #03 wire-wound coating rod. The film was dried under ambient conditions for 1 h and then at 80 °C for 1 h. After drying, the thickness of VBT–VPS film is expected to be about 680 nm. The FTIR spectra of the resulting film were obtained. Then the VBT–VPS film coated on PET substrate was irradiated with a short-wave UV lamp (254 nm) through a patterned UV-opaque mask from a distance of 1 cm. The film was then rinsed with hot water and Softsoap Antibacterial Liquid Hand Soap and then cold water in order to remove the non-cross-linked polymer. The dried UV-exposed films were measured by NC-AFM and FTIR.

Results and Discussion

UV-induced photo-cross-linking of VBT–VPS films coated on substrates causes the immobilization of the polymer on the substrate. The areas of the polymer that have not been exposed to the UV radiation can be easily washed away, much like conventional negative photoresists. The polymer investigated here provides the added benefit of being nontoxic as well as water-soluble, therefore precluding the necessity for the use of organic solvents. To explore the possibility of using this material for photoresist applications, it is important to understand the film formation process and the UV–irradiation dose-dependent immobilization of the resist due to cross-linking. ATR FTIR is a convenient method to monitor the film formation process. Since a flexible PET substrate was used for this study, the thickness of the photoresist film formed on UV exposure could only be monitored by a noncontact technique such as NC-AFM. The combination of these techniques has been useful in obtaining complementary information on the cross-linked photoresist film.

Characterization of VBT–VPS Film Using FTIR Spectroscopy. The FTIR spectra of bare PET film and of VBT–VPS film coated on silicon wafer are shown in Figure 1. VBT–VPS film was neither irradiated nor rinsed. It can be clearly seen that PET absorption bands are overlapping with the VBT–VPS absorption bands. The strong PET absorption bands around 3000 cm⁻¹, corresponding to both aromatic and aliphatic C–H stretching, around 1700 cm⁻¹, corresponding to C=O stretching and around 1250 and 1120 cm⁻¹, corresponding to C–O stretching, make it complicated to extract information about VBT–VPS coatings on PET from FTIR spectra.²⁴ Therefore, we decided to concentrate

(24) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; John Wiley and Sons: New York, 1958.

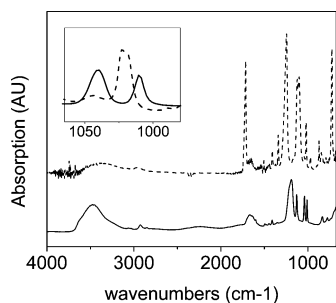


Figure 1. FTIR spectra of bare PET film in ATR mode (---) and of VBT-VPS film coated on silicon wafer in transmission mode (—).

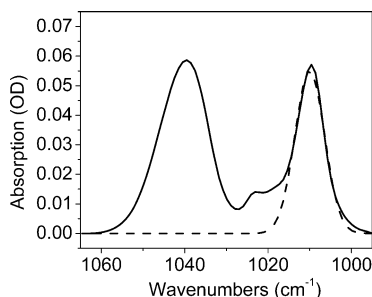


Figure 2. S=O stretching region of the ATR spectrum of VBT-VPS film coated on PET substrate (—); S=O symmetric stretching band (---).

on the 980–1070 cm^{-1} region, which is presented on the insert. Two weak absorption bands at 1045 and 1020 cm^{-1} can be attributed to the C–H in-plane deformation modes of para-substituted aromatic compounds,²⁴ while two strong absorption bands at 1040 and 1010 cm^{-1} correspond to asymmetric and symmetric S=O stretching bands in VPS, respectively.²⁵ Since the bands at 1045 and 1040 cm^{-1} are situated too close to each other to be resolved satisfactorily, we concentrated on the 1010 cm^{-1} band.

The thickness of VBT-VPS film coated on PET substrate is expected to be about 680 nm (prior to irradiation and rinse). To verify this, an ATR spectrum was obtained. The S=O stretching region of the ATR spectrum of VBT-VPS film coated on a PET substrate is presented in Figure 2. The VBT-VPS film thickness was estimated using bulk approximation²⁶ using the following assumptions. Since the typical refractive index of polymers is around 1.5, this value was used for both VBT-VPS and PET. Further, the VBT-VPS film was assumed to be uniform. Absorbance of the symmetric S=O stretching band at 1010 cm^{-1} was defined as the area under the peak and was determined to be 0.49 cm^{-1} . The $[\epsilon c]$ from FTIR transmission measurements was found to be 9254 cm^{-2} , where ϵ is the molar absorptivity and c is the concentration of S=O groups in the VBT-VPS. From the above considerations the VBT-VPS film thickness was found to be about 650 nm, which is close to the expected value of 680 nm within experimental uncertainty. We conclude that the parameters used for the calculation allow accurate estimation of the VBT-VPS film thickness from its ATR spectrum. It should be pointed out that both the

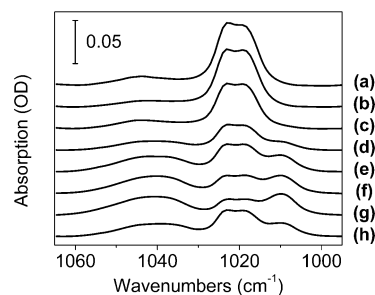


Figure 3. S=O stretching region of the ATR spectra of (a) bare PET film and (b–g) VBT-VPS films coated on PET substrate, exposed to short-wavelength UV for (b) 0 min, (c) 1 min, (d) 2 min, (e) 3 min, (f) 5 min, (g) 7 min, and (h) 10 min, washed, and dried.

expected and the calculated value are rough estimates only, the expected one due to the uncertainty inherent to the coating with the wire-wound metering rod²⁷ and the calculated one due to the distortion of the FTIR ATR absorption bands in thick films.²⁶

Effect of Irradiation Dosage on the Properties of the Cross-linked VBT-VPS Film. The S=O stretching region of the ATR spectra of VBT-VPS films coated on a PET substrate, exposed to various doses of UV irradiation, and washed is shown in Figure 3. The intensity of the S=O band is in all cases significantly lower than that presented in Figure 2, which shows the spectrum taken prior to irradiation and washing. It can clearly be seen that the spectrum of bare PET film is similar to the spectrum of VBT-VPS coated PET film that was washed without being exposed to the UV radiation. It can be rationalized by pointing out that un-cross-linked VBT-VPS is water-soluble and since in the absence of UV irradiation no cross-linking was expected to occur, there is no expectation that a significant amount of VBT-VPS will be immobilized on the PET substrate. Therefore, almost the entire VBT-VPS is removed from the surface by the aqueous wash and no increase in absorbance at 1010 cm^{-1} is observed. The minor increase of absorbance at 1040 cm^{-1} and the decrease of absorbance at 1020 cm^{-1} relative to the bare PET spectra can be attributed to either experimental error or trace amounts of VBT-VPS. In the latter case we could suggest that the PET substrate orients VBT-VPS in such a way that the S=O asymmetric stretching band absorption is enhanced relative to that of the S=O symmetric stretching band.

Only minor effect was observed for VBT-VPS irradiated for 1 min; however, as irradiation time (and therefore dose) increases, the cross-linking progresses further, and the VBT-VPS gets immobilized on the PET substrate. This is clearly seen by the increase in the intensity of S=O signal intensity. It should be pointed out that the S=O absorption signal reaches its maximum at 7 min irradiation, and at larger irradiation times it starts declining. This effect can be attributed either to a decrease in VBT-VPS layer thickness due to possible UV-induced damage to the polymer backbone or to destruction of photoactive sulfonate groups as the result of prolonged exposure to short-wavelength UV irradiation. In any event immobilization is achieved well before significant photodegradation occurs.

(25) (a) Chen, S.-A.; Hwang, G.-W. *Polymer* **1997**, *38*, 333. (b) Chen, S.-A.; Hwang, G.-W. *Macromolecules* **1996**, *29*, 3950. (c) Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K. J.; Samuelson, L. *J. Am. Chem. Soc.* **1999**, *121*, 71–78.

(26) Harrick, N. J. *Internal Reflection Spectroscopy*; John Wiley and Sons: New York, 1967.

(27) MacLeod, D. M. In *Coating Technology Handbook*; Satas, D., Ed.; Marcel Dekker: New York, 1991.

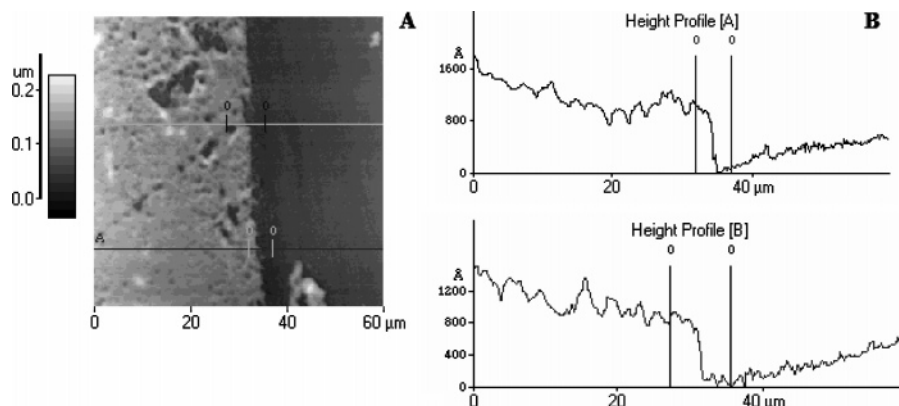


Figure 4. (A) NC-AFM image of VBT-VPS film on PET substrate. (B) Line-profile measurements of the VBT-VPS film image. The measured thickness of VBT-VPS film was around 90 nm (Height Profile [A] 94.3 nm and Height Profile [B] 90.7 nm).

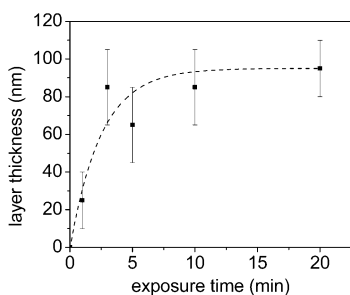


Figure 5. VBT-VPS film thickness versus irradiation time measured using NC-AFM.

To further investigate the effect of the dose of UV radiation on the thickness of the film formed, NC-AFM was used to measure film thickness.

Surface Topography and Film Thickness Measurements Using NC-AFM. AFM imaging was carried out on VBT-VPS films coated on a PET substrate, irradiated through a UV-opaque mask for various exposure times, washed, and dried. Figure 4A represents an image of VBT-VPS film exposed for 20 min. The cross-linked and immobilized VBT-VPS polymer is seen on the left side of the image while the right side of the image reveals the unexposed part where the polymer has been washed away, leaving behind the bare PET substrate. Although the morphology of the cross-linked polymer on PET appears to be coarse and coverage is incomplete at some locations, the interface is clearly visible. The width of the interface is of the order of a few micrometers. But it should be noted that these films were coated on PET manually with a coating rod and washed by scrubbing by hand. The defects in the polymer film are expected, given the method of preparation. The quality of the cross-linked polymer films as well as the interface can be significantly improved by employing more reliable coating, irradiation, and washing techniques. Figure 4B provides the line-profiles measurement at an arbitrary location on the image. The thickness of the polymer was found to be around 90 nm as estimated by averaging the thickness obtained from line-profile measurements from 10 different locations on the image.

Similar measurements were performed for VBT-VPS films irradiated for lower exposure times. The results are presented in Figure 5. It can clearly be seen that the thickness of the VBT-VPS films reaches its maximum value after

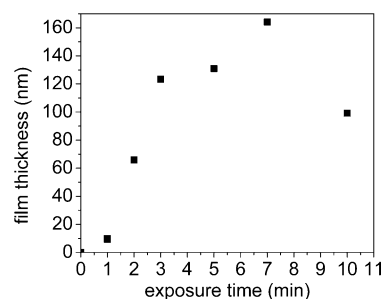


Figure 6. VBT-VPS film thickness at various exposure times estimated from FTIR ATR spectra.

about 3 min of irradiation and does not decrease with longer duration of irradiation. Therefore, one can conclude that the decrease in the sulfonate absorption at prolonged exposure time is due to the UV-induced damage to the pendant sulfonate groups rather than due to reversal of the cross-linking or any damage to the polymer backbone.

Comparison of FTIR ATR and NC-AFM Results. To correlate the results of film thickness measured using NC-AFM with the FTIR ATR results, the VBT-VPS film thickness was estimated from the spectra presented in Figure 3 using the same assumptions as those for interpreting the spectrum in Figure 2. The calculated film thickness for various exposure times is shown in Figure 6. The spectra (d)–(h) presented in Figure 3 correspond to films with thickness $\geq 10\%$ of the ATR light penetration depth (about 660 nm at 1000 cm^{-1} for the ATR crystal used). Films of thickness comparable to the ATR light penetration depth are expected to have distorted spectra, which could explain the discrepancy between the NC-AFM and ATR results, giving an overestimated film thickness in the latter case (for irradiation times of 2–7 min). It should be pointed out that the decrease in calculated film thickness at 10 min exposure is most likely caused by UV-induced damage to sulfonates in VPS. The photodegradation of sulfonates has been reported to be effective only in the presence of catalysts, for instance, metal oxides such as TiO_2 or ZnO^{28} or potassium peroxydisulfate,²⁹ as indicated by chromatographic studies. However, we observe the photodegradation in the absence of

(28) Hidaka, H.; Nohara, K.; Ooishi, K.; Zhao, J.; Serpone, N.; Pelizzetti, E. *Chemosphere* **1994**, *29*, 2619–2624.

(29) Zerbini, O.; Pittavino, S. *Environ. Sci., Pollut. Res.* **2003**, *10*, 395–398.

photocatalysts. We attribute this to the enhanced surface sensitivity of the FTIR ATR technique used to monitor the sulfonate groups.

From Figures 5 and 6 it is clear that the AFM and FTIR ATR results correlate very well in the thickness measured. Both techniques agree in general on the points such as there is no quantifiable VBT–VPS immobilization in the absence of irradiation, the amount of immobilized VBT–VPS reaches saturation after about 3 min of irradiation under the specified conditions, and the thickness of immobilized VBT–VPS film is around 100 nm. However, while FTIR ATR was used to monitor the absorption signal of sulfonate functional groups in the immobilized polymer film, which depends on both the thickness of the film and on the amount of sulfonate groups in the film, NC-AFM provided information on film thickness, supporting the estimate of film thickness obtained from FTIR ATR measurements as well as helping in interpreting qualitative information on the changes in VBT–VPS composition, namely, attributing the decrease of the sulfonate signal as a result of extremely prolonged exposure to photodecomposition of the pendant groups only rather than to actual reduction of film thickness.

Conclusions

A novel class of environmentally benign negative photoresists based on water-soluble polymer (VBT–VPS) has been developed. The selective photoinduced immobilization of VBT–VPS was studied by coating the aqueous solution of the polymer on PET substrates and exposing the polymer to

UV light at 254 nm through a standard mask. FTIR ATR and NC-AFM have been used to study the thickness and composition of VBT–VPS polymer films formed upon photoirradiation. Our preliminary investigations reveal that the thickness of the immobilized films saturate at around 100 nm after 3 min of exposure under specified conditions. These results clearly demonstrate that VBT–VPS polymer can potentially be used as a negative photoresist in a variety of applications. Efforts are underway to adopt a more reliable coating and development techniques to significantly improve the film quality as well as the ultimate resolution of the photoresist.

Acknowledgment. Authors thank Pfizer Corporation for financial support (Pfizer Green Chemistry Postdoctoral Fellowship), Polaroid Corporation for donating PET film base, Dr. Arthur Coury and Dr. Li Ping Yu for help with SEC/MALLS analysis, and Mr. Kevin Dye for useful discussions. Financial support for AFM instrumentation from the Office of Naval Research (ONR) is gratefully acknowledged.

Supporting Information Available: 250 MHz ^1H and ^{13}C NMR spectra of VBT–VPS copolymer in D_2O (PDF), ATR FTIR spectra of VBT–VPS copolymer compared with the ATR FTIR spectra of pure PSS polymer taken at various stages of cure and development, and UV–vis spectra of VBT–VPS copolymer exposed to a range of irradiation doses. This information is available free of charge via the Internet at <http://pubs.acs.org>.

CM0515303