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Cecilia Kiarie[a]; Jason Bianchini[a]; Sofia Trakhtenberg[a]; John C. Warner[a]
[a] Center for Green Chemistry, School of Health and the Environment, University of Massachusetts Lowell, Lowell, MA, USA

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Methylene Blue Adsorption on Thymine Based Polyvinylphenylsulfonate Films

CECILIA KIARIE, JASON BIANCHINI,
SOFIA TRAKHTENBERG, AND JOHN C. WARNER

Center for Green Chemistry, School of Health and the Environment, University of Massachusetts Lowell, Lowell, MA, USA

The immobilization of thymine-containing copolymers of vinylphenylsulfonate (VPS) and vinylbenzylthymine (VBT) on a nonreactive substrate has been investigated. These polymers are environmentally benign, water-soluble and when irradiated with low levels of UV light undergo a $2\pi + 2\pi$ photodimerization reaction of the thymine moieties. These photoinduced dimers form a crosslinked network that renders the polymer significantly less soluble in water. Consequently the irradiated polymer is immobilized on the substrate, allowing removal of unexposed regions by simple aqueous wash. Visualization of the photoresist is done by "toning" the remaining anionic copolymer with the cationic dye methylene blue. By evaluating the color density of the crosslinked, toned films by UV-Vis spectroscopy, this report describes the impact of copolymer composition and curing conditions on polymer photoreactivity. Mechanistic rationale is proposed.

Keywords crosslink, adsorption, green chemistry, photodimerization, thymine

Introduction

The use of *bioinspired* mechanisms in order to create environmentally benign alternatives to traditional materials has recently attracted a bit of attention (1). One area of significant effort is in environmentally benign photoprocessing materials. It has been previously demonstrated that preformed, environmentally benign, thymine-containing water-soluble photopolymers can be used to pattern substrates with either polyanionic or polycationic material while minimizing the exposure to toxic monomers, crosslinking agents and high energy radiation (2).

The photocrosslinking mechanism is inspired by $2\pi + 2\pi$ photodimerization reaction of thymine bases in DNA (3). In our synthetic analogs, thymine groups are incorporated into the polymer by copolymerizing the novel vinylbenzylthymine (VBT) monomer with either anionic or cationic styrene derivatives to achieve water solubility (4). The resulting copolymers can be immobilized on a variety of substrates by exposing them to low levels of UV [<285 nm] irradiation. After irradiation, a simple aqueous wash removes the non-

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Address correspondence to John C. Warner, Center for Green Chemistry, School of Health and the Environment, University of Massachusetts Lowell, 3 Solomont Way, Suite 4, Lowell MA, USA 01854. E-mail: john_warner@uml.edu

crosslinked polymer. This unreacted polymer can be collected and reused. The range of possible applications of these coatings varies from antibacterial polycationic surfaces (5) to polyanionic substrates for the enzyme catalyzed templated polymerization of conductive polyaniline under mild conditions (6).

Since the photoimmobilized copolymer film is very thin [$<1\ \mu$m] and transparent, the immobilized polymer coatings are typically visualized by exposing the resulting patterned films to a solution or suspension of an oppositely charged dye. The dye selectively adsorbs on the polymer, providing clear contrast from the regions of unreacted, cleanly washed substrate. This process is important both by itself because of possible photolithographic applications and also as a model of other processes involving adsorption of various materials on coated surfaces. The amount of adsorbed dye can be monitored by UV-Vis spectroscopy and a correlation between the amount of adsorbed dye and the amount of immobilized charged groups on the surface can be made. The goal of the present work is to quantitatively assess the effects of polymer molecular weight and composition as well as irradiation dose on the adsorption of dye onto the polymer surface. The polymer composition was controlled by varying starting amounts of the monomers and verified by elemental analysis. The molecular weight of the polymers was controlled by varying the amount of polymerization catalyst. The system chosen for the study includes anionic polymers and cationic methylene blue dye.

Experimental

Materials and Methods

All reagents and materials, unless specifically noted, were purchased from Sigma-Aldrich in its purest available form and used as received. Vinylbenzylthymine (VBT) was synthesized from thymine and vinylbenzyl chloride as described previously (7). Vinylphenylsulfonate sodium salt (VPS) was purchased from Fluka, and methylene blue was purchased from Fisher Scientific.

Gel-subbed hydrophilic treated polyethylene terephthalate (PET) film was donated by Polaroid. Coatings were done using milled coating rods, purchased from RDS Corp. (Webster, NY). Irradiations were performed using Spectrolinker XL-1000 UV Crosslinker manufactured by Spectronics Corp. (Westbury, NY). UV-Vis spectra were taken on Agilent 8453 spectrometer and NMR spectra were taken on Bruker 250 MHz and Bruker 300 MHz NMR spectrometers. Elemental analysis was performed using the classical modified Pregl/Dumas technique on an Exeter Analytical 240 analyzer at Umass, Amherst.

Polymer Synthesis

The amounts of VBT, VPS and AIBN are given in Table 1. Vinylbenzylthymine (VBT) and vinylphenylsulfonate sodium salt (VPS) were dissolved in 250 mL of a 50% (v/v) aqueous solution of isopropanol. The solution was heated to 65°C while stirring and 2,2′-azobisisobutyronitrile (AIBN) was added. Stirring was continued for 16 h while the temperature was maintained at 65°C. The reaction mixture was cooled to room temperature and concentrated to 125 mL *in vacuo*. The polymer was precipitated by adding the aqueous solution to 1 L of acetone. Subsequently, the solid precipitate was filtered and then dried under vacuum for 2 days. H^1 NMR spectroscopy was used to confirm the absence of unreacted monomer and elemental analysis was used to confirm copolymer ratio.

Table 1
Synthesis of VBT-VPS copolymers

Polymer	VBT:VPS ratio	VBT (g)	VPS (g)	AIBN (g)
1c	1:4	5.0	17.0	0.11
2a	1:1	11.9	10.1	0.22
2b	1:2	8.2	13.9	0.22
2c	1:4	5.0	17.0	0.22
2d	1:8	2.8	19.2	0.22
2e	1:16	1.5	20.5	0.22
3c	1:4	5.0	17.0	0.44
8e	1:1	11.9	10.1	0.88
8b	1:2	8.2	13.9	0.88
8c	1:4	5.0	17.0	0.88
8d	1:8	2.8	19.2	0.88
8e	1:16	1.5	20.5	0.88

Coating Procedures

First the PET film was pretreated by immersion in 1M aqueous solution of NaOH for 2 h following by rinsing with water and drying under ambient conditions. A 6.8 μm thick layer of 10% aqueous solution of each of the VBT-VPS polymers of various compositions was coated onto the PET film using a coating rod. The film was dried under ambient conditions for 1 h, and then at 80°C for 1 h.

Irradiation and Toning

The samples were irradiated with a short-wave UV (254 nm). The exposure levels varied between 0 and 360 mJ/cm^2. The samples were then immersed into a solution of 0.5 g of methylene blue dye and 1 g sodium carbonate in 1 L of DI water for 10 s. Then, in order to remove the noncrosslinked polymer and weakly attached dye, the samples were rinsed with water, immersed in a solution of 5 mL of DAWN Liquid Detergent (Procter & Gamble) in 1L DI water for 20 s. and finally rinsed with water. The samples were dried by hot air and visually examined for uniform coloring. UV-Vis spectrum of each sample was taken using the corresponding bare substrate as a reference.

Results and Discussion

Figure 1 shows the 450–800 nm region of UV-Vis spectra of toned [1:8 VBT:VPS] polymer **2d** at various irradiation doses. Since the polymers are colorless and transparent in this region of the UV-Vis spectrum, the absorbances result solely from physisorbed methylene blue. The absorption band at 662 nm corresponds to dye monomers and the band at about 613 nm corresponds to combination of dimers and higher aggregates of methylene blue (8).

It can be clearly seen from the spectra that the total amount of adsorbed methylene blue increases with irradiation dose. The relative impact from the monomeric dye

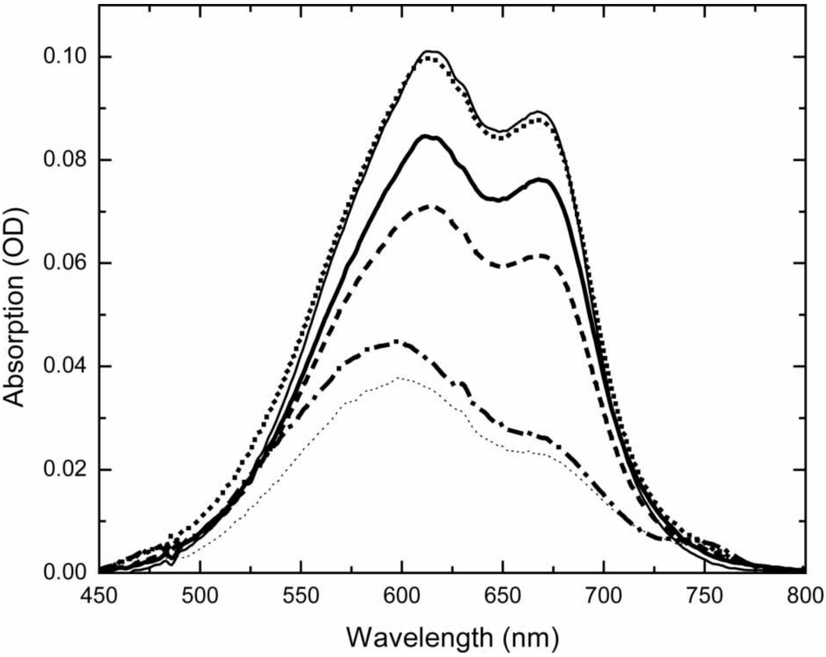

Figure 1. UV-Vis spectra of methylene blue adsorbed on [1:8 VBT:VPS] polymer **2d** at various irradiation doses: (···) 0 mJ/cm^2; (-··-) 5 mJ/cm^2; (--) 30 mJ/cm^2; (—) 60 mJ/cm^2; (···) 100 mJ/cm^2; (—) 120 mJ/cm^2.

signal (662 nm) into the total methylene blue signal increases with the irradiation dose, though most of the increase comes from the aggregate band signal (613 nm). These observations are consistent with a situation where the increased amount of irradiation is causing an increase in the number of crosslinking events - which in turn increases the amount of the polymer adsorbed on the substrate. The positively charged methylene blue molecules and aggregates are adsorbed on the polyanionic immobilized polymer; the amount of adsorbed methylene blue is positively correlated to the amount of adsorbed polymer and therefore also increases. The thicker the polymer layer is the more difficult it is for larger aggregates to penetrate into its pores, therefore the relative amount of adsorbed dye monomers increases.

It was also observed that when the irradiation dose is increased above certain level (50 mJ/cm^2) the amount of adsorbed Methylene blue reaches saturation and does not increase anymore. This effect can be rationalized by assuming that the diffusion of the relatively large methylene blue molecules into a thick polymer layer is somewhat ineffective and therefore an increase of polymer layer thickness above certain level does not affect the toning and thus the additional adsorption of dye. Also, the sulfonate groups, which serve as adsorption sites for methylene blue, are known to be photoactive and their amount can be expected to decrease with irradiation dose, reducing the number of effective sites for methylene blue adsorption. On the other hand, ongoing FTIR-ATR and AFM measurements of the VBT-VPS coatings demonstrate that the amount of immobilized polymer also reaches saturation at certain irradiation dose. This could be explained by taking into account the fact that the polymer absorbs UV and therefore, the amount of irradiation that is reaching the underlying layers of the polymer is much lower than that which is absorbed by the top layer.

It is important to also note that the crosslinking process is reversible, and the reverse process is induced by the short-wave UV. At low irradiation doses most of the thymine groups are not crosslinked and therefore the reverse process is insignificant. When the irradiation dose increases, the amount of crosslinked groups increases proportionately and eventually the reverse process does become significant. Another consideration is the nature of the immobilization process itself. At 0 mJ/cm^2 irradiation dose, obviously no crosslinking occurs and the polymer chains are fully soluble in water and are removed from the surface by aqueous wash. However some polymer may still be adsorbed on the hydrophilic substrate, which can explain the presence of trace amounts of methylene blue in unexposed regions. Furthermore, the bare PET film has some affinity to the dye. At low irradiation doses most of the $2\pi + 2\pi$ photodimerization events where the thymine pendants belong to different polymer chains will achieve crosslinking between the two previously non-crosslinked chains [this effectively increases the polymer molecular weight and thus decreases its solubility while increasing the strength of intermolecular interactions between the polymer and the substrate]. As the irradiation dose increases, the $2\pi + 2\pi$ photodimerization events, where the thymine pendants belong to different polymer chains, which are already crosslinked either directly or through other chains, occur more frequently. However these events do not change the effective molecular weight of the polymers and therefore do not affect polymer immobilization on the surface. All these processes contribute to explain the saturation phenomenon.

Similar measurements were made for all other VBT-VPS polymers studied and similar effects were observed. Figure 2 shows the total intensity of methylene blue

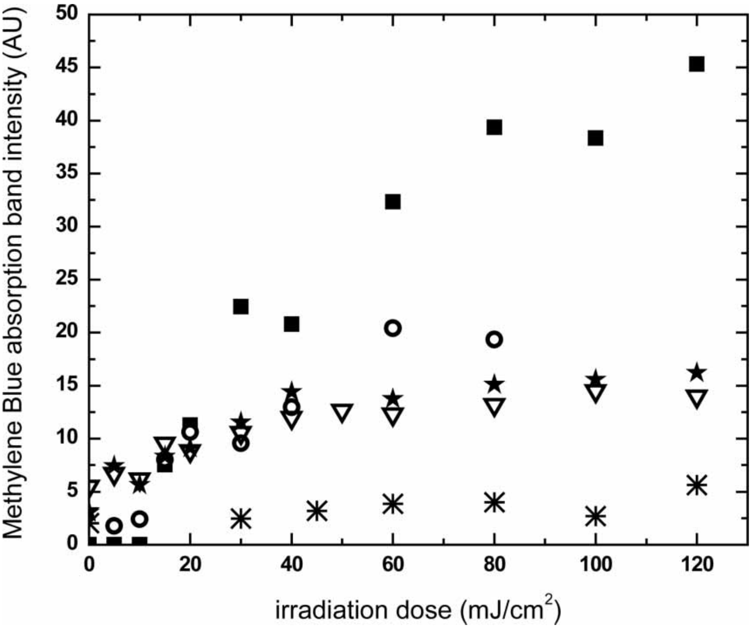

Figure 2. The intensity of methylene blue absorption band as function for irradiation dose for VBT-VPS polymers: (■) **2a**; (○) **2b**; (★) **2c**; (▽) **2d**; (✳) **2e**.

signal as function of irradiation dose for polymers **2a**–**2e** with similar MW, but different VBT to VPS ratios. One can immediately see that the greater the proportion of VPS to VBT, the larger the irradiation dose required to immobilize the polymer on the surface, and the lower is the amount of dye adsorbed on the polymer after saturation.

The spectra of methylene blue adsorbed on polymers **2a**–**2e** exposed to the irradiation dose of 80 mJ/cm^2, which is enough for saturation, are presented on Figure 3. It can clearly be seen that an increase in VPS content, onto which the dye adsorbs, does not lead to an increase in dye adsorption as would be expected, in contrast the amount of adsorbed dye is decreasing. However, since we observe more adsorbed methylene blue on polymers with lower VPS content we conclude that the thickness of these polymer coatings is higher than that of the ones with higher VPS content. This is the additional evidence of the role of thymine photocrosslinking in the formation of the polymer layer. The polymers with lower VPS content have more thymine groups and as a result undergo more efficient crosslinking at the given irradiation dose forming thicker polymer coatings.

Polymers prepared with higher amounts of initiator are expected to have lower molecular weights. They were tested under the similar conditions as the higher molecular weight polymers described above. Increased irradiation doses were in fact required in order to achieve saturation as shown on Figure 4; however at saturation they exhibited similar trends as their higher molecular weight counterparts.

These phenomena can be rationalized by considering the fact that in order to immobilize a polymer on the surface one needs to increase its effective molecular weight by crosslinking. The degree of crosslinking is increasing with irradiation dose and with amount of thymine groups in the polymer.

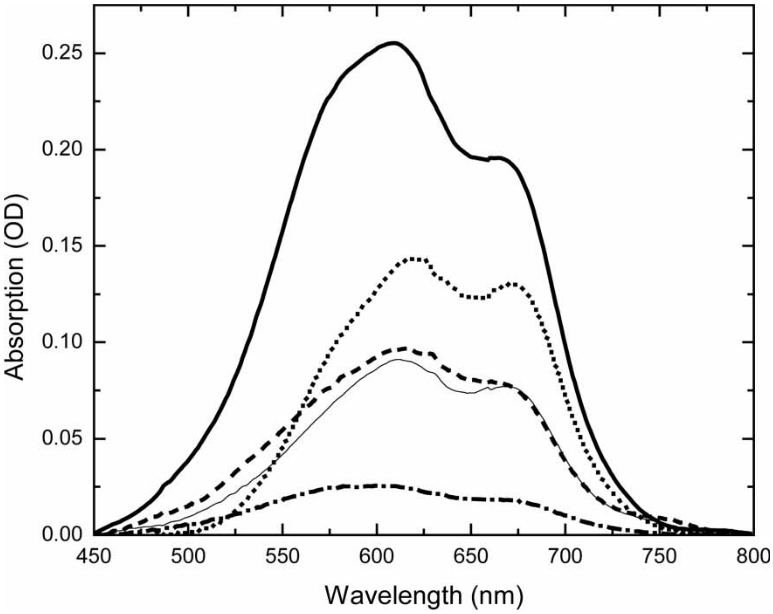

Figure 3. UV-Vis spectra of methylene blue adsorbed on VBT-VPS polymers at 80 mJ/cm^2 irradiation dose: (—) **2a**; (···) **2b**; (---) **2c**; (—) **2d**; (-·-) **2e**.

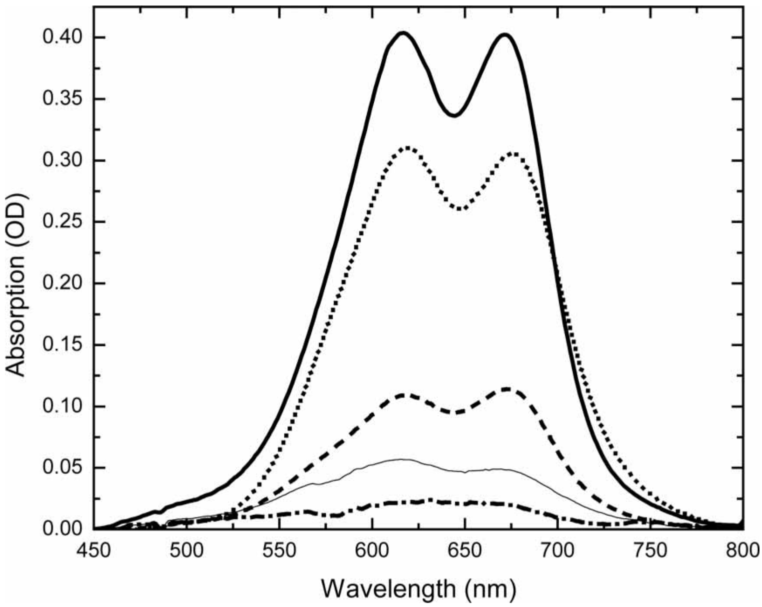

Figure 4. UV-Vis spectra of methylene blue adsorbed on VBT-VPS polymers at 240 mJ/cm^2 irradiation dose: (—) **8a**; (···) **8b**; (--) **8c**; (—) **8d**; (-··-) **8e**.

Conclusions

The adsorption of methylene blue dye on the surface of thymine based photoresist polymers was studied by UV-Vis spectroscopy. It was demonstrated that the amount of adsorbed dye can be controlled by varying photoresist composition, molecular weight and UV irradiation dose. It was also shown that increasing the amount of thymine-containing pendant groups in the polymer increases the amount of adsorbed dye. Increased amount of irradiation first increases the amount of adsorbed dye until the saturation value is reached. Higher molecular weight of the polymer also increases the dye adsorption at the same thymine concentrations and irradiation doses.

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References

1. Anastas, P.T. and Warner, J.C. (1998) *Green Chemistry: Theory and Practice*; Oxford University Press: London.
2. Lloyd-Kindstrand, L. and Warner, J.C. (2003) Thymine Containing Styrene Polymers as Environmentally Benign Photoresists. In *Biopolymers*; Matsumura, S. and Steinbüchel, A., eds.; Wiley: Weinheim, Germany; Vol. 9, 165–174.
3. (a) Blackburn, G.M., Davies, R.J.H. (1966) The Structure of Thymine Photo-dimer. *J. Chem. Soc. C.*, 23: 2239–2244; (b) Lamola, A.A. and Mittal, J.P. (1966) Solution Photochemistry of Thymine And Uracil. *Science*, 154 (756): 1560–1561.

4. (a) Grasshoff, J.M., Taylor, L.D., and Warner, J.C. Copolymeric Mordants and Photographic Products and Processes Containing Same. US Patent 5,395,731, March 7, 1995; (b) Grasshoff, J.M., Taylor, L.D., and Warner, J.C. Vinylbenzyl Thymine Monomers. US Patent 5,455,349, October 3, 1995; (c) Grasshoff, J.M., Taylor, L.D., and Warner, J.C. Method of Imaging using a Polymeric Photoresist Having Pendant Vinylbenzyl Thymine Groups. US Patent 5,616,451, April 1, 1997; (d) Grasshoff, J.M., Taylor, L.D., and Warner, J.C. Copolymers Having Pendant Functional Thymine Groups. US Patent 5,708,106, January 13, 1998.
5. El-Hayek, R. (2004) Bacteriostatic Polymeric Film Immobilization. MS Thesis in Chemistry, UMASS, Boston.
6. Trakhtenberg, S., Hangun-Balkir, Y., Warner, J.C., Bruno, F., Kumar, J., Nagarajan, R., and Samuelson, L.A. (2005) Photocrosslinked Immobilization of Polyelectrolytes for Enzymatic Construction of Conductive Nanocomposites. *J. Am. Chem. Soc.*, 121 (25): 9100–9104.
7. Cheng, C.M., Egbe, M.J., Grasshoff, M.J., Guarrera, D.J., Pai, R.P., Taylor, L.D., and Warner, J.C. (1995) The Synthesis of 1-[Vinylbenzyl]thymine, a Very Versatile Monomer. *J. Polymer Sci., Part A: Polymer Chem.*, 33 (14): 2515–2519.
8. Kobayashi, M., Maeda, Y., Hoshi, T., Okubo, J., and Tanizaki, Y. (1989) Analysis of the Electronic Absorption Spectrum of Adsorbed Layers of Methylene Blue. *Journal of the Society of Dyers and Colourists*, 105 (10): 362–368.