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Influence of pH and Salt on the Photocrosslinking in Polyelectrolyte Thymine-Containing Films

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Photocrosslinking of thymine-based water-soluble polymer films was investigated at varying preparation conditions. Adding salt or decreasing the pH of the solution from which the films were cast resulted in the decreased efficiency of photoimmobilization, while increasing the pH was found to increase the photoimmobilization efficiency. A mechanistic rationale for the observed effects is proposed.

Keywords: green chemistry; bioinspiration; thymine; photocrosslinking

1 Introduction

Polyelectrolytes, high molecular weight compounds containing ionizable groups, have recently become the focus of much attention due to the great abundance of polyelectrolytes among biological macromolecules and the wide variety of technological applications of synthetic polyelectrolytes (1). In aqueous medium counterions dissociate from the polyelectrolyte molecule, leaving behind a polyion containing a large number of charged monomers which repel each other due to the arising Coulombic electrostatic interaction. This repulsion results in extended conformation of the polyion chains or so-called coils (2). The strength of the electrostatic repulsion can be fine-tuned by changing the properties of the solution, such as ionic strength and pH. Increasing the ionic strength causes Debye screening of the interaction between the charged monomers, thus resulting in the collapse of the extended chain structure and consequent formation of globules (3, 4). This process is referred to as coil-globule transition (5). Varying the pH of the solution may affect the degree of dissociation of the polyelectrolyte, thus changing the number of interacting charged monomers within the polyion, which in turn affects the structure of the polyion chain. A number of theoretical and experimental studies of the properties of polyelectrolytes in solutions were carried

out recently (2–8). However, due to the long-range nature of the Coulombic forces a complete understanding of polyelectrolytes' behavior in polar solutions has not yet been achieved (3).

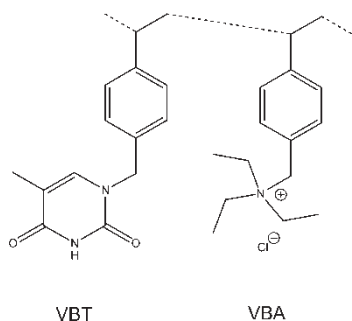
The primary focus of the present study was to determine how the pH and the ionic strength of the polyelectrolyte solution affect the properties of the polyelectrolyte film cast from that solution. Specifically, the efficiency of short UV ($\lambda \sim 254$ nm) irradiation-induced immobilization of a vinylbenzylthymine-vinylbenzyltriethylammonium chloride copolymer (VBT-VBA) was investigated. The structure of the copolymer is presented in the Scheme 1.

VBA monomer contains an ionizable quaternary ammonium functional group; hence the VBT-VBA copolymer is an electrolyte. VBT monomer contains thymine, a DNA base. The pK_a of the N-3 hydrogen in thymine is 9 (9). Therefore, under neutral and acidic conditions most of VBT monomers are not dissociated and have no charge. As the pH increases above the pK_a the number of VBT monomers which have dissociated and acquired negative charge increases.

When exposed to ultraviolet light, two adjacent thymines can undergo a photodimerization reaction and form a photodimer (10). This process is very common in DNA (11). The structure of thymine photodimer depends on the mutual orientation of the thymines prior to the photoreaction (12). In irradiated DNA the most abundant thymine photodimer is *cis-syn* isomer as presented in Scheme 2 (13).

The prevalence of the *cis-syn* isomers in DNA is attributed to the overwhelming majority of thymine photodimerizations occurring between neighboring thymines which belong to the same DNA strand (14). DNA photocrosslinking is rare *in vivo*, although it has been observed in DNA (15–17).

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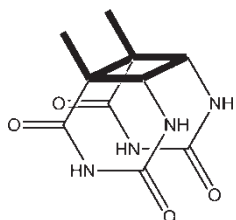


Sch. 1. The structure of VBT-VBA copolymer.

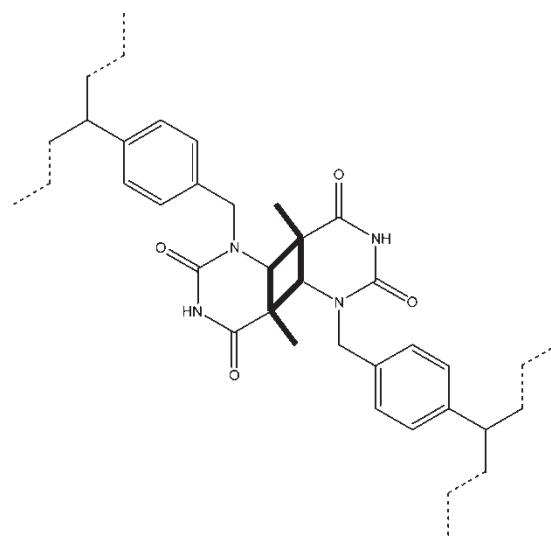
Thymine dimers which are formed from thymines belonging to different DNA strands and therefore resulting in DNA photocrosslinking are expected to be either *cis-anti* or *trans-anti* isomers (14).

In VBT polymers the orientation of thymines is random, in contrast to the well-defined DNA structure. Therefore one can expect all four isomers of thymine photodimer to be formed. If the thymines belong to two different polymer chains, the photodimerization results in crosslinking as shown in the Scheme 3 (9). The *trans-anti* isomer presented on the Scheme 3 is the least sterically constrained but is not likely to be the only isomer formed as result of irradiation of VBT polymers and copolymers.

The higher the irradiation dose, the more such dimers are formed, and the higher is the degree of photocrosslinking. Initially the photocrosslinking and the resulting increase in average molecular weight of the polymers do not affect solubility. However, as the degree of photocrosslinking reaches a certain threshold value referred to as “gel point”, large numbers of polymer chains connected together by thymine dimers form “infinite” molecular weight networks which make up the insoluble fraction of the photocrosslinked polymer (18). In frontally irradiated films, the gelation (insolubilization) process starts at the top of the irradiated layer, and as the irradiation dose increases further it propagates into the depth of the film. When the insoluble network is formed at the bottom of the film, adjacent to the substrate, the insoluble fraction of the film becomes immobilized and cannot be removed by an aqueous wash which does remove the soluble fraction of the film. The minimum irradiation dose required to achieve polymer immobilization is referred to as a speedpoint (19–21).



Sch. 2. The thymine *cis-syn* photodimer.



Sch. 3. VBT polymer crosslinking via thymine photodimerization.

The kinetics of polymer immobilization via crosslinking is described by the Flory theory of network formation, which postulates that the probability of intramolecular reactions leading to the formation of cyclic structures is negligible compared to the probability of intermolecular reactions resulting in crosslinking (22–27). This assumption implies a high degree of chain interpenetration in the polymer matrices and has been confirmed experimentally for a number of photocrosslinkable polymers (28).

In the present study, the conformation of polymer chains was altered by varying pH and salt content of the solution. It was assumed that although the structure of the polymer chains in solution is not likely to be preserved while casting a film, there still might be a general resemblance between the shapes of polymer chains in solution and in the solid film. In other words, the extended polymer chains (coils) are likely to form an interpenetrated, easily crosslinkable solid matrix when cast from solution onto the substrate, while the collapsed polymer chains (globules) are less likely to interpenetrate each other. In the latter case the photocrosslinking and resulting immobilization is expected to be less efficient than in the former case (28).

2 Experimental

2.1 Materials and Methods

All the reagents were purchased from Sigma-Aldrich and used as received unless otherwise specified. Vinylbenzyl thymine (VBT) and vinylbenzyltriethylammonium chloride (VBA) were synthesized as described before (9). Copolymerization and subsequent purification of VBT-VBA was performed under the same conditions as in the previous study (29). The PHB-209 bench-top pH-meter (Omega Engineering) was used for pH measurements. Wire-wound milled

coating rods (#03) were purchased from R. D. Specialties Inc. The hydrophilic PET-X4C1 film base (Dupont) was used as received. UV irradiations at $\lambda \sim 254$ nm were performed in the Spectrolinker XL-1000 UV Crosslinker. The FD&C approved dye Green 3 was obtained from Warner Jenkinson Co, Inc. and used as received. The color density of the samples was measured using the X-Rite 528 Spectrodensitometer (X-Rite).

2.2 Preparation of VBT-VBA Solutions

Solutions with NaCl concentrations ranging between 1 M and 0.001 M were prepared by adding 2.9 g (50 mmol) NaCl to 50 mL of deionized (Millipore) water and subsequent dilutions of the resulting 1.0 M solution. Solutions with pHs ranging between 0.7 and 5.7 were prepared by adding 1.0 g (10.2 mmol) of concentrated sulfuric acid (H_2SO_4) to 50 mL of deionized water and subsequent dilutions of the resulting solution. Solutions with pHs ranging between 12.6 to 7.4 were prepared by adding 0.2 g of NaOH (5 mmol) to 50 mL of deionized water and subsequent dilutions of the resulting solution. The pH of water used for the experiments was found to be 6.2.

For each of the solutions described above (including deionized water), 0.1 g of VBT-VBA polymer were added to 2 mL of solution, stirred for 10 min, and left overnight. The VBT-VBA polymer dissolved in each of the solutions except for one with pH 12.6. That sample was not used in the experiments described below.

2.3 Coating, Irradiation, Development and Toning

Polyethylterephthalate (PET) was used as a substrate. Samples of PET film were secured to a flat surface, and polymer solutions were applied along the top edge of the samples. The solutions were spread on the PET surface using #03 wire wound milled coating rod, which resulted in coatings with wet thickness of 6.8 μm (30). The coatings were allowed to dry overnight under ambient conditions.

Next, the coatings were exposed to UV irradiation doses ranging between 5 and 70 mJ/cm^2 . After irradiation, the samples were rinsed with deionized water for one minute, exposed to toning solution (0.25 g of FD&C Green 3 dye in 500 mL of deionized water) for one minute, briefly rinsed with deionized water again and left overnight to dry.

Finally, color density of each sample was measured. Overall visual density as well as its cyan, magenta, and yellow components were monitored.

3 Results and Discussion

The VBT-VBA films are colorless. In order to quantify the extent of their photoimmobilization on the substrate the films were toned with anionic dye. The dye molecules have low affinity to the PET substrate but are readily adsorbed

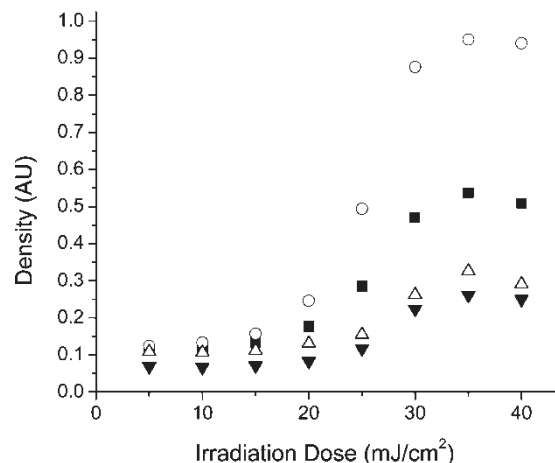


Fig. 1. The color density values (■ visual, ○ cyan, △ magenta, ▽ yellow) of the irradiated, developed, and toned VBT-VBA films as function of the irradiation dose.

on the immobilized, oppositely-charged, polycationic VBT-VBA. It was demonstrated earlier that the amount of adsorbed dye correlates strongly with the thickness of the adsorbed VBT-VBA polymer film (31).

Figure 1 shows the color density of the toned samples, for which deionized water was used as a solvent, as a function of irradiation dose.

At irradiation doses below 20 mJ/cm^2 , the color density of the samples (corresponding to the amount of the adsorbed dye which is correlated to the amount of the immobilized VBT-VBA) is very low and is virtually independent of the irradiation dose. As the irradiation dose reaches 20 mJ/cm^2 , the color density increases with the irradiation dose until it reaches saturation at about 30 mJ/cm^2 . This is a typical shape of a characteristic curve of a crosslinking photoresist (19). As can be seen in Figure 1, the hue of the adsorbed dye remains constant, indicating that the structure of adsorbed dye molecules is likely to be independent of the thickness of immobilized VBT-VBA film. This is different from the previous study (32) where cationic Methylene Blue dye was adsorbed on the immobilized polyanionic VBT copolymers, and the dye aggregation associated with the shift of the Methylene Blue absorption band was detected. Thus, the independence of the adsorbed dye color hue on the VBT-VBA film thickness allowed us to monitor only the largest (cyan) component of the samples' color density.

Next, the effect of added salt (NaCl) on the VBT-VBA photoimmobilization was investigated. In Figure 2, the color density cyan component of samples exposed to 30 mJ/cm^2 of ultraviolet light, developed, and toned is presented as function of the NaCl concentration in the VBT-VBA solutions from which they were coated.

Clearly, as more salt is added, the VBT-VBA immobilization becomes less efficient. This can be explained in the following way. In absence of salt, the ionized VBA groups

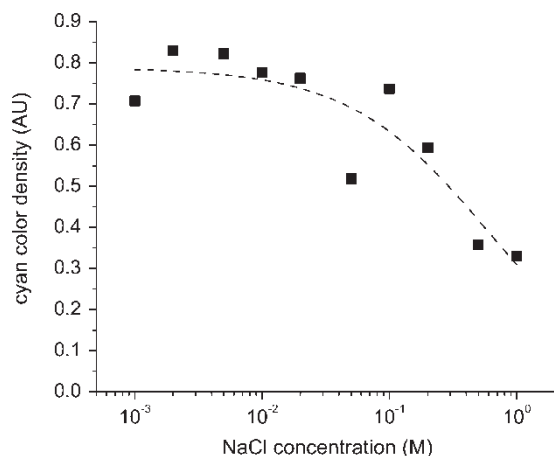


Fig. 2. The color density cyan component of samples exposed to 30 mJ/cm^2 of ultraviolet light, developed, and toned as function of the NaCl concentration; The data points are represented by squares, line is intended to serve as guide for eye only.

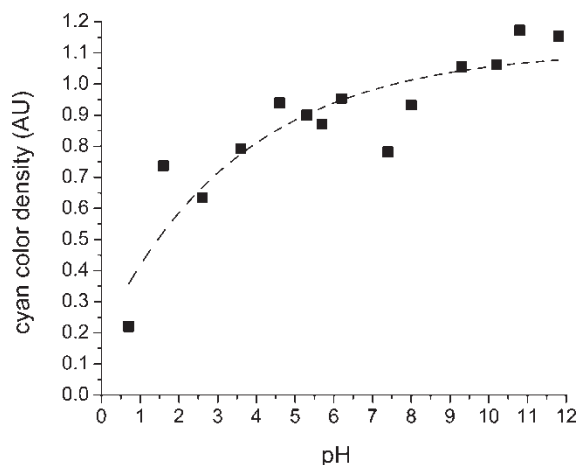


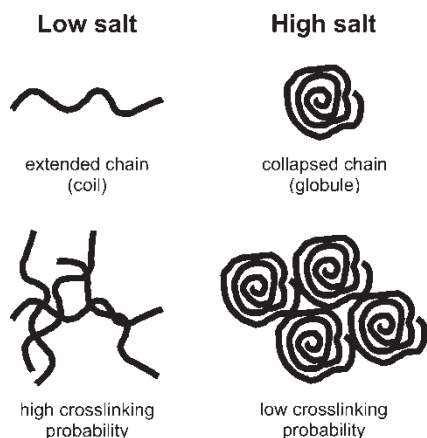
Fig. 3. The color density cyan component of samples exposed to 30 mJ/cm^2 of ultraviolet light, developed, and toned as function of the pH. The data points are represented by squares; line is intended to serve as guide for eye only.

repel each other and the polymer chains are extended. As the amount of salt increases, the polymer chains contract (33). Eventually, the polymer chains collapse and acquire globule structure (5). Such globules are less likely to interpenetrate than the extended chains as presented on the Scheme 4.

Thus, under low salt conditions, the majority of thymine photodimerisation reactions in the extended VBT-VBA chains result in crosslinking of the previously unconnected chains and increase of the polymer molecular weight. Under high salt conditions, the probability of thymine photodimerization being “non-productive”, i.e., connecting two thymine groups belonging to the same collapsed VBT-VBA globule becomes non-negligible, and therefore crosslinking becomes less efficient. Finally, the effect of pH on the photoimmobilization of VBT-VBA was investigated. In the Figure 3 the color density cyan component of samples,

exposed to 30 mJ/cm^2 of ultraviolet light, developed, and toned, is presented as a function of the pH of the solutions in which the VBT-VBA was dissolved. It should be noted here that upon addition of VBT-VBA to the solutions their pH was likely to change; however the pH of the resulting solutions could not be monitored due to technical reasons, namely that the limited amount of the VBT-VBA polymer was insufficient for preparing volumes of solutions large enough to allow the pH measurements.

It is evident from the data presented in Figure 3 that the acidic medium hinders crosslinking, while the basic medium promotes crosslinking. For acidic solutions, the reduced efficiency of photocrosslinking may be explained using the same arguments as for high salt solutions, especially if one takes into account that dissociation of sulfuric acid results in divalent anions whose contribution to the ionic strength of the medium is larger than that of monovalent ions present in the NaCl solutions of equal concentrations (34). However, in basic solutions adding NaOH and consequent increase of the ionic strength of the medium evidently did not result in hindering of photocrosslinking. This could be attributed to partial dissociation of the VBT monomers as a result of which the VBT-VBA becomes a polyampholyte containing both positively charged ionized VBA groups and negatively charged ionized VBT groups. The decrease of the overall charge on each polymer chain results in decreased repulsion between chains, which allows for greater chain interpenetration.



Sch. 4. Interpenetration of extended (coils) and collapsed (globules) polymer chains.

4 Conclusions

Photoimmobilization of water-soluble thymine-containing photopolymers was investigated in various media. It was

demonstrated that immobilization is most efficient when polymer films are cast from basic solution and least efficient when polymer is deposited from acidic solution. Adding salt also resulted in decreased efficiency of photoimmobilization. A mechanistic explanation of the observations is proposed. This study provides useful information necessary for optimizing coating conditions for environmentally benign water-processable photoresists.

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