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### The Effects of Irradiation Dose and of Photopolymer Composition on the Dissolution of Entrapped Dyes

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# The Effects of Irradiation Dose and of Photopolymer Composition on the Dissolution of Entrapped Dyes

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*Dissolution kinetics of dyes entrapped in photocrosslinked polymer matrix were investigated. Films containing thymine-based bioinspired photopolymers and non-toxic dyes were deposited on the polyethylterephthalate (PET) substrate from aqueous solutions. The films were cured by exposure to various UV-irradiation doses ( $\lambda = 254$  nm) and developed in a weakly acidic aqueous medium. The UV-Vis spectra of the films before and after curing and development were taken and the intensities of the bands corresponding to the absorbance of the respective dyes entrapped in the films were monitored for a variety of irradiation doses, development times, polymer compositions and two different dyes.*

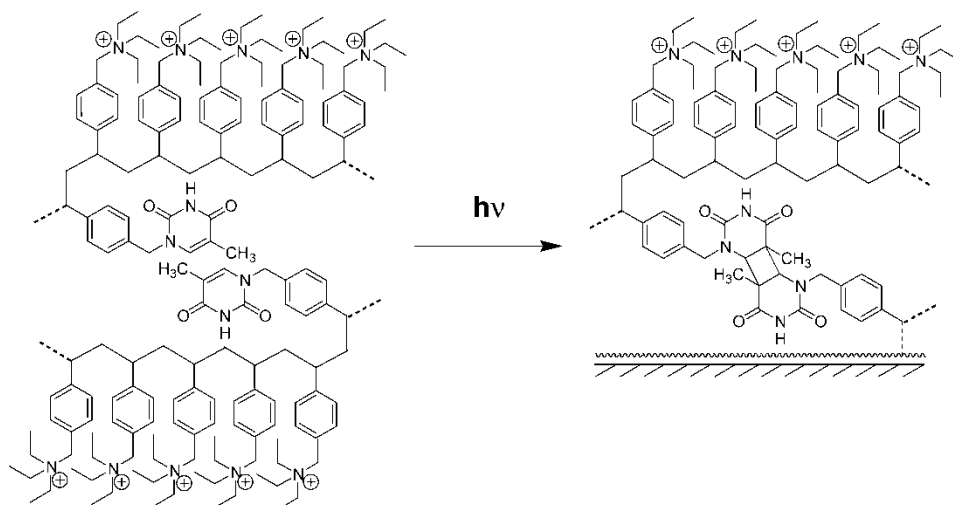
**Keywords** crosslink, photodimerization, thymine, Green Chemistry, dissolution kinetics

## Introduction

When a drug is administered into a body or a fertilizer is deposited onto the ground, it is often important to control the rate of its release. Typically this is done by encapsulating the guest drug or fertilizer in some other material with desired solubility. Sometimes a combination of materials with different solubilities can be used. Our group has developed a family of bioinspired thymine-based photopolymers (1–15). Thymine, one of the DNA bases, is known to dimerize both *in vivo* and *in vitro*, under irradiation with ultraviolet light (16, 17). Grafting thymine pendant groups onto the backbone of a polymer with desired properties, such as aqueous solubility, allowed us to create a water-soluble environmentally benign photoresist.

Upon irradiation photodimerization of the thymine groups causes the polymer chains to crosslink. Crosslinking results in decreased solubility of the polymer and, as the irradiation dose increases, nearly total insolubilization and immobilization of the polymer (Scheme 1).

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**Scheme 1.** UV-induced crosslinking and insolubilization of thymine-based polymer.

By varying the irradiation dose one can alter the solubility of the irradiated polymer. Using such polymers as carriers for drugs or fertilizers could eliminate the need to have a variety of carriers with different solubilities. Selecting the right irradiation dose would allow fine-tuning the polymer solubility for the desired application. It is advantageous to add the guest species (drug, or fertilizer) to the polymer prior to irradiation, which renders the polymer less soluble and therefore, less processable. It was demonstrated in earlier work (15) that adding a strongly UV-absorbing model guest species in quantities exceeding the amount of thymine in the polymer did not hinder photocrosslinking. Films containing water-soluble thymine-based photopolymer and various dyes were successfully immobilized on a substrate by exposure to ultraviolet irradiation.

The goal of the present study was to investigate the effects of irradiation dose on the dissolution kinetics. Two photocrosslinkable polymers with different copolymer ratios and two different dyes as model guest species were used for this study. Polymer-dye films were prepared and exposed to a range of irradiation doses (cured) and rinsed (developed) for a range of different times. UV-vis spectra of the films were taken before and after curing and development to monitor the dissolution of the dye released from the films.

## Experimental

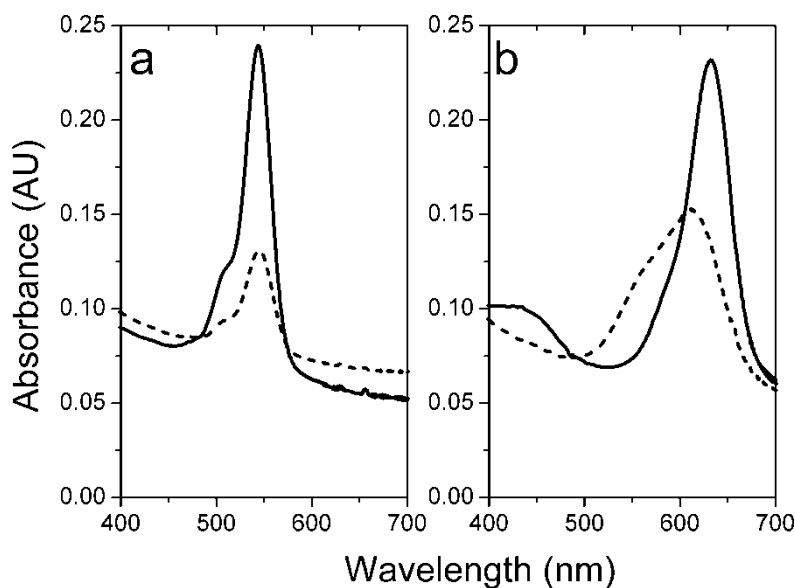
Para-substituted vinylbenzylthymine (VBT) and vinylbenzyltriethylammonium chloride (VBA) were synthesized as described previously (2). Copolymers (VBT)(VBA)<sub>2</sub> and (VBT)(VBA)<sub>8</sub> were synthesized in isopropanol at 65°C via 2,2'-azobisisobutyronitrile (AIBN) initiated free radical polymerization. After polymerization the reaction mixture was concentrated by rotary evaporation and the polymers were precipitated from the solution by cold acetone. Absence of the monomers was confirmed by <sup>1</sup>H-NMR. The solutions were prepared in the following way. 1 gram of the polymer (either (VBT)(VBA)<sub>2</sub> or (VBT)(VBA)<sub>8</sub>) and 200 mg of the dye (either FD&C red #3 or FD&C Green #3) were added to 10 mL of deionized water and stirred until a homogeneous solution was obtained. The resulting solutions were coated on the PET substrate pretreated

by the manufacturer to be rendered hydrophilic. Wire wound milled coating rod #3 (wet film thickness  $\sim 6.8 \mu\text{m}$ ) was used for coating (18). The films were allowed to dry under ambient conditions and the UV-Vis spectrum of each sample was recorded. Agilent 8453 Spectrophotometer was used for all the UV-Vis measurements. Samples were exposed to various irradiation doses in the Spectrolinker XL-1000 UV Crosslinker, using short wavelength UV light of  $\lambda \sim 254 \text{ nm}$ . After exposure, the samples were rinsed for varying amounts of time in 1% aqueous solution of acetic acid and then briefly immersed into deionized water. Finally, the samples were allowed to dry and the UV-Vis spectra were taken again.

## Results and Discussion

In Figure 1a the visible range of the typical spectra of the film containing (VBT)(VBA)<sub>2</sub> and Red #3 dye are presented before irradiation (solid line) and after the irradiation and rinse (dashed line). Since the VBT-VBA polymer is colorless, the absorbance band centered at  $\lambda = 545 \text{ nm}$  is attributed to the dye. It can be seen that after irradiation and rinse the signal decreased by  $\sim 65\%$ . Hence, about 35% of the initial amount of dye was not rinsed off, but stayed entrapped in the crosslinked polymer matrix.

The next step was to determine whether the difference between the two spectra is real and results from the dye being rinsed off the surface, or whether it results from experimental error caused by changing the position of the sample in the spectrometer. To determine the experimental error a sample was chosen randomly and ten UV-Vis spectra were taken at different locations on the sample and the intensities of the absorption bands at 545 nm were compared. It was observed that all measured intensities were within 3% of the mean. Therefore, decrease of absorption is real and is attributed to the release of the dye from the film. In Figure 1b, the corresponding spectra of the film containing

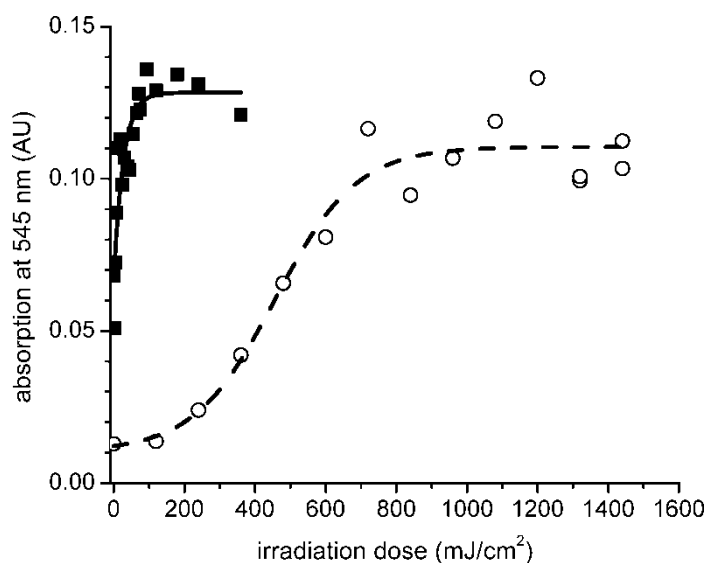


**Figure 1.** Typical UV-Vis spectra of (VBT)(VBA)<sub>2</sub>-dye film before (—) and after (---) irradiation and development. (a) FD&C Red #3. dye; (b) FD&C Green #3. dye.

(VBT)(VBA)<sub>2</sub> and Green #3 dye are presented before and after the irradiation and rinse, demonstrating the same effect.

Next, the effect of polymer composition on the irradiation induced entrapment of the Red #3 dye was investigated. Two polymers: (VBT)(VBA)<sub>2</sub> and (VBT)(VBA)<sub>8</sub> were used. For these measurements, the samples with initial absorbance of  $0.155 \pm 0.005$  AU at 545 nm were selected. The samples were exposed to various doses of UV irradiation and developed for 60 sec. The intensity of the dye absorption band at 545 nm after irradiation and development are presented in Figure 2. It can be seen that the amount of the trapped dye increases with irradiation dose until it reaches saturation, while for (VBT)(VBA)<sub>2</sub> the saturation is reached faster and both the initial and the saturation values are higher than those for (VBT)(VBA)<sub>8</sub>. This can be rationalized if it is taken into account that the dissolution of the dye is related to the dissolution of the polymer. Prior to irradiation (irradiation dose of  $0 \text{ mJ/cm}^2$ ) the polymer, as well as the dye, is fully water soluble. Nevertheless, (VBT)(VBA)<sub>2</sub> dissolves slower than (VBT)(VBA)<sub>8</sub> due to higher concentration of water-insoluble VBT in the former and under same rinsing conditions one would expect more (VBT)(VBA)<sub>2</sub> to remain on the surface. Affinities of the dye to the polymers and of the polymers to the substrate are responsible for non-zero absorbance at zero irradiation doses, while the difference in polymers solubility is responsible for the difference in the initial absorbance values.

As the irradiation dose increases the thymine groups in VBT undergo photodimerization. When the thymine groups are on different polymer chains, dimerization results in crosslinking. Crosslinking of the polymer chains causes a fraction of the polymer to become insoluble and stay immobilized on the surface due to increased molecular weight and acquired network structure. When all the polymer chains are connected the saturation is reached and continued irradiation does not cause any additional decrease in



**Figure 2.** Absorption intensity at 545 nm of the (VBT)(VBA)<sub>2</sub>-FD&C Red #3. dye films (■) and of the (VBT)(VBA)<sub>8</sub>-FD&C Red #3. dye films (○) after exposure to various irradiation doses and 60 s development. The lines are intended as guide for eye only. Initial absorption intensity of each sample was  $0.155 \pm 0.005$  AU.

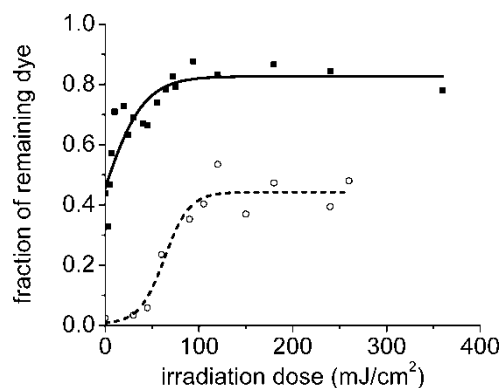
solubility. Since the fraction of the photocrosslinkable VBT monomer is larger in (VBT)(VBA)<sub>2</sub> than in (VBT)(VBA)<sub>8</sub>, photocrosslinking of the former is more readily achieved and it reaches saturation earlier. Dye is prevented from dissolution by both its electrostatic interactions with polycationic immobilized polymer and by the difficulty of diffusion through the crosslinked polymer matrix in which it is entrapped.

The irradiation dose dependence of entrapment efficiency of Red #3 dye in (VBT)(VBA)<sub>2</sub> was compared to that of the Green #3 dye. Since the initial absorbance of the red dye (at 545 nm) and of green dye (at 632 nm) were different, the absorption band intensities were normalized to the initial values, and the results are presented in Figure 3 in terms of the fraction of the respective dyes remaining in the film after irradiation and development.

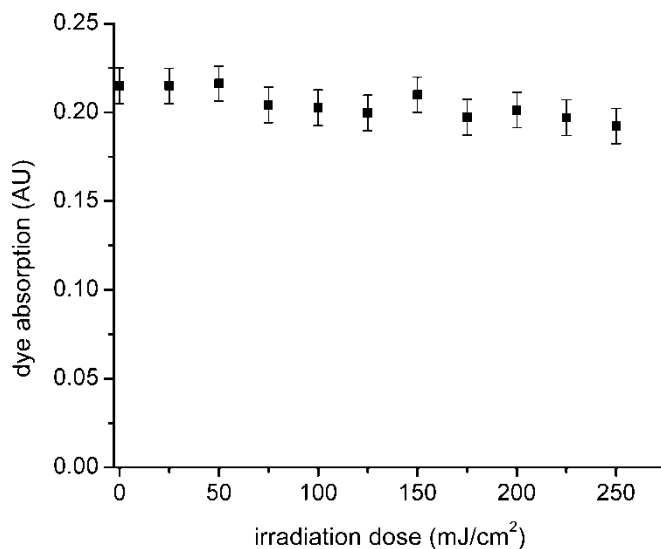
It can be seen that the levels of both dyes reach saturation at the same irradiation dose of about 100 mJ/cm<sup>2</sup>. Presumably this is the dose at which the insoluble fraction of (VBT)(VBA)<sub>2</sub> reaches saturation. At saturation, while more than 80% of the Red #3 dye is retained in the film, only about 40% of the Green #3 dye stays immobilized under the same irradiation and development conditions.

To test the possibility that Green #3 dye was bleaching when exposed to UV irradiation, a sample of Green #3 dye in the (VBT)(VBA)<sub>2</sub> was irradiated repeatedly without rinsing, with UV-Vis spectra taken after each irradiation and the absorption intensities at 632 nm presented in Figure 4 as a function of the irradiation dose. It can be seen clearly that bleaching of the Green #3 dye does occur. The magnitude of the bleaching (about 10% reduction in the intensity) however cannot explain the loss of ~60% of the initial dye absorption as seen in Figure 3.

The structures of the dyes are shown in Scheme 2. The molecular weight of Red #3 dye is 880 g/mol and it has only two ionized groups. Green #3 dye has a lower molecular weight of 808 g/mol and four ionized groups. These two factors combined may account for the stronger van der Waals interaction between Red #3 dye and the polymer than that between Green #3 dye and the polymer as well as the apparently higher affinity of Green #3 dye to water compared to that of Red #3. This would explain the more efficient entrapment of Red #3 dye in the polymer and the quicker dissolution of Green #3 dye.

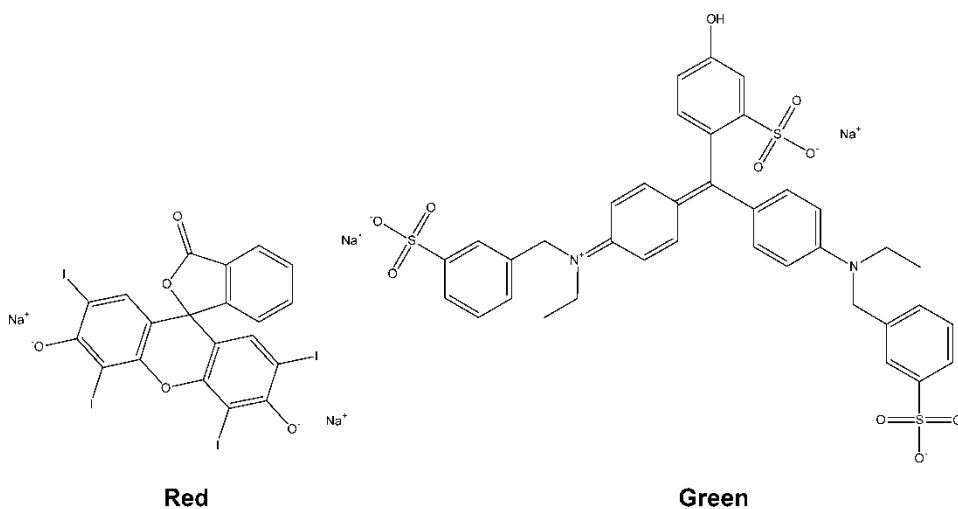


**Figure 3.** Normalized absorption intensity at 545 nm of the (VBT)(VBA)<sub>2</sub>-FD&C Red #3. dye films (■) and at 632 nm of the (VBT)(VBA)<sub>2</sub>-FD&C Green #3. dye films (○) after exposure to various irradiation doses and 60 s development. The lines are intended as guide for the eye only.

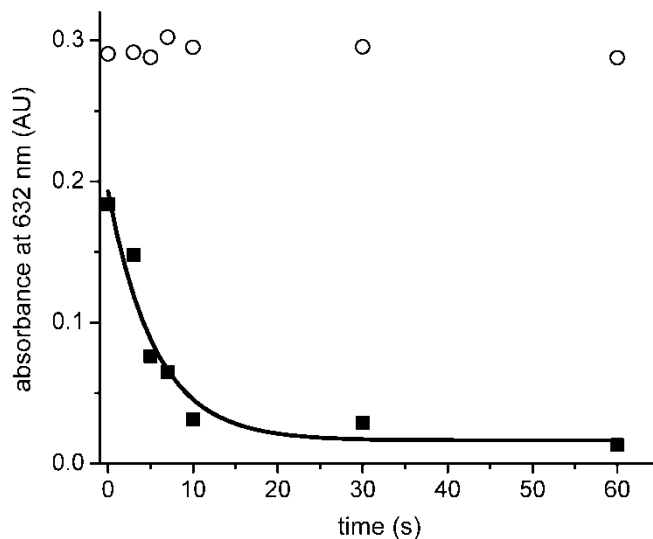


**Figure 4.** Absorption intensity at 632 nm of the (VBT)(VBA)<sub>2</sub>-FD&C Green #3. dye films (■) after exposure to various irradiation doses.

Next the dissolution kinetics of Green #3 dye in crosslinked (VBT)(VBA)<sub>2</sub> after rinsing for varying times was studied to determine the percentage of dye retained in the polymer. First, all the samples were exposed to the irradiation dose of 60 mJ/cm<sup>2</sup>, which as seen in Figure 3, is not enough to reach saturation. Then, the samples were immersed in the 1% solution of acetic acid for varying amounts of time (0–60 sec), after which each sample was briefly immersed into deionized water and allowed to dry. The UV-Vis spectra of all the samples were taken and the intensity of the absorption band at 632 nm was monitored. The results are presented in Figure 5. The decay of the



**Scheme 2.** Structures of FD&C Red #3 and FD&C Green #3 dyes.



**Figure 5.** Absorption intensity at 632 nm of the (VBT)(VBA)<sub>2</sub>-FD&C Green #3. dye films before (○) and after (■) exposure to irradiation dose of 60 mJ/cm<sup>2</sup> and various development times. The line represents an exponential decay fit.

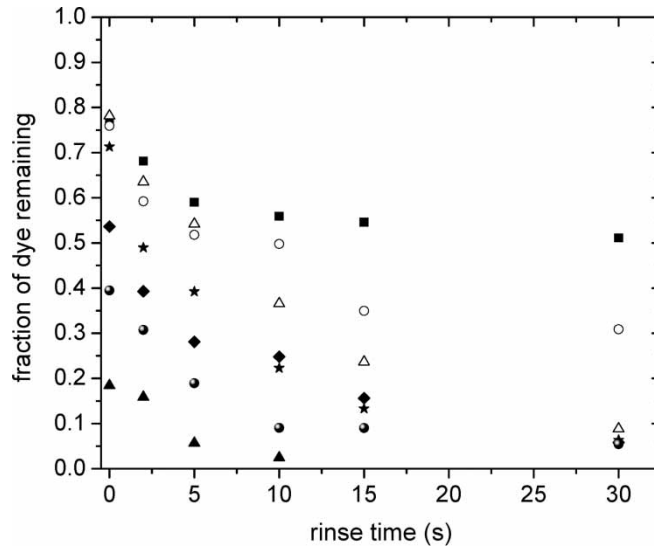
dye absorption, corresponding to the dissolution of the dye, was fitted with an exponential decay curve and the characteristic decay time was determined to be  $\sim 5.6$  s.

Next the dissolution kinetics were studied for samples exposed to an irradiation dose of 120 mJ/cm<sup>2</sup>, which is enough to achieve saturation, and for samples exposed to an irradiation dose of 30 mJ/cm<sup>2</sup>, which is not enough to immobilize any appreciable amount of dye. In both cases, the dissolution of dye occurred faster than when the irradiation dose was 60 mJ/cm<sup>2</sup>. The characteristic adsorption times were 3.5 s and 1.8 s, respectively. This result can be rationalized if two ideal cases are considered: no crosslinking, with no polymer-polymer or polymer-substrate interactions, which would result in immediate dissolution of both dye and polymer and in the second case, a fully immobilized polymer network with the dye securely trapped within. In this second case, the only dissolution one could expect is from the surface of the polymer film where the dye molecules are immediately exposed to the solution and the dye-polymer interactions are considerably weaker. Here the dissolution would be limited neither by diffusion of the dye through the polymer film, nor by the dissolution of the polymer itself and would be expected to occur very quickly. In the intermediate case, when only a fraction of the polymer is immobilized, the less crosslinked polymer chains will slowly dissolve. This would allow the dye molecules which are electrostatically attached to the dissolving polymer chains to escape the immobilized polymer film. Additionally, as some polymer chains are dissolving, the remaining film is likely to become more porous and this should facilitate diffusion of the dye molecules within the polymer film.

Similar experiments were performed for a different polymer-dye system, namely (VBT)(VBA)<sub>8</sub> and Red #3 dye. The absorption at 545 nm corresponding to the red dye was monitored. The results are presented in Figure 6.

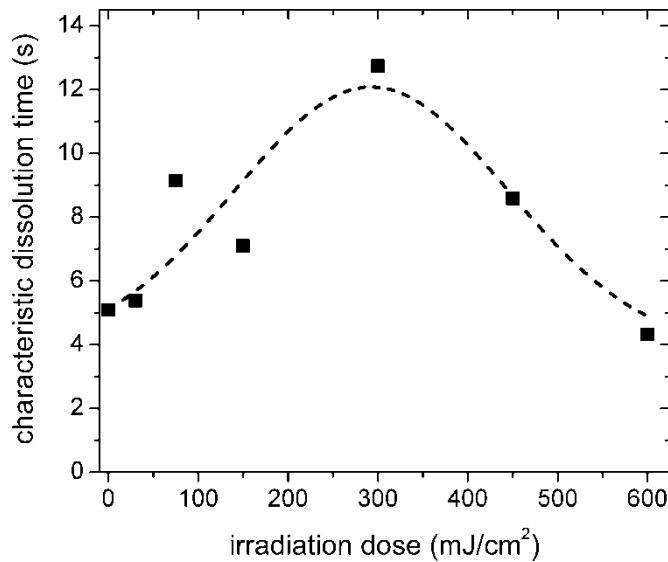
As before, the experimental data were fitted to exponential decay curves and the characteristic times were plotted as a function of irradiation dose as shown in Figure 7.





**Figure 6.** Normalized absorption intensity at 545 nm of the (VBT)(VBA)<sub>8</sub>-FD&C Red #3. dye films after exposure to irradiation doses of 600 mJ/cm<sup>2</sup> (■), 450 mJ/cm<sup>2</sup> (○), 300 mJ/cm<sup>2</sup> (△), 150 mJ/cm<sup>2</sup> (★), 75 mJ/cm<sup>2</sup> (◆), 30 mJ/cm<sup>2</sup> (●), 0 mJ/cm<sup>2</sup> (▲) and various development times.

Here the characteristic dissolution times range between 4 and 13 sec, exhibiting a maximum at irradiation dose of  $\sim 300$  mJ/cm<sup>2</sup>, which, as evident from Figure 2, is enough to immobilize some fraction of the dye (and the polymer), but not enough for saturation.



**Figure 7.** Characteristic dissolution times obtained by fitting the data presented on the Figure 6 with exponential decay curves. Line is intended as a guide for the eye only.

It should be noted here that if the development of the heavily crosslinked films is prolonged farther, even crosslinked polymer chains might begin to swell and that might allow further dissolution of the dye. Since polymer swelling usually occurs on a very different time scale (hours or even days) from the experiments described, this phenomenon was not observed.

## Conclusions

Dissolution kinetics were studied for a model system including bioinspired non-toxic water-soluble photocrosslinkable thymine-based polymers and FD&C. approved dyes. Effects of irradiation dose, polymer composition and dye structure were investigated. It was demonstrated that by varying these parameters one can control the dissolution rate of the dye from the polymer matrix. This study was intended to explore the use of thymine-based polymers for controlled release applications.

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