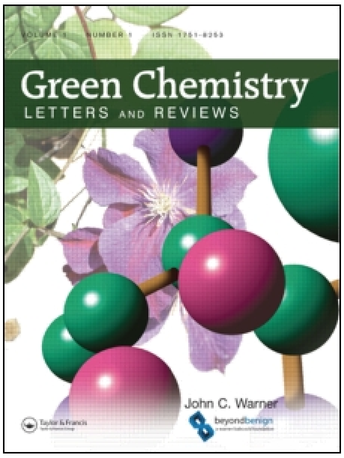

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RESEARCH LETTER

The effect of light intensity, film thickness, and monomer composition in styrene-based bioinspired polymers

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The effect of irradiation light intensity, film thickness, and polymer composition upon photo-irradiation of water-soluble polymers containing thymine was studied by ultraviolet (UV)-vis spectroscopy. Coatings of aqueous solution of the polymer on PET substrates were exposed to UV light at 254 nm through a standard mask. The effect of irradiation dose is similar to the typical behavior of photo-resists: the degree of crosslink increases over the time until it reaches saturation. The polymer composition effect shows an expected trend on the curing process, the more vinylbenzylthymine (VBT) content in the copolymer the higher the degree of crosslinking, a situation that agrees with the fact the VBT is the monomer playing the main role in the photo-reaction. It was observed that the effect of film thickness was as expected, the thicker the film the slower the immobilization of the polymer on the substrate. It was demonstrated that by varying these parameters one could control the crosslinking rate of the polymer.

Keywords: bioinspired polymers; crosslink; green chemistry

Introduction

Identifying naturally occurring mechanisms that can be extrapolated to synthetic systems, is one way of developing environmentally benign materials using the "12 Principles of Green Chemistry" (*1,2*). Thymine, one of the DNA nucleic bases, is known to dimerize both *in vivo* and *in vitro* under irradiation with ultraviolet (UV) light through a $[2\pi + 2\pi]$ photocycloaddition reaction. The carbon–carbon double bonds of proximal thymine bases react to form a cyclobutane ring disrupting the helical structure of DNA. The interruption of the normal cellular processing of DNA leads to a complex web of biological responses, including apoptosis, immune suppression, and carcinogenesis (*3–5*). Thymine bases in DNA are tethered to the sugar-phosphate backbone, and this tethering restricts the achievable orientations of the reacting double bonds that are needed for the reaction to occur. DNA is highly dynamic, and motions such as the stacking and unstacking of bases, base-pair breathing and opening, torsional oscillations, and helix bending will incessantly bring a given thymine into and out of favorable geometries for dimerization. The photo-dimerization is a reversible reaction and the photo-dimer splits very efficiently to make available the original thymines upon irradiation at a shorter wavelength (240 nm) (*6*).

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 photo-resist. Upon irradiation a photo-dimerization reaction of the pendant thymine units causes the polymer chains to crosslink (Scheme 1). Crosslinking results in a decreased solubility of the polymer and a nearly total insolubilization of the polymer occurs when the irradiation dose increases. Selecting the right irradiation dose would allow fine-tuning of the polymer solubility for a desired application. The selective immobilization of polymers by photo-crosslinking on various non-reactive substrates to create thin three-dimensional relief images, provide the technological basis for the electronics industry. The substrates may include inorganic semiconductors, fabric glass as well as metal, depending on the desired applications. Thymine-based polymers are currently being extensively used for a wide variety of applications such as conducting surfaces, antibacterial surfaces, hair style products, nail polish, controlled drug release devices, recycle materials, and photo-resist materials including microelectronic and circuit boards (*7–19*).

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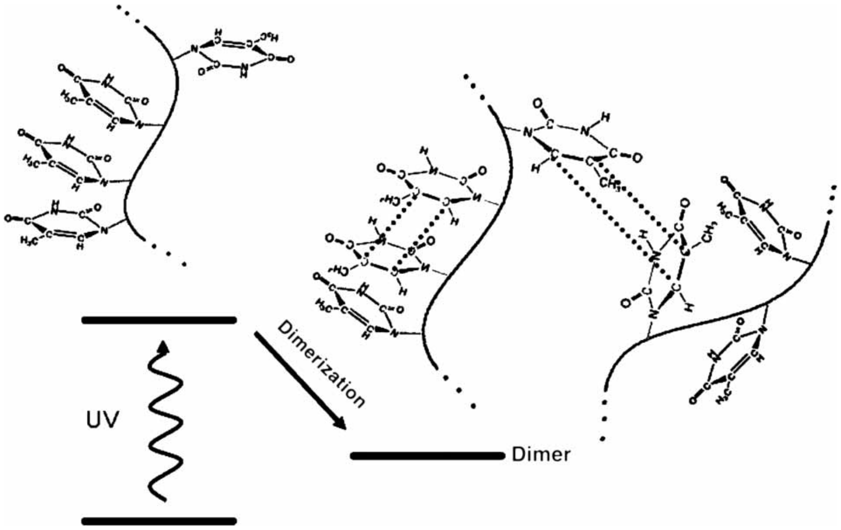


Scheme 1. Photodimerization of polymer chains. Styrene backbone is shown in grey.

The goal of the present study was to investigate the effects of light intensity, film thickness and monomer ratio on the crosslinking kinetics of bioinspired synthetic copolymers based on styrene and containing thymine units. Three photo-crosslinkable polymers with different copolymer ratios were used for this study. Polymer films were prepared, exposed to a range of irradiation doses (cured) and rinsed with water (developed). UV-vis spectra of the films were taken after curing and development to monitor the crosslinking of the polymer.

Experimental section

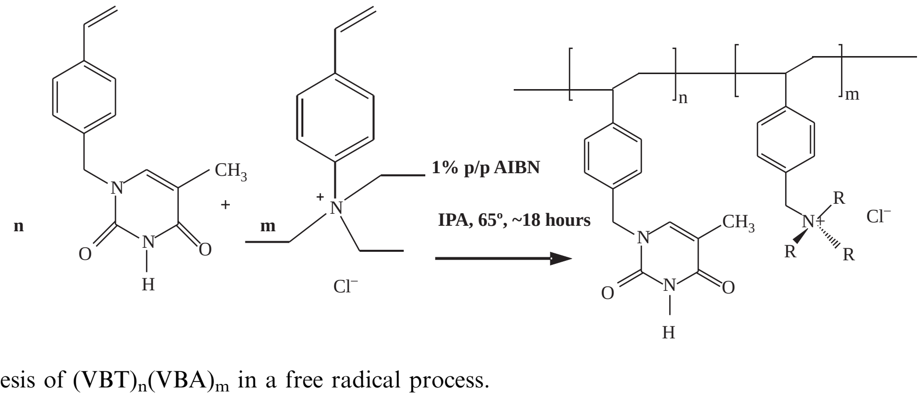
Synthesis of vinylbenzylthymine (VBT)–vinylbenzyltriethylammonium chloride (VBA) polymers

All reagents and materials were obtained from Sigma-Aldrich in their purest available form and used as received. Para-substituted VBT was synthesized from thymine and vinylbenzyl chloride, while VBA was obtained from vinylbenzyl chloride and triethylamine as described previously (*7–9*).

In order to produce water-soluble polymers, VBT was copolymerized in a free radical process with the cationic monomer VBA. The ratio of the comonomers influences the behavior of the VBT polymeric system and varies depending on the application. Copolymers $(VBT)(VBA)_1$, $(VBT)(VBA)_4$, and $(VBT)(VBA)_8$ were synthesized in isopropanol at 65°C via 2,2'-azobisisobutyronitrile (AIBN) initiated free radical polymerization (*8*) (Scheme 2). After about 18–20 hours of polymerization, the reaction mixture was concentrated by rotary evaporation and the polymers were crashed from the solution by cold acetone, obtaining a fine white powder (95% conversion). The absence of unreacted monomers was confirmed by 1H NMR (Bruker 250 MHz).

Coating, irradiation, development, and toning

Homogeneous aqueous solutions (10% in water) of $(VBT)(VBA)_1$, $(VBT)(VBA)_4$, and $(VBT)(VBA)_8$ copolymers were distributed homogeneously onto a solid substrate of polyethyleneterephtalate, PET (PET-X4C1-Dupont). Wire-round milled coating rods #3, #6 and #12 (R. D. Specialties Inc., Webster,



Scheme 2. Synthesis of $(VBT)_n(VBA)_m$ in a free radical process.

NY) were used for coating. The wet film thicknesses are approximately 6.8 μm, 13.7 μm and 27.4 μm for rods #3, #6 and #12 according to coating rod specifications. The films were allowed to dry under ambient conditions for 1 hour and in the oven at 80°C for another hour. Samples were exposed to short wavelength UV light of $\lambda \sim 254$ nm (Spectroline UL, model ENF 260c) through a patterned UV-opaque mask. Irradiation times varied from 0 to 35 minutes and light intensities from 0.9×10^{-3} W/cm^2, 1.1×10^{-3} W/cm^2, and 1.3×10^{-3} W/cm^2. The irradiation process leads to an immobilization of the polymer, allowing the removal of the unexposed regions by a simple aqueous wash. The films were then rinsed 60 seconds in deionized water in order to remove the non-crosslinked polymer (unreacted material can be recovered and reused in subsequent applications). In order to visualize the UV crosslinked material, the solid support is then immersed for 60 seconds in aqueous solution of anionic dye FD&C Red N° 3 (RFC-[0.001 mol/L]), generating the final image after removing the photo-resist. Finally, the samples were allowed to dry at room temperature and the degree of crosslinking was determined measuring the absorption spectra of the RFC at $\lambda \sim 545$ nm using a UV-vis spectrometer (Lambda 20 Perkin Elmer).

Film thickness and light intensity measurements

The film thickness of (VBT)(VBA)$_4$ coatings which we made using different rods were measured using an interferometer (angstrometer Sloan M-100, resolution 2.72×10^{-7} m). The films were made following the procedure described above but using pretreated silicon wavers (500/1500 Ω/cm) as solid support instead of PET. After being dried, the films on the silicon wavers were aluminized to avoid the presence of different refractive indexes that facilitates the measurements of the thickness. From these experiments, the obtained thickness values are 590 nm for rod #3 and 2652 nm for rod #12, values in very close agreement with the expected values of about 680 nm and 2700 nm for rods #3 and #12, respectively. On the other hand, the thicknesses of the VBT–VBA film obtained with rod #3 was estimated to be of about 650 nm from FTIR spectra in ATR mode (*21*), which is close to our measured value of 590 nm within experimental uncertainty. The resolution of coatings prepared with rod #6 was not good enough, and we only can assure that the film thickness is about 1300 nm, which is in the range of the expected value.

The light intensity at different distances from the source was measured with a power-meter (International Light INC, IL 1700, with detector SED240 N° 4277, diffuser W N° 7722 and filter NS254 N° 16793). Stable values for the light intensity were obtained after five minutes of having the lamp turned on.

Results and discussion

The vinylbenzylthymine (VBT)–vinylbenzyltriethylammonium chloride (VBA) films are colorless. In order to quantify the extent of their photo-immobilization on the substrate the films were toned with anionic dye. The dye molecules have low affinity to the PET substrate, but are readily adsorbed on the immobilized oppositely charged polycationic VBT–VBA. Dye is restrained 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. It was demonstrated earlier that the amount of adsorbed dye correlates strongly with the thickness of the adsorbed VBT–VBA polymer film (*16*).

Figure 1 shows the intensity of the UV-vis absorption peak at 545 nm (corresponding to the

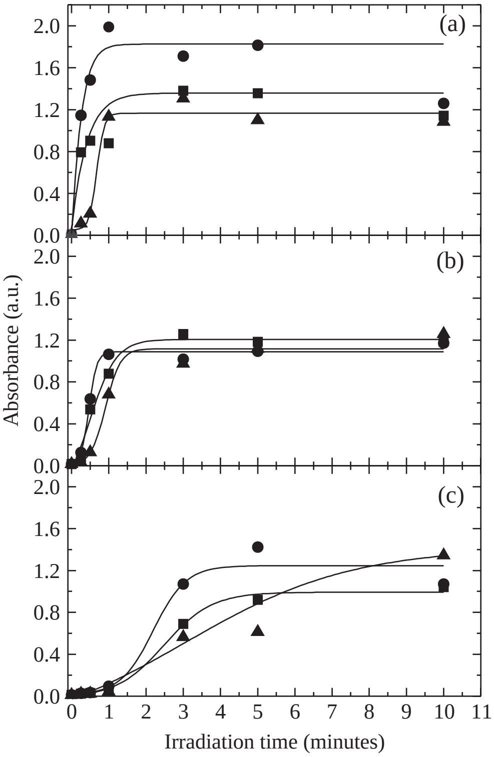


Figure 1. Time dependence of the absorption peak intensity at 545 nm of coatings of (a) (VBT)(VBA)$_1$, (b) (VBT)(VBA)$_4$, and (c) (VBT)(VBA)$_8$, irradiated at $\lambda = 254$ nm for different times and light intensities, (●) 1.3×10^{-3} W/cm^2, (■) 1.1×10^{-3} W/cm^2, (▲) 0.9×10^{-3} W/cm^2, washed with deionized water for 60 seconds and immersed in RFC solution for 60 seconds. Lines are for visual guidance.

RFC dye absorption) in function of irradiation time for copolymers $(VBT)(VBA)_1$, $(VBT)(VBA)_4$ and $(VBT)(VBA)_8$ exposed to UV light ($\lambda = 254$ nm) at three different light intensities, washed with water and dyed with RFC for 60 sec. Lines in the graph do not represent a fitting they are only used as visual guides. In all the cases it was observed that the amount of trapped dye increases with irradiation time until it reaches saturation. The higher the irradiation dose, the more dimers are formed, and therefore, the higher is the degree of crosslinking. Initially the photo-crosslinking and the resulting increase in average molecular weight of the polymers do not affect solubility. However, as the degree of photo-crosslinking reaches a certain threshold value, large numbers of polymer chains connected together by thymine dimers form "infinite" molecular weight networks, which make up the insoluble fraction of the photo-crosslinked polymer.

At shorter times, there is a high probability that the dimerization process occurs between thymines belonging to different polymer chains, causing 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 saturation is reached and more irradiation does not cause any additional decrease in solubility. This behavior is typical for photo-resist materials (*20*). For all molar compositions $(VBT)(VBA)_1$, $(VBT)(VBA)_4$ and $(VBT)(VBA)_8$, it was observed that the immobilization time is shorter at higher light intensity, but for $(VBT)(VBA)_4$ the effect is very small. In Figure 1(a) it can be seen that the higher the light-intensity the faster the immobilization process is produced. Specifically, at higher light intensity (1.3 mW/cm^2) the crosslink was observed after 15 seconds, and increasing the irradiation time the amount of immobilized polymer increases until it reaches saturation around one minute. This behavior was also observed at lower light intensities but the speed of the immobilization process of the polymer is slower. These circumstances were expected since when more energy is given to the copolymer films, extra thymine groups in VBT undergo photo-dimerization causing the polymer to become insoluble, and therefore less irradiation time is required to stay immobilize on the surface of the substrate.

In Figure 2 it is clearly shown that for each light intensity, when more fraction of the photo-crosslinkable VBT monomer compared with VBA monomer is present in the copolymer $(VBT)(VBA)_1 > (VBT)(VBA)_4 > (VBT)(VBA)_8$, less irradiation time is required to immobilize the polymer on the substrate surface and higher absorption values are reached. This difference is more noticeable for higher light intensities. This was expected in view of the fact that VBT is the monomer responsible for the crosslinking. Therefore, increasing VBT concentration will result in thymine molecules closer to each other and in consequence a faster and more efficient crosslink.

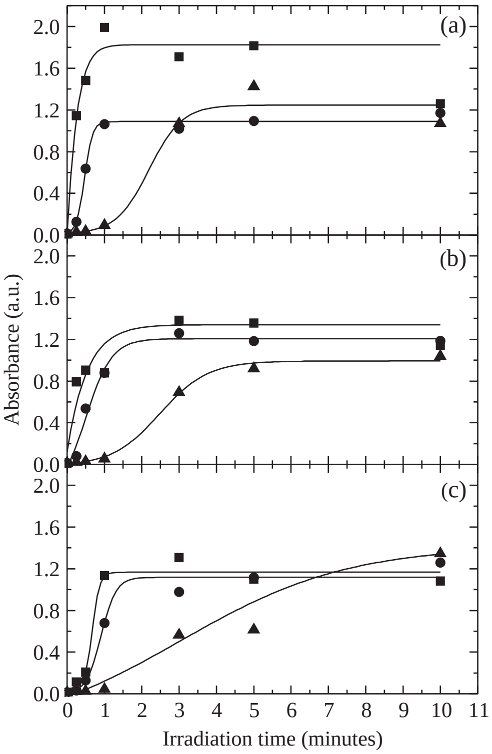


Figure 2. Time dependence of absorption peak intensity at 545 nm for different light intensities: (a) 1.3×10^{-3} W/cm^2; (b) 1.1×10^{-3} W/cm^2; and (c) 0.9×10^{-3} W/cm^2, for coatings of (■) $(VBT)(VBA)_1$, (●) $(VBT)(VBA)_4$, and (▲) $(VBT)(VBA)_8$, irradiated at $\lambda = 254$ nm for different times, washed with deionized water for 60 seconds and immersed in dye aqueous solution for 60 seconds. Lines are intended as visual guides only.

Figure 3 shows the time dependence of the UV-vis absorption peak intensity at 545 nm for copolymers $(VBT)(VBA)_1$ and $(VBT)(VBA)_4$, irradiated at $\lambda = 254$ nm and 1.1×10^{-3} W/cm^2, when coated with different film thicknesses of (a) 590 nm; (b) 1300 nm; and (c) 2652 nm, washed with deionized water for 60 seconds and immersed in a RFC aqueous solution for another 60 seconds.

It can be 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 are likely to form interpenetrated, easily crosslinkable solid matrix when cast from solution onto the substrate. In

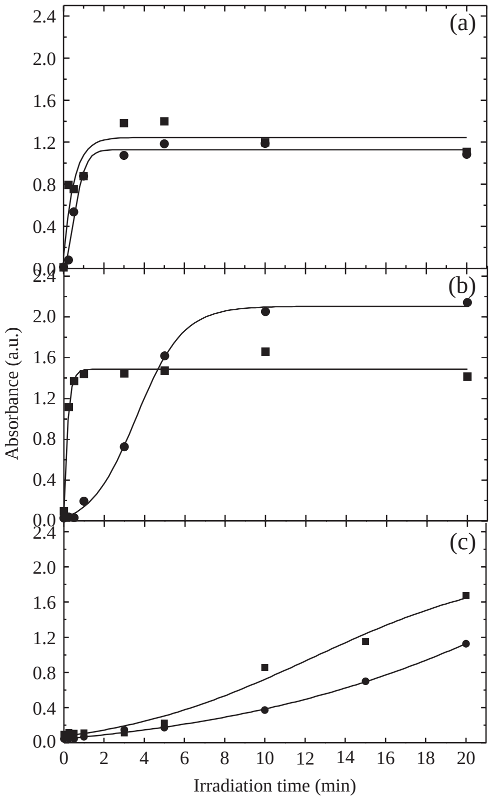


Figure 3. Time dependence of the absorption peak intensity at 545 nm for coatings of (■) (VBT)(VBA)$_1$, and (●) (VBT)(VBA)$_4$ for different film thickness (a) 590 nm, (b) 1300 nm, and (c) 2652 nm, irradiated at $\lambda = 254$ nm and 1.1×10^{-3} W/cm^2, washed with deionized water for 60 seconds and immersed in RFC solution for 60 seconds. Lines are intended as visual guide only.

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. For thin layers of polymers (590 nm), both copolymers crosslink after 30 seconds irradiation time and the kinetics are very similar, only a minor effect on the amount of immobilized polymer can be observed (Figure 3(a)). When the thickness of the film increases to 1300 nm there is a noticeable difference between (VBT)(VBA)$_1$ that crosslink very rapidly (comparable to thinner layers), and (VBT)(VBA)$_4$ that takes about three minutes to start being immobilized on the substrate (Figure 3(b)). A very slow process was observed for (VBT)(VBA)$_1$ and (VBT)(VBA)$_4$ coatings of 2652 nm thickness, where only after five minutes of irradiation the crosslinking progresses and the polymer gets immobilized on the PET substrate (Figure 3(c)).

Figure 4 shows the time dependence of the absorption peak intensity at 545 nm for (VBT)(VBA)$_4$ copolymer coatings having different film thickness of 590 nm; 1300 nm and 2652 nm, irradiated at $\lambda = 254$ nm and 1.1×10^{-3} W/cm^2, washed with deionized water for 60 seconds and immersed in a RFC aqueous solution for another 60 seconds. For the thinner film the immobilization time was very short, and it can be seeing that the speed of the curing process decreases when the thickness of the film increases. For films of 590 nm, the saturation point was reached after 1 minute irradiation time while for films of 1300 nm this time was longer than 5 minutes. Moreover, for films of 2652 nm, the saturation point was not still reached even after 20 minutes irradiation. It can be observed that with an intermediate thickness a higher absorbance value was reached while the speed of the process is faster for the thinner coatings.

This behavior is a result of a poor photodimerization of the polymer chains that are in close contact with the substrate. When the film thickness become larger the top layers absorb light easily and get crosslinked, leaving less amount of irradiation light available to get through the top layers and reach the bottom chains. Therefore, it takes more irradiation time to crosslink the lower chains that are in contact with the substrate. Furthermore, the uncrosslinked polymer from the bottom chains together with the crosslinked polymer from the top layers will be removed from the surface by the aqueous wash.

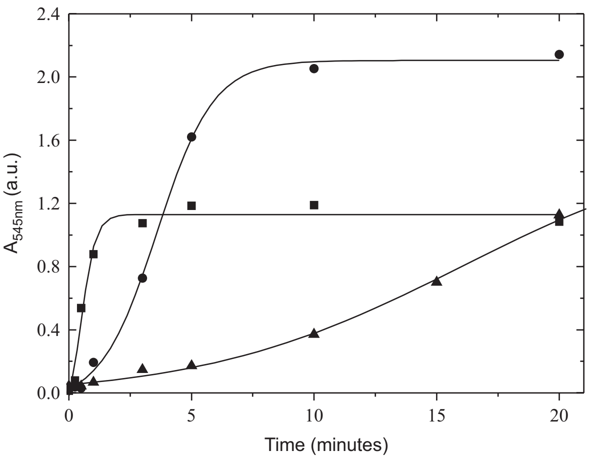


Figure 4. Time dependence of the absorption peak intensity of (VBT)(VBA)4 coatings for different film thickness (■) 590 nm, (●) 1300 nm, and (▲) 2652 nm, irradiated at $\lambda = 254$ nm and 1.1×10^{-3} W/cm2, washed with deionized water for 60 seconds and immersed in RFC solution for 60 seconds. Lines are only as visual guide.

Conclusions

The selectively photo-induced immobilization process of water-soluble polymers containing thymine was studied by coating aqueous solutions of the polymer on PET substrates and exposing the polymer to UV light at 254 nm. UV-vis spectroscopy has been used to study the effect of irradiation light intensities, film thicknesses and polymer compositions upon photo-irradiation. The effect of irradiation dose is similar to the typical behavior of photo-resists: the degree of crosslink increases over the time until it reaches saturation. Our investigations reveal that the required irradiation time to immobilize the polymer on the substrate is shorter at higher light-intensities; in other words, higher light intensity cause the photo-immobilization process to occurs faster. The polymer composition effect shows an expected trend on the curing process, the more VBT content in the copolymer the higher the degree of crosslinking, a situation that agrees with the fact that VBT is the monomer playing the main role in the photo-reaction. The effect of film thickness was found to be as expected: the thicker the film the slower the immobilization of the polymer on the substrate; due to a poor photo-dimerization of the polymer chains in close contact with the substrate was observed.

It was demonstrated that by varying these parameters one could control the crosslinking rate of the polymer and therefore explore the use of thymine-based polymers for specific applications. This study provides useful information necessary for optimizing coating conditions for environmentally benign water-processable photo-resists.

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