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Lithography Based on Memory Effects Resulting from Photoinduced Self-Assembly of Pyrene Dimers in Thin Polymer Films

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Pulsed laser irradiation of pyrene in thin films through lithographic masks leads to blue fluorescent images characteristic of pyrene excimer emission. The images are stable at room temperature and are readily observable using fluorescence microscopy. For a constant energy dose, the images are stronger and better resolved at the shorter laser wavelengths and cannot be recorded with continuous wavelength (CW) light sources. Images are easier to obtain with high Tg films, while polymers with Tg below room temperature image only when the laser also causes polymer cross-linking. It is proposed that laser excitation generates excited singlet pyrene and simultaneously causes a temperature change that facilitates diffusion and thus excimer formation. Following excited state (monomer and excimer) decay, the polymer matrix cools down and prevents the separation of the pyrene pairs, that are preserved by the rigid polymer matrix. Some of the images can be thermally erased by annealing above Tg. The method may find applications in imaging and information storage.

Introduction

The photophysics of pyrene is a well-understood system in which emission from pyrene monomer occurs at low concentration, while at moderately high concentrations (typically millimolar) this emission is accompanied by fluorescence from the pyrene excimer, resulting from association of an excited singlet pyrene with a molecule of pyrene in the ground state.[1−7] Emission from pyrene has been studied in different media such as Langmuir−Blodget films,[8−10] clays,[11,12] zeolites, and micelles.[13,14] Due to its sensitivity to the medium, pyrene has been used as fluorescent probe to monitor phase transitions in polymers, either as a physical mixture[15−17] or chemically attached to polymer chains.[18] It has also been used as sensitizer in laser induced ablation of polymers,[19] and it has been shown that pyrene molecules used as dopant in polymer films can absorb more than ten photons when exposed to laser radiation at 248 nm, without significant damage.[20] In thin polymer films aggregation occurs differently at the interface between the film and substrate compared to aggregation within the film.[2] In the vast majority of cases, the system has no "memory" for the past events or experimental conditions. There are exceptions to this statement, for example, inclusion of pyrene in zeolites, the initial microheterogeneous distribution can be "remembered" for weeks.[21] Similarly, the redistribution of dodecyl pyrene in micelles can take days.[22] Both examples manifest themselves in the shape and relative intensity of monomer and excimer (or aggregate) emission; these examples generally illustrate the dynamics with which a given system changes from a nonrandom initial distribution toward a random (and thermodynamically favored) distribution of pyrene molecules. The kinetics for these processes are specific to a given

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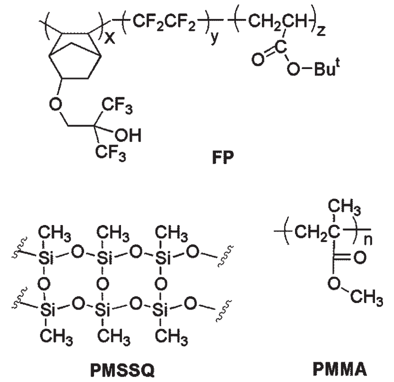
Chart 1. Chemical Structures of the Polymers Employed in This Study: the Fluorinated Polymer Especially Designed for Optical Lithography at 157 nm (FP), Poly(methylmethacrylate) (PMMA), and Polymethylsislsesquioxane (PMSSQ)



supramolecular system, such as in the case of zeolites and micelles.

Evolution from a statistical distribution toward a non-statistical one is rare. Perhaps the exception is the case of triplet−triplet annihilation of pyrene in solution, where the delayed fluorescence is more excimer-rich than anticipated. The result reflects the generation of pyrene-pairs during triplet−triplet annihilation; many of these pairs form the excimer before separation in solution takes place. The "memory" for the triplet-mediated encounters only lasts for microseconds, mirroring the triplet lifetime.[23]

In this contribution we report that pulsed laser excitation of pyrene in thin polymer films leads to memory effects, with laser-induced formation of pyrene pairs or aggregates that persist for long times at room temperature (e.g., weeks). This laser-promoted aggregation can be used for imaging purposes that may find applications in lithography and in information storage. These ideas are demonstrated with images generated by laser excitation and recorded using fluorescence microscopy. Images of this type cannot be obtained using lamp irradiation.

These images are attributed to pyrene photoinduced aggregation that is initiated by excited state encounters leading to excimer formation at the same time that the polymer matrix has been softened by laser-induced local heating. As this sample cools down by heat exchange with the substrate, the aggregates are preserved and become readily detectable by fluorescence microscopy, as they are already predisposed for efficient excimer formation.

Studies in these polymers with different T_g values (chemical structures displayed in Chart 1) and optical absorption properties, as well as with three excimer laser wavelengths (157, 248, and 308 nm), demonstrated that the imaging sensitivity, as well as its permanence, can be tuned.[24] For example, some images can be readily erased thermally, while others persist under similar heating conditions.

Experimental Section

Materials. Pyrene (Aldrich) was recrystallized from ethanol. Poly(methylsilsesquioxane) (PMSSQ) and the fluorinated terpolymer (FP) were a generous gift from Rohm and Haas. Poly(methylmethacrylate) (PMMA) ($M_w \sim 1.0\times10^6$, polydispersity ~ 1.1) was purchased from Polysciences Inc. and used as received. The solvent 2-heptanone (Aldrich) was used as received.

Film Preparation. The thin films were obtained by spin coating solutions containing polymer and pyrene dissolved in 2-heptanone, on one-inch diameter quartz discs at 2000 rpm (rotations per minute) for 20 s, using a spin coater from Specialty Coatings, Inc. The thickness of the polymer films was measured with a TFA-11 thin film analyzer from Luzchem Research. The spin coated solutions contained: (a) 80% weight 2-heptanone, 20% weight fluorinated polymer (FP), and pyrene 0.5 wt % from dry polymer weight, (b) 15% weight PMMA, 85% weight 2-heptanone, and pyrene 0.33% weight from dry PMMA weight, (c) 80 wt % 2-heptanone, 20 wt % PMSSQ, and pyrene 0.5 wt % from PMSSQ weight. After coating, the films were subjected to 60 s postapplication bake (PAB) over an aluminum plate in an oven at 95−98 °C, allowing evaporation of the solvent. The concentrations of pyrene in the spin coated solutions were 4.5×10^{-3} M in the FP solution and 2.1×10^{-3} M for PMMA.

T_g Measurements. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis of FP were performed with 12.76 mg samples and recorded with 2960 SDT V3.0F equipment, STD-MS method. The heating rate was 20 °C/min, between room temperature and 1000 °C under an air flow of 100 mL/min.

UV Exposure. Laser exposure was done using GSI-Lumonics Pulsemaster model 846 excimer lasers using F_2 or F_2/Kr mixtures for 157 and 248 nm, respectively, and a Lumonics Excimer-500 laser containing Xe/HCl for 308 nm. Continuous wavelength exposure was done with a Hybrid Technology Group (HTG) exposure unit using a mercury−xenon lamp and filter such that the light wavelength was centered at 249 ± 5 nm, with energy of 0.82 W/ m^2, as determined with the Luzchem SPR-1 spectroradiometer. The energy of the incident laser beam was measured with a JD2000 joulemeter radiometer and a Coherent J45LP-MB photon detector. In order to obtain the patterns, copper masks with hexagonal holes were placed on top of the films. The centers of the hexagons were 60 μm apart. The transmitting part of the mask was required to have actual holes because laser radiation at 157 nm is absorbed by almost any material. The 157 nm exposures were done under nitrogen. For all the other wavelengths, the exposure was done under air, in the laboratory atmosphere. Continuous wavelength exposure was done in the HTG exposure unit mentioned above.

Fluorescence Spectroscopy. Fluorescence emission of the films was recorded using a Perkin-Elmer LS 50 fluorimeter in a front-face setup and variable slits for emission and excitation.

Optical Fluorescence Microscopy. Fluorescence microscopy images were recorded using a Leica DMLS optical microscope, with a 50 W mercury lamp which provided the excitation light, and a Leica DFC 300 FX camera. The software used to record images was IM50 version 4 release 117 from Leica. An XF-02 filter cube (excitation centered at 367 nm, emission long pass 470 nm) from Omega Optics was used to monitor fluorescence of pyrene excimers. The optical spectrum of the excitation light was recorded with a Luzchem Spectroradiometer SPR-1. (see the Supporting Information) The copper mask was removed from the top of the polymer films prior to recording images with the fluorescence microscope.

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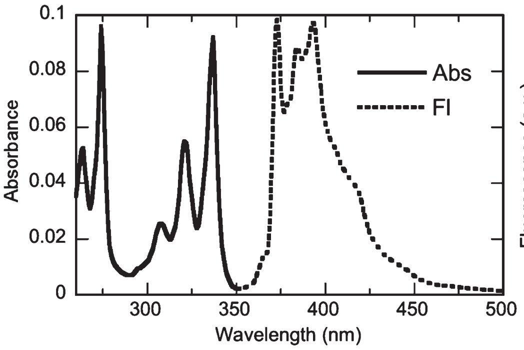

Figure 1. Absorption (continuous line) and fluorescence (dashed line) of pyrene in a 930 nm thick film of PMMA. The excitation wavelength for the fluorescence spectrum was 330 nm. The pyrene loading represented 0.33% wt relative to PMMA.

Image Color Analysis. Color analysis of images from fluorescence microscopy were analyzed by examining the contribution of fundamental colors red, green, and blue to the final color with a software application from Apple Computer Inc., namely DigitalColor Meter v. 3.0. This application determines the color value of any pixel in the images using the RGB scale.

Results

Exposure of High T_g Polymer Films (FP and PMMA) to Pulsed Laser Radiation. Selection of polymers was done taking into account their T_g. Bulk PMMA has a T_g of 104−105 °C.[25] The T_g of FP is ~216 °C, as measured with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC; see the Supporting Information). PMMA films with a thickness of 930 nm show an absorbance of 0.18 centered at ~218 nm, while films of FP and PMSSQ with thicknesses of 441 and 476 nm, respectively, are practically transparent in the interval 190−300 nm (see the Supporting Information).

Typical absorption and fluorescence spectra of pyrene in polymer films are shown in Figure 1. The initial stock solution contained PMMA (15% wt) dissolved in 2-heptanone (85% wt), to which we added pyrene 0.33% relative to PMMA weight. It is a common practice in the semiconductor industry to express the amounts of additional compounds as a percent relative to the mass of polymer. In this case, the molar concentration of pyrene was 2.1×10^{-3} M. A few drops of solution were spin-coated on quartz discs, then baked at 96 °C for 60 s to ensure evaporation of the solvent, followed by rapid cooling to room temperature on a metallic surface.

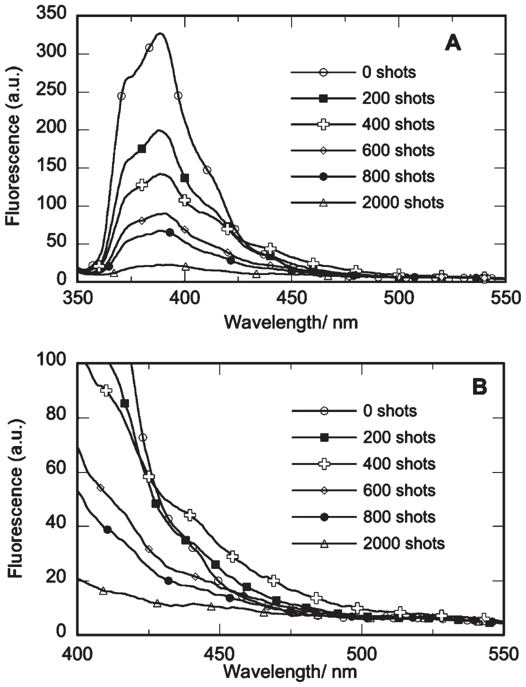

Figure 2. Fluorescence of pyrene containing FP films (~440 nm thick) exposed to laser radiation at 157 nm, 1.7 mJ/cm^2 per shot, 15 shots/s (A); the expanded region between 400 and 550 nm (B). The excitation wavelength was 330 nm.

We noticed that exposure of pyrene containing FP films to laser radiation at 157 nm causes a decrease in emission of the monomer centered at 390 nm, accompanied with an increase in emission at 470 nm, the region characteristic for excimer emission; Figure 2. The vibrational bands in the fluorescence spectra are not so visible in Figure 2 compared to the emission in Figure 1 due to a slightly different orientation of the sample holder inside the fluorimeter and the front-face recording of the spectrum. This causes reflections (and interference) of incident radiation on the film surface to be captured by the monochromator and detector and distorts finer details of the spectrum. The increase is evident until a certain dose is delivered, and then, the intensity of 470 nm emission decreases. A solution containing FP (20 wt %), 2-heptanone (80 wt %), and pyrene 0.5 wt % relative to FP weight was spin coated on a quartz disk, then soft baked, and cooled. The film was exposed to 157 nm laser radiation, delivered in series of 200 shots up to a total of 2000 shots, with a frequency of 15 shots/s, 1.7 mJ/(cm^2 shot). The fluorescence was recorded after every 200 shots, and the fluorescence excitation wavelength was 330 nm. One can notice a decrease in the monomer fluorescence centered at 390 nm as a function of incident dose. Initial monomer fluorescence, when no laser exposure was performed, is 1.66, 2.40, and ~15 times higher than the monomer emission after 200, 400, and 2000 shots, respectively. The decrease in monomer emission is accompanied by an increase in the excimer region for the initial 400 shots. Past 400 laser shots, the excimerlike emission decreases as well. Thus at 470 nm, the intensity of excimer emission after 200, 400, 800, and 2000 shots is 1.3, 2.0, 1.0, and 0.8 times the initial emission, when no laser exposure of the film was performed. After 400 shots, the intensity of the excimer increases by a factor of 2 compared to the initial excimer emission. Above 400 shots, the excimer fluorescence intensity decreases and reaches the initial level after 800 shots, decreasing to 0.8 of the initial intensity after 2000 shots. Experiments performed at different frequencies (1, 2, 5, 8, 10, 12, 15, and 20 shots/s) showed a similar pattern of increasing/decreasing emission for both monomer and excimer, suggesting that this behavior was independent of the rate of

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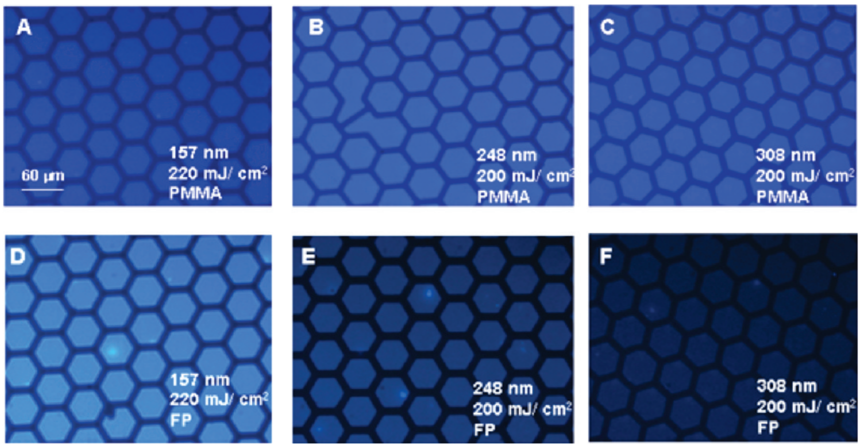

Figure 3. Emission of exposed and unexposed areas of polymer films of PMMA (A−C) and FP (D−F) containing pyrene and exposed through a mask to 220 mJ/cm^2 at 157 nm (A and D), 200 mJ/cm^2 at 248 nm (B and E), and 200 mJ/cm^2 at 308 nm (C and F). The pyrene loading was 0.5% from FP weight and 0.33% from PMMA weight, respectively. The fluorescence excitation beam was centered at 367 nm. The total incident laser energy was as follows: 4.3 mJ/cm^2 per shot at 308 nm at a frequency of 3 shots/s, 4.4 mJ/cm^2 per shot at 248 nm at 3 shots/s, and 1.1 mJ/cm^2 per shot at 157 nm at 5 shots/s.

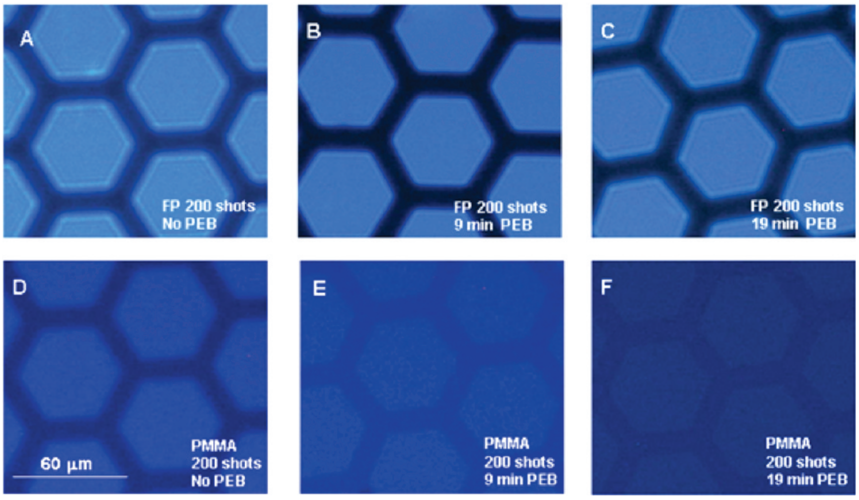

Figure 4. Fluorescence images of FP (A−C) and PMMA (D−F) films containing 0.5% and 0.33% pyrene relative to the polymer weight, exposed to 200 shots at 157 nm (1.1 mJ/cm^2 per shot 5 shots/s). The images were recorded with nonbaked films (A and D), those baked for 9 min (B and E), and those baked for 19 min, respectively (C and F).

energy delivery. For example, the fluorescence of the monomer decreased three times, while the emission at 470 nm increased 1.5 times, compared to the initial excimer emission at zero shots, when 200 shots of laser radiation [7 mJ/(cm^2 shot)] at 157 nm were delivered at frequencies of 5 and 20 shots to pyrene in 440 nm thick FP films.

Absorption spectra of FP films show an overall increase of absorption, accompanied by a broadening of the peaks. The increase in absorption is much more pronounced between 200 and 250 nm, probably due to chemical modification of the polymer matrix.

Since fluorescence is much more sensitive than absorbance, we decided to exploit this and focused our attention on the emission of these films using fluorescence microscopy. Fluorescence images from FP and PMMA films exposed to 157, 248, and 308 nm laser excitation are shown in Figure 3.

Since the highest contrast between exposed and unexposed regions of the FP films was obtained with 157 nm, we selected this wavelength for in-depth exploration of the effects of laser radiation on pyrene-doped polymer films. Films of FP and PMMA containing pyrene were exposed to 157 nm radiation (220 mJ/cm^2 delivered in 200 shots with a frequency of 5 shots/s). Fluorescence images were recorded immediately after exposure, prior to post exposure bake (PEB), and then at different PEB times; Figure 4. The images reveal that while FP films retain the emission of pyrene excimer in the exposed areas after 9 and 19 min of baking at 98 °C, the emission in exposed areas of the PMMA film gradually fades during baking, until eventually the exposed and unexposed areas become almost indistinguishable.

A PMMA film containing pyrene was subjected to double exposure at 157 nm, with the hexagonal mask placed in a different position during the second exposure, resulting in three regions: unexposed (3), exposed once (1) to 200 shots (220 mJ/cm^2), and exposed twice (2) (total 400 shots, 440 mJ/cm^2). The fluorescence images were recorded after one exposure, and then, another series of

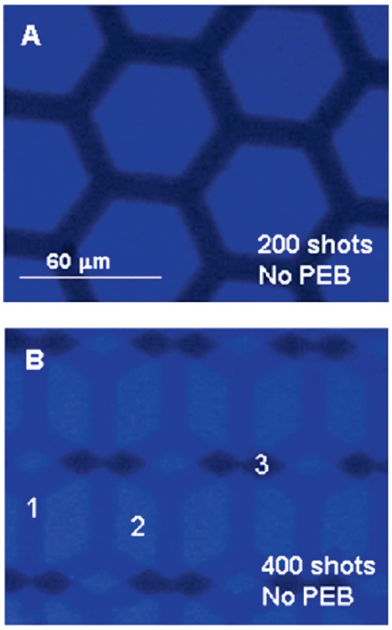

Figure 5. Images of fluorescence emission of PMMA films containing pyrene (0.33 wt % relative to PMMA) exposed to 220 mJ/cm^2 (A) and 440 mJ/cm^2 (B) at 157 nm. The energy was 1.1 mJ/(cm^2 pulse), and the frequency was 5 shots/s. The excitation light was centered at 367 nm; the second exposure was performed after moving the mask.

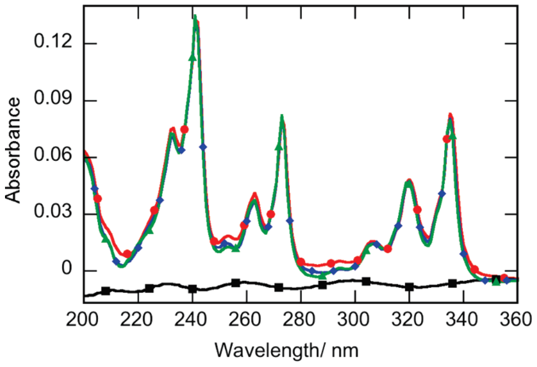

Figure 6. Absorption spectra of PMSSQ films containing pyrene (0.5% relative to PMSSQ): nonsandwiched 1 min PAB (■, black), sandwiched no PAB (●, red), sandwiched 2 min PAB (♦, green), and sandwiched 4 min PAB (▲, blue). The baseline was recorded with two sandwiched uncovered quartz discs, causing a slightly negative signal for the sample with just one quartz plate. PAB at 98 °C.

200 shots was performed after moving the mask. The images (Figure 5) show the possibility of further imaging the unexposed areas.

Exposure of Low T_g Polymer Films (PMSSQ) to Pulsed Laser Radiation. PMSSQ has a T_g below room temperature, and pellets of PMSSQ become a viscous liquid when removed from the fridge (4 °C). The influence of the T_g of the polymer on the emission of pyrene was studied in films of PMSSQ containing pyrene using the same methodology as for FP and PMMA. Recording of absorption spectra following PAB at 100 °C reveals the absence of pyrene signals; Figure 6. A simple experiment with a PMSSQ film containing pyrene sandwiched between two quartz discs, baked at 98 °C for 4 min shows the characteristic absorption spectrum of pyrene. We conclude that pyrene sublimes from the PMSSQ films during PAB, unlike in the case of PMMA and FP. The same behavior was recorded with fluorescence microscopy when PMSSQ films containing pyrene underwent PAB prior to 157 nm exposure: no excimer or monomer emission from the exposed areas was observed. Exposure of PMSSQ films containing pyrene to 157 nm radiation through the copper grid, but without being subjected to PAB, gave the clear hexagonal patterns also noticed for PMMA and FP films. Fluorescence spectroscopy of the baked and unbaked films revealed the same behavior: no emission of pyrene when the films were excited with 330 nm following PAB, while those which were not submitted to PAB showed the characteristic emission of pyrene monomer.

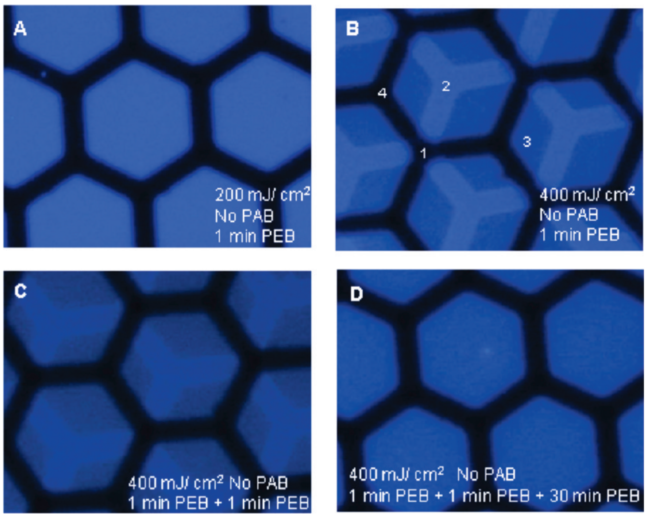

Figure 7. Fluorescence images of pyrene-containing PMSSQ films subjected to 157 nm exposure through the copper mask and to thermal treatment: 200 mJ/cm^2 incident energy, no PAB, 1 min PEB (A), 400 mJ/cm^2, 1 min PEB, no PAB (B), 400 mJ/cm^2, 2 min PEB, no PAB (C), and 400 mJ/cm^2, no PAB, 32 min PEB (D). The energy was delivered in a series of 200 shots, 1.0 mJ/cm^2 per shot, 5 shots/s. The exposed film was 460 nm thick, and the excitation wavelength was 367 nm.

Fluorescence microscopy revealed that PEB for 10 min of pyrene-containing PMSSQ films (no PAB after spin coating), following exposure to 157 nm through the copper masks, did not erase the blue color in the exposed areas, nor did it cause any fading, unlike in the case of pyrene-containing PMMA films. However, the unexposed areas are completely dark, no emission of the pyrene monomer being detected; this result is consistent with sublimation in unexposed areas.

Fluorescence microscopy images of double-imaged PMSSQ pyrene-containing films subjected to thermal treatment are shown in Figure 7. The same film is imaged in all four pictures, A–D. Without PAB, the film was exposed 157 nm laser radiation for a dose of 200 mJ/cm^2, 1.0 mJ/(cm^2 shot), at a frequency of 5 shots/s, followed by 1 min PEB, and then the fluorescence image was recorded; Figure 7A. A second exposure to 200 mJ/cm^2 (400 mJ/cm^2 in total) was performed with the copper mask in a different position; Figure 7B. One can distinguish four distinct regions: no exposure (region 1), exposed only the first time (region 2), exposed both times (region 3), and unexposed the first time but exposed a

Table 1. Ratios of the Intensities of Blue, Green, and Red Colors in the Exposed vs Unexposed Regions of PMMA and FP Films Containing Pyrene (0.33 and 0.5 wt % Relative to PMMA and FP, Respectively)[a]

color	PMMA 157 nm	PMMA 248 nm	PMMA 308 nm	FP 157 nm	FP 248 nm	FP 308 nm
red	1.2	1.7	1.2	1.8	1.8	1.2
green	1.4	2.0	1.5	2.5	2.1	1.3
blue	1.6	1.6	1.6	2.2	2.0	1.4

[a] The films were exposed through hexagonal copper masks to laser radiation at 157 nm (220 mJ/cm^2), 248 nm (200 mJ/cm^2), and 308 nm (200 mJ/cm^2).

second time (region 4). Next, the film was baked for another minute at 98 °C and cooled to room temperature on a metallic surface, and its fluorescence was recorded; Figure 7C. Further heating of the film at 98 °C for 30 min leads to the complete erasure of the pattern obtained during the second exposure; Figure 7D.

Continuous Wave Exposure. Exposure of pyrene-containing FP and PMMA films to a mercury−xenon lamp in an HTG exposure unit for up to 500 s did not cause any change in the fluorescence and absorption spectra; Figure S5 in the Supporting Information. The exposure was performed through a band-pass filter, 249 ± 5 nm, with incident power of 0.082 mW/cm^2, to a total of up to 41 mW/cm^2. The spectrum of the incident radiation is available in the Supporting Information.

Discussion

Upon exposure to UV light, pyrene and the polymer matrix undergo a series of physicochemical transformations. Excimer formation, covalent bonding to the medium, and solvent photolysis were reported to occur.[26−34]

In the present experiments, pyrene plays a double role: sensitizer and fluorescent probe. Thus following absorption, pyrene either fluoresces or releases the energy to the environment as heat; depending on the wavelength, this function is shared with the polymer itself. Softening of the polymer matrix allows pyrene molecules to diffuse within the film, leading to excimer-formation; the resulting pyrene pairs are then trapped in the cooled polymer matrix. The fluorescence increases at 470 nm due to the excimer and the monomer fluorescence decreases are possible only if two molecules diffuse toward each other and form an excimer. Since the excimer emission is not observed before exposure to laser radiation, it is safe to conclude that exposure assists excimer formation. Diffusion is controlled, among other parameters, by the T_g of the polymer, that is in turn influenced by the presence of pyrene, by the thickness of the polymer films, and is lower in thin films compared to bulk polymers.[34,35] The optimal distance between pyrene molecules forming an excimer is ~3.5 Å.[36] Assuming a uniform distribution in the film, and that all the solvent was removed during spin coating and baking, for the three polymers used, pyrene molecules are between 3.5 and 4.5 nm average distance, or about 10 times the molecular dimensions. The distribution will of course be random, but the distances are large enough to prevent random excimerlike pairs, yet sufficiently short for such pairs to form upon laser excitation/heating.

The excimer fluorescence intensity after 400 laser shots at 157 nm, Figure 2B, proves that pyrene excimers are formed during irradiation. The intensity decreases during prolonged irradiation, probably reflecting degradation of the polymer matrix, photodarkening of the polymer being previously reported,[37,38] and quenching of fluorescence by species formed during exposure.

Monitoring the contribution of red, green, and blue to the formation of colors in the exposed and unexposed areas of pyrene containing films reveals a shift of emission toward longer wavelengths, consistent with excimer formation.[31] The results are displayed as ratios between each color's intensity in the exposed and unexposed areas of PMMA and FP films exposed through the copper masks to 157, 248, and 308 nm; Table 1. The data corresponds to the images from Figure 3.

Formation of pyrene excimers is attributed to photochemical and photothermal effects of laser radiation. Ablation of PMMA films at 248 nm with pyrene as dopant was studied by Fujiwara et al., who discovered that when exposed to 248 nm, 150 mJ/cm^2, each pyrene can absorb up to ten photons, form higher excited states (S_n, T_n, excited state ions), and yet not be destroyed.[20,39,40] These molecules return to S_1 or T_1 through fast vibrational relaxation releasing the energy as heat and may absorb again, a process termed *cyclic multiphoton absorption* by Fukumura.[40] Analysis of a PMMA film containing pyrene, and following 308 laser excitation, showed that pyrene was not destroyed.[39] Our work involves exposure at lower energy doses, allowing us to assume that pyrene was not

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significantly destroyed during exposure and, thus, that the decrease in monomer emission (at least in PMMA) may be caused by several factors beyond formation of excimers or aggregates, such as quenching of fluorescence through various mechanisms, or simply by sublimation. Fluorescence may be quenched by photoproducts resulting from polymer chain or side group scission as previously reported in acrylate polymers.[41] Film damage may play a role in the decrease of monomer and excimer emission at higher energy doses (above 400 shots), as seen in Figure 2.

The images from Figure 3 and the ratios of intensities of different colors from Table 1 may be interpreted by taking into account the absorbances at the exposure wavelengths and the T_g of the polymers. The higher the absorbance, the more photons are absorbed and consequently more energy is released to the polymer matrix, thus softening it. For PMMA films, the greatest increase in red, blue, and green in the exposed areas is achieved with 248 nm exposure. At 248 nm, PMMA absorbs (Figure 1A) slightly more compared to 308 nm where PMMA is practically transparent. At 157 nm, both pyrene and PMMA have very large absorbances.

FP is a terpolymer especially designed for photolithography at 157 nm, with C_2F_4 units, Chart 1, which lowers the overall absorbance. However, other units in FP introduce some absorbance at 157 nm, enough that the polymer absorbs some light. This absorption combined with that of pyrene creates an ideal environment, which facilitates formation of excimers when exposed to 157 nm, compared to 248 and 308 nm. At 248 and 308 nm, FP is virtually transparent, only pyrene absorbs slightly. The low absorbance of FP combined with its very high T_g do not create a fluidlike environment for pyrene migration, and this is reflected also in the contribution of green and blue in FP exposed to 308 and 248 nm. The highest increase in green and blue is for areas of FP exposed to 157 nm.

The images recorded in Figure 4 during a control experiment clearly show the influence of T_g on the formation of excimers. In lower T_g films (PMMA), the image formed during exposure is largely erased during PEB at 98 °C for 19 min; Figure 4. The erased pattern proves that pyrene vicinal pairs are eliminated during baking, when softening of the polymer matrix allows these pairs to diffuse apart; thus, these neighbors are not covalently bound to a common structure. Pyrene does not leave the film during baking since in another control experiment a fluorescence image of a PMMA film containing pyrene, but unexposed to 157 nm, has the same color and appearance. The baking temperature is very close to the reported T_g of bulk PMMA but well below the T_g of FP (206 °C). We speculate that in FP the excimer precursor pairs do not diffuse apart since the polymer matrix is still rigid at 98 °C; other contributory aspects may be grafting of pyrene to polymer chains, a phenomenon well-documented in prior literature reports, and cross-linking of polymer chains. The ratio of the intensities of red, green, and blue ($I_{\text{exp}}/I_{\text{unexp}}$) between the exposed and unexposed regions for the pyrene-containing PMMA films exposed to 157 nm and then baked at 98 °C for 19 min are close to unity, 1.07, 1.17, and 1.01, respectively (see the Supporting Information). In the case of FP films, the ratio did not change significantly; in fact, it increased for the blue component, suggesting that the excimer pairs were not affected by baking well below the T_g of FP.

Films of PMMA containing pyrene imaged easily and could be readily erased by PEB near T_g (Figure 4). Double exposure experiments (Figure 5) revealed that regions exposed only once can be imaged further and that unexposed areas remain photosensitive.

The low T_g polymer, PMSSQ, shows a different behavior compared to the high T_g polymers when subjected to the same photochemical treatment at 157 nm. Fluorescence images of PMSSQ films baked for 1 min after spin coating, and prior to exposure, displayed only a dark background, and fluorescence spectra did not show the characteristic peak of monomer emission. Studies of the absorption spectra reveal that pyrene sublimes during PAB after just 1 min. Indeed, when a quartz disk is placed on top of the PMSSQ film containing pyrene, protecting it, the pyrene signal is preserved even after 4 min of baking at 98 °C; Figure 6. PMSSQ films containing pyrene first exposed to radiation at 157 nm and then baked even for 10 min at 98 °C, clearly displayed the hexagonal pattern of the copper mask (images not shown). This behavior suggests that during exposure pyrene is either trapped within or bonded to the polymer. A likely mechanism involves cross-linking of the polymer, which has been previously shown to occur when PMSSQ is subjected to thermal curing (100−450 °C), thus preventing pyrene from escaping the film.[29] Another plausible explanation is that in this system pyrene is attached to the polymer matrix through covalent bonds. This is supported by images that were not erased even after PEB for 32 min, Figure 7D, unlike the case of PMMA. Unfortunately, these experiments do not reveal to what extent the chemistry occurs directly during exposure or during prolonged baking. Previous literature reports show that aromatic molecules may chemically bind to certain polymer matrixes following exposure to UV and γ radiation.[26−28,30−33] Thomas et al. reported on covalently bound pyrene to polyethylene in films irradiated with γ rays at room temperature[14,26] and proposed that pyrene traps radical species formed by scission of polymer bonds. Weiss et al. also reported on pyrene molecules covalently attached to the polymer in low density polyethylene (LDPE) films irradiated under nitrogen.[30] Due to the very small volumes of films employed in these experiments, there was not enough material to perform an NMR or GPC analysis of the exposed samples. However, literature reports are consistent with our spectroscopic data and give us enough information to rationalize the processes that occur during exposure.

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Double exposure experiments, Figure 7, reveal the difference between PMSSQ and PMMA films containing pyrene. The second exposure of PMSSQ films clearly shows that the regions unexposed during the first exposure could not be imaged (region 4). This is due to the fact that pyrene in the unexposed regions had sublimed during PEB. Compared to PMMA films (higher T_g), in PMSSQ the exposed areas retain their color even after 32 min of baking, whereas for PMMA, 19 min of baking were enough to erase the imaged areas.

Continuous wave exposure did not induce any changes in the absorption or emission spectra of polymer films containing pyrene, unlike the exposures to laser radiation. The high peak power of the laser beam is needed to soften the polymer matrix and to allow sufficient diffusion of pyrene molecules.

Conclusions

Thin films of various polymers containing pyrene showed formation of excimers that persist as vicinal pairs when exposed to laser radiation with various wavelengths (157, 248, and 308 nm). Continuous wave exposure did not cause excimer formation. Low T_g PMSSQ behaves different compared to high T_g PMMA and FP. The formation of excimers is favored by softening of the polymer matrix induced by the energy released by excited pyrene and, in some systems, the polymer itself. Thermal erasure of the fluorescence images in the case of PMMA upon baking at a temperature close to T_g shows that pyrene is not covalently attached to the polymer matrix. In the case of PMSSQ, the images where not thermally erased after baking at a much higher temperature than T_g. This is attributed to formation of a cross-linked network structure which prevents the pre-excimer pairs from diffusing apart during heating, or by covalently bonding to the polymer matrix. One can envision applications of these results in the design of recordable substrates with applications in optical storage of data and in photolithography.

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Supporting Information Available: Absorption spectra for the three polymer films in the 190−300 nm region; tables of digital color measurements based on fluorescence images; spectra of light sources used for flood exposure and for fluorescence excitation; TGA and DCS data for polymer FP. This material is available free of charge via the Internet at http://pubs.acs.org.