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Aromatic Monoazines as Fluorescent Sensors for Photoacid Generation in Thin Polymer Films

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This paper reports a novel approach to monitor photoinduced acid generation in polymer films of the type used in microlithography. We have employed fluorescent acid-sensitive sensors to monitor the progress of photoacid generation in solution and in thin polymer films. We have studied the effect of *p*-toluenesulfonic acid on the spectral properties of 2-phenylpyridine, 2-phenylquinoline, and acridine in diglyme solution and in poly(methyl methacrylate) (PMMA) films using absorption and fluorescence spectroscopy. In both cases a bathochromic spectral shift and an increase in fluorescence quantum yield are observed upon protonation. In samples containing a photoacid generator, the acid production upon irradiation could be monitored by observing the increase in fluorescence intensity with proceeding irradiation time in both solution and PMMA films. This new acid-monitoring method may find application in the study of diffusional processes in polymer films.

Introduction

In integrated circuit fabrication, microlithography is used to image the various thin-film materials which build up the device on a semiconductor substrate. The primary step of the microlithographic process is the delineation of the desired circuit design in a resist layer, which generally consists of a photosensitive thin polymer film spin coated on the semiconductor material. This image-transfer process is usually achieved by UV exposure through a photomask containing the circuit pattern. Depending on the chemical nature of the resist material, the exposed regions of the photoresist become *more* or *less* soluble than the unexposed areas, and subsequent development of the latent image yields a *positive* or *negative* three-dimensional relief image of the circuit layout on the substrate.[1−3]

Responding to the ever-increasing circuit density, new high-resolution exposure technologies such as deep-UV, e-beam, and X-ray lithography have been developed. However, these new technologies require departure from the conventional diazoquinone/novolac based resists widely used today.[3] Therefore, several new classes of chemically amplified resists have been developed,[4−9] all of which utilize a photoacid generator (PAG), i.e., a substance that produces acid as one product of photolysis. In these formulations, during a postexposure baking step, an acid-catalyzed reaction is initiated that modifies the properties of the matrix to achieve the required difference in solubility between the exposed and unexposed resist areas.

It is important to develop techniques to easily monitor the generation of acids in thin (∼1 μm) polymer films. We believe that fluorescence spectroscopy is the suitable tool for this purpose. Further, with the minimum feature size expected to approach the 0.1 μm mark within the next decade, preserving the integrity of the latent image becomes more and more critical. Diffusion of the photogenerated acid during the period of time between exposure and development can cause contrast loss and ultimately loss of the latent image. This is especially relevant for chemically amplified photoresists that require a postexposure baking step, which in turn facilitates the diffusion of the acid due to the high temperature normally employed. Due to the ever-decreasing feature size, diffusion of the photogenerated acid within the photoresist material leading to the deterioration of the latent image has recently become a matter of great concern in microlithography. Thus, for the ability of microlithography to keep pace with the demand for higher resolution imposed by microelectronics, the need for detailed knowledge of acid generation and diffusion processes in photoresist systems will increase dramatically during the next few years. It is thus important to develop spatially resolved techniques to monitor the photogeneration of acid in these thin polymer films; fluorescence spectroscopy may eventually allow the extension of these methods for the determi-

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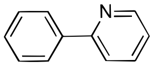
nation of diffusion coefficients in thin films (typically ~1 μm) with features in the submicron range.

While many molecules with pH-dependent fluorescence properties are known, most of them find applications in fluorimetric titrations or as probes for intracellular pH determinations, i.e., they are used in aqueous media. For resist applications it is more important to develop sensors that are soluble in organic solvents of moderate polarity and that are compatible with applications in thin polymer films.[10,11]

It has been known for a long time that aromatic monoazines such as acridine and quinoline are essentially nonfluorescent in non-hydrogen-bonding solvents, whereas the protonated forms of these molecules were found to be highly fluorescent, at least in aqueous solutions.[12−16]

These findings make this class of molecules an interesting candidate for potential acid sensors. Thus, we employed 2-phenylpyridine (**1**), 2-phenylquinoline (**2**), and acridine (**3**) for our study.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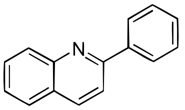
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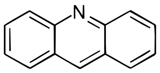
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The phenyl derivatives provide a bathochromic spectral shift compared to the unsubstituted molecules. The long-wavelength emission characteristic of the sensor is required to avoid overlap with the fluorescence of the phenolic polymers that are widely used in microlithography. We preferred the 2 isomers over the 3 and 4 isomers since a recent study of phenylpyridines by Testa et al.[17] indicated that they provide the most desirable combination of properties with respect to our application, i.e., both the highest absolute fluorescence quantum yield and the most pronounced increase in fluorescence quantum yield upon protonation.

Since, except for Mataga's[12] seminal work, no studies dealing with the fluorescence properties of the protonated forms of these substrates in nonaqueous solutions have been published, we have first investigated the effect of acid on the absorption and fluorescence properties in diglyme solution, employing both direct addition of *p*-toluenesulfonic acid and photoacid generation using 1,2,3-tris(toluenesulfonyloxy)benzene,[18] a PAG yielding *p*-toluenesulfonic acid. Diglyme was the solvent of choice since it is a good coating solvent for the materials used. In a second step we extended our studies to thin polymer films using poly(methyl methacrylate) (PMMA) as a model polymer. PMMA was the polymer of choice for this work because of its excellent spectroscopic properties. In particular, PMMA is UV-transparent and does not have the background fluorescence that characterizes other polymers such as novolac.

Experimental Section

Materials. Diglyme (bis(2-methoxyethyl) ether, spectrophotometric grade), poly(methyl methacrylate) (average MW 120,000), *p*-toluenesulfonic acid monohydrate, 2-phenylpyridine, 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole and 1,1,4,4-tetraphenyl-1,3-butadiene were purchased from Aldrich and used as received. The acridine (Aldrich) was recrystallized from hexane and ethanol followed by treatment with activated charcoal and then sublimed. The 2-phenylquinoline (Aldrich) was first sublimed and then recrystallized several times from methanol and 2-(1-naphthyl)-5-phenyloxazole (Fluka) was used without further purification. The PAG 1,2,3-tris-(toluenesulfonyloxy)benzene (**4**) was prepared according to literature procedures.[18]

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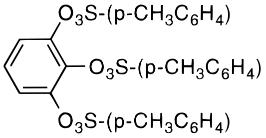

General Techniques. Absorption spectra were recorded using a Varian Cary 1E spectrophotometer. Fluorescence spectroscopy was carried out using a Perkin-Elmer LS-50 luminescence spectrometer. To obtain the fluorescence spectra in thin polymer films a front face attachment (~45° excitation) was employed.

Thin polymer films were spin coated at 3000 rpm (20 s) from 25% w/v diglyme solutions, onto 1 in. quartz disks using an Integrated Technologies Inc. P-6000 spin coater. Typical film thickness was ~1 μm.

UV irradiation was performed at room temperature in a photoreactor equipped with four RPR-254 nm lamps from the Southern New England Ultraviolet Co.

Experiments in Solution. Solutions of the three fluorescent sensors in diglyme were prepared to give an absorbance of 0.1−0.2 at the excitation wavelength. From these solutions, two sets of samples were made, one in which *p*-toluenesulfonic acid (0.05 M) was added directly and one with PAG added (0.01 M). The latter set of samples was irradiated at 254 nm in a photoreactor for various time intervals and fluorescence spectra were taken after each period of irradiation.

The fluorescence quantum yields of **1**−**3** in diglyme were measured relative to 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD, $\Phi_f = 0.69$),[19] 2-(1-naphthyl)-5-phenyloxazole (α-NPO, $\Phi_f = 0.78$),[19] and 1,1,4,4-tetraphenyl-1,3-butadiene ($\Phi_f = 0.52$)[20] in cyclohexane, respectively. In these experiments, the absorbance of all samples at the excitation wavelength did not exceed 0.1, and the emission spectra were corrected for photomultiplier response between 380 and 650 nm. All experiments in solution were carried out with deaerated samples using sealed 1 cm × 1 cm Suprasil quartz cells.

Experiments in PMMA Films. Samples of **1**−**3** were prepared in a 25% w/v solution of PMMA in diglyme to give an absorbance between 0.1 and 0.4 at the excitation wavelength. Again, two sets of samples were prepared as described above and spin-coated onto quartz disks. After being baked at 90 °C for 10 min, the samples containing PAG (0.2 M in the coating solution) were irradiated at 254 nm with RPR-254 lamps for various time intervals and fluorescence spectra were taken. Thin-film interference effects are anticipated to

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[10] An attempt to use the fluorescence from acid-sensitive polymers as acid sensors has been reported: Carey, W. P.; Jorgensen, B. S. *Appl. Spectrosc.* **1991**, *45*, 834.

[11] McKean et al. used a merocyanine dye as a sensor to monitor acid generation in thin polymer films. However, contrary to our approach using *fluorescence* spectroscopy, this method was based on the changes in the *absorption* spectrum of the dye upon protonation: McKean, D. R.; Schaedeli, U.; MacDonald, S. A. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3927.

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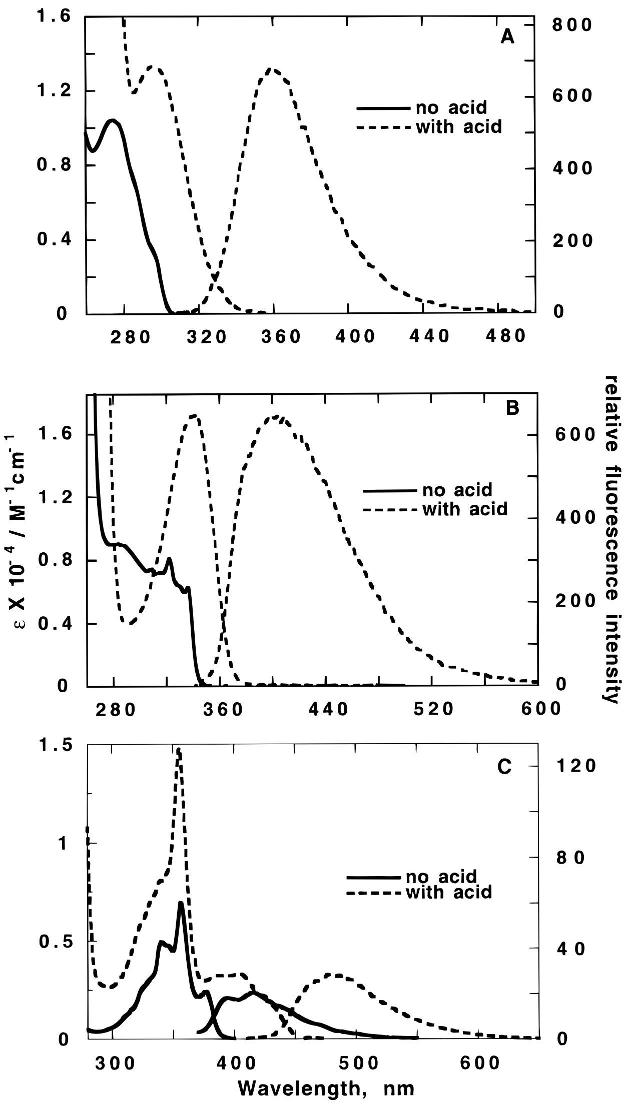

Figure 1. (A) Absorption and fluorescence (normalized to the longest wavelength absorption band) spectra of 2-phenylpyridine with and without *p*-toluenesulfonic acid in diglyme at room temperature. No fluorescence signal due to **1** was observed in the absence of acid. (B) Same as (A) for 2-phenylquinoline. No fluorescence signal due to **2** was observed in the absence of acid. (C) Same as (A) for acridine with and without *p*-toluenesulfonic acid in diglyme at room temperature.

be minimal due to the use of impure monochromatic light, a transparent substrate (quartz), and a nonreflective aluminum backing.

Results and Discussion

Experiments in Solution. Figure 1 shows the effect of 0.05 M *p*-toluenesulfonic acid on the absorption/fluorescence spectra of **1**−**3** in diglyme. The absorption spectra of each of the three compounds show both a bathochromic shift of the ^1L_a band and an increase in intensity of the ^1L_b band relative to the samples without acid.[21] The fluorescence spectrum of acridine exhibits the same bathochromic shift that is observed in the absorption spectrum. No fluorescence due to the unprotonated species could be detected for **1** and **2** with our instrument, indicating that the fluorescence quantum yield of these molecules in diglyme must be very low (<0.0001). These findings are in accordance with Testa's results, who was unable to detect any fluorescence for **1** in several organic solvents. The fluorescence quantum yields of all three compounds are listed in Table 1. Since a very similar behavior has been found to be characteristic for monoazines upon protonation in aqueous solution,[13,15] we conclude that the observed changes are due to the protonation of these molecules caused by the *p*-toluenesulfonic acid. Thus, it should be possible to monitor the photogeneration of acid in diglyme by simply monitoring the change in fluorescence intensity. To check whether this is correct, we employed 1,2,3-tris(toluenesulfonyloxy)benzene (**4**), a PAG yielding *p*-toluenesulfonic acid, to monitor the photoacid generation upon irradiation at 254 nm. Figure 2 shows the fluorescence spectra of 2-phenylquinoline and acridine in the presence of PAG in diglyme

Table 1. Fluorescence Band Maxima (λ_{max}), Quantum Yields (Φ_f), and Excitation Wavelengths Used for the Fluorescence Spectra in Figure 1 (All Data in Diglyme at Room Temperature)

sensor molecule	fluorescence λ_{max}/nm	ϕ_f	excitation wavelength/nm
2-phenylpyridine[a]		<0.0001	
2-phenylpyridinium cation	359	0.031	300
2-phenylquinoline[a]		<0.0001	
2-phenylquinolinium cation	409	0.016	340
acridine	414	<0.001	365
acridinium cation	480	0.31	415

[a] No fluorescence could be detected with our instrument (see text).

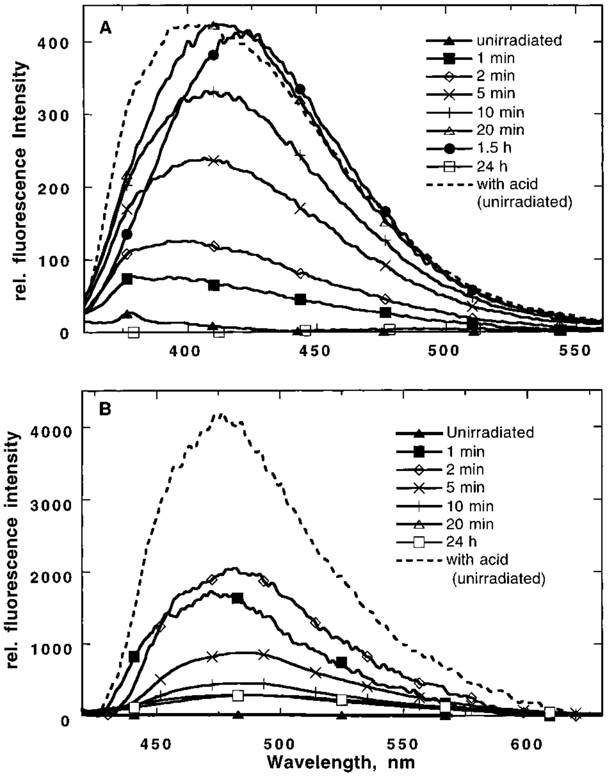

Figure 2. (B) Changes in fluorescence spectra of 2-phenylquinoline in diglyme (room temperature) in the presence of PAG upon irradiation at 254 nm for various irradiation time intervals. Also depicted is the fluorescence spectrum of **2** (same concentration) without PAG but with *p*-tolenesulfonic acid added (unirradiated). The excitation wavelength was $\lambda_{ex} = 340$ nm. (B) Same as (A) for acridine; $\lambda_{ex} = 415$ nm.

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[21] The spectra of the protonated forms are dominated by the absorption of the acid below 290 nm.

taken upon subsequent intervals of irradiation time. The increase in fluorescence intensity upon irradiation observed for both compounds indicates acid production.

Due to the relatively small spectral shift upon protonation observed for **2**, the 2-phenylquinolinium cation could not be excited selectively. The weak fluorescence observed for the unirradiated sample is due to trace impurities.

In the case of 2-phenylquinoline, no further increase in fluorescence intensity was observed for irradiation times longer than 20 min, indicating that all sensor molecules had been protonated at this time. This is supported by the finding that the fluorescence intensity observed after 20 min and in the experiment where the acid was added directly to the same solution are essentially the same.[22] Furthermore, this implies that photodegradation of the sensor due to irradiation is negligible at this point, and even the spectrum recorded after 1.5 h of irradiation shows only a slight decrease in fluorescence intensity accompanied by a bathochromic shift. This is at least partially due to the high concentration of PAG (which acts as an UV screen at 254 nm) rather than to the photostability of **2**, since in an irradiation experiment without PAG the 2-phenylquinoline was found to photodegrade much faster. After 24 h of irradiation the photodegradation of the sensor is nearly complete, and the observed weak fluorescence maximizing around 480 nm is probably due to a photoproduct.

In contrast to **2**, under the same conditions, acridine was found to photodegrade very quickly in diglyme solution (Figure 2B). After 5 min, the fluorescence intensity is already decreasing, maximizing between 2 and 5 min of irradiation time. Although we did not monitor the exact maximum in fluorescence intensity, the value corresponding to complete protonation of all sensor molecules without photodegradation (broken line) is not reached. This is inferred from the analogue experiment with 2-phenylquinoline where it was shown that it takes at least 20 min to achieve complete protonation.[23] Taking into account the difference in both optical density and the spectral power distribution of the xenon lamp at the excitation wavelengths, the higher fluorescence intensity observed for **3** relative to **2** in these experiments roughly reflects the difference in fluorescence quantum yields of both sensors.

Experiments in Films. Since fluorescence properties can be strongly dependent on the environment, it was important to determine whether these results could be reproduced in a thin polymer film. Again, first the effect of directly added *p*-toluenesulfonic on the absorption and fluorescence spectra was examined. Figure 3 shows that both the change in intensity and spectral shifts are essentially identical with those observed for the absorption spectra in solution, indicating that it is possible to protonate these monoazines in a PMMA film using *p*-toluenesulfonic acid. Although we did not determine the exact values of the fluorescence quantum yield in films, the qualitative changes in the fluorescence spectra parallel those observed in solution. The poor signal-to-noise ratio observed for the fluorescence spectra in film compared to the spectra in solution is due to the fact that a front face setup had to be used in these experiments.

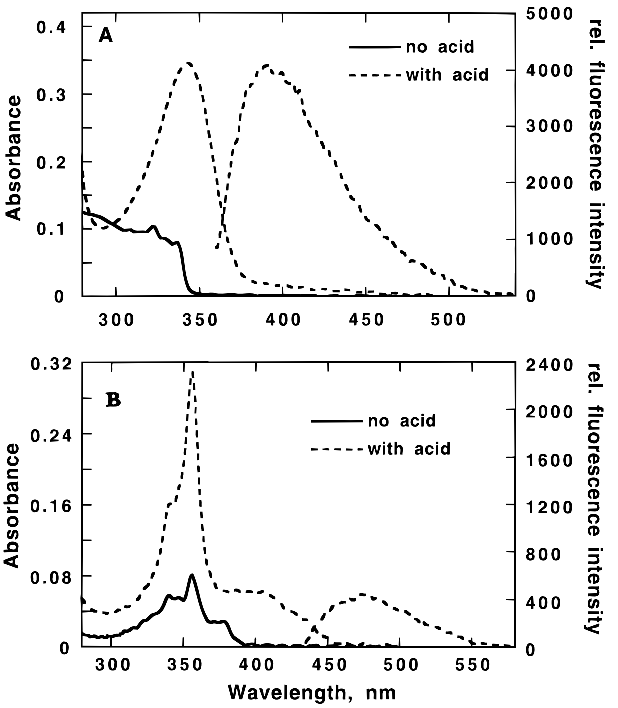

Figure 3. (A) Absorption and fluorescence (normalized to the longest wavelength absorption band) spectra of 2-phenylquinoline with and without *p*-toluenesulfonic acid in PMMA film at room temperature. No fluorescence signal due to **2** was observed in the absence of acid. (B) Same as (A) for acridine.

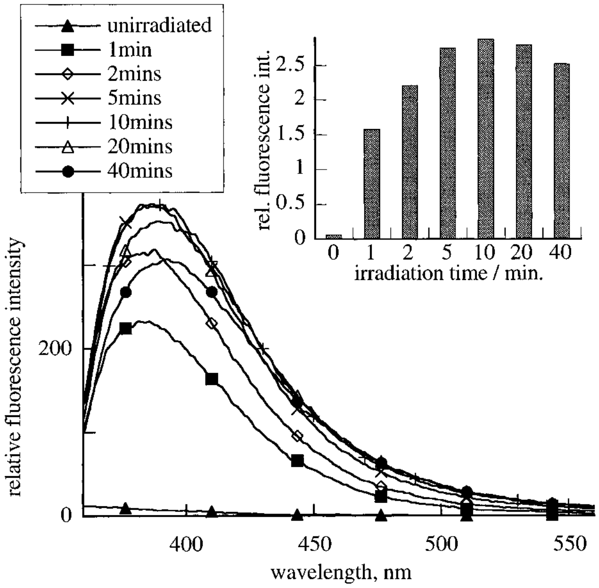

Figure 4. Changes in fluorescence spectra of 2-phenylquinoline in PMMA film (room temperature) in the presence of PAG upon irradiation at 254 nm for various irradiation time intervals; λ_{ex} = 340 nm. Inset: Bar graph of the changes in fluorescence intensity of 2-phenylquinoline in PMMA film (room temperature) in the presence of PAG upon irradiation at 254 nm for various irradiation time intervals. The bars represent the area under the respective fluorescence spectrum between 360 and 520 nm.

Finally, the photogeneration of acid in PMMA films was employed to test the suitability of the investigated sensors under conditions that come close to real photoresist applications. Again, the results (Figures 4 and

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[22] The small spectral shift between these two spectra is caused by the PAG. The same shift could be induced by just adding PAG to the solution containing sensor and acid.

[23] This must be regarded as a lower limit since the concentration of the acridine sample was approximately 4 times the concentration used in the experiment with 2-phenylquinoline.

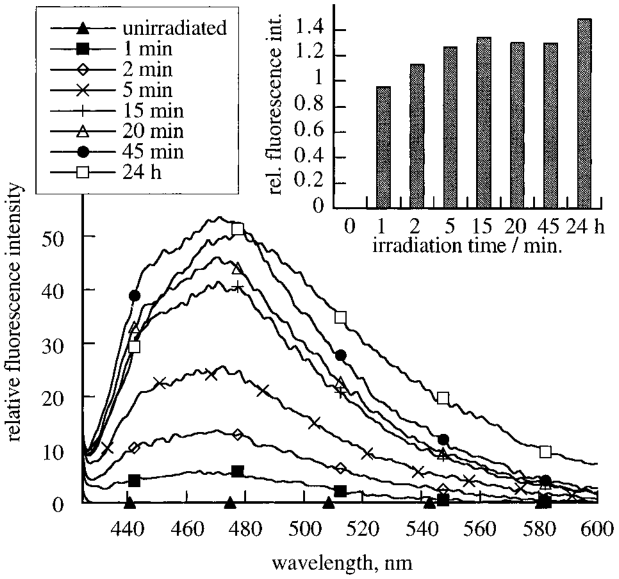

Figure 5. Changes in fluorescence spectra of acridine in PMMA film (room temperature) in the presence of PAG upon irradiation at 254 nm for various irradiation time intervals. Inset: Bar graph of the changes in fluorescence intensity of acridine in PMMA film (room temperature) in the presence of PAG upon irradiation at 254 nm for various irradiation time intervals; $\lambda_{ex} = 415$ nm. The bars represent the area under the respective fluorescence spectrum between 430 nm and 600 nm.

5) show close resemblance with those obtained in solution, clearly indicating the buildup in acid concentration in the film upon irradiation. However, in contrast to the experiments in solution, the peak value of fluorescence intensity for *both* sensors is reached before significant photodegradation takes place. Furthermore, the fluorescence intensity observed for the acridine sample is lower than for the 2-phenylquinoline. This is unexpected since the greater extinction coefficient at the excitation wavelength ($\epsilon_{340}(\mathbf{2}) = 17\ 100$ M^{-1} cm^{-1}, $\epsilon_{415}(\mathbf{3}) = 2600$ M^{-1} cm^{-1}) of **2** should not even compensate for its lower fluorescence quantum yield (taking into account the difference in both optical density and the spectral power distribution of the xenon lamp at the excitation wavelengths). Apparently, the ratio of the fluorescence quantum yields of **2** and **3** changes going from diglyme solution to PMMA film, thereby indicating that the results obtained in solution might be of only limited use for predicting the behavior in polymer films.

The results show that within the group of molecules studied here acridine is the most promising sensor with respect to applications in phenolic polymers such as poly(vinylphenol) (PVP) or novolac. This is mainly due to the spectral range of the acridinium ion fluorescence which, in contrast to the fluorescence of the 2-phenylquinolinium and especially the 2-phenylpyridinium cation, does not overlap with the fluorescence emission of these polymers containing phenolic groups. Moreover, the emission in the visible range also allows the use of a fluorescence microscope to study the acid diffusion in the polymer film directly. Furthermore, the large spectral shift upon protonation observed for acridine allows the selective excitation of only the protonated form. However, in terms of extinction coefficient at the excitation wavelength the 2-phenylquinoline proved to be superior to acridine. As mentioned above, a high excitation coefficient (i.e., high absorbances) at the excitation wavelength is needed to get a good signal-to-noise ratio even in a thin polymer film. This problem cannot be solved by just increasing the sensor concentration since the acid consumption by the sensor cannot exceed a certain limit without influencing the effectively of the imaging chemistry.

In general, an essential property of a potential sensor molecule is an increase in quantum yield and/or a significant change in spectral range of fluorescence upon protonation in a polymer matrix. Furthermore, the ideal sensor should exhibit a fluorescence spectrum at wavelengths greater than 450 nm as well as a high fluorescence quantum yield, a short singlet lifetime, and a high extinction coefficient at the wavelength used for excitation, i.e., in the region >300 nm. In contrast, the extinction coefficient at 254 nm should be small to minimize photodegradation, although it has been shown in this work that in films, this point is only of minor importance, at least for the molecules studied here. However, still a certain level of photostability is required. Moreover, the molecule should be of high molecular weight and, even more important, of moderate polarity in order to minimize the diffusion of the sensor molecule itself. Finally, the molecule must exhibit a moderate solubility in diglyme (>0.001 M), which excludes highly polar or charged molecules. Finally, thermal stability in the polymer matrix up to 90 °C is required for the molecule to survive the baking step.

Conclusion

An investigation of the spectral properties of 2-phenylpyridine, 2-phenylquinoline, and acridine in diglyme indicated that these aromatic monoazines can be protonated by *p*-toluenesulfonic acid in diglyme. The observed spectral changes and the increase in fluorescence quantum yield upon protonation make these compounds suitable sensors to monitor photoacid generation in PMMA films by fluorescence spectroscopy. 2-Phenylquinoline and acridine proved to be superior to 2-phenylpyridine, mainly because of the poor absorption/fluorescence characteristics of the latter, which makes it unsuitable for an application in the phenolic polymers which are of industrial importance. We anticipate that by using these sensors it may be possible to quantify the production of acid in photoresists and to develop techniques to study the diffusion of acid in thin polymer films.

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