A Novel Photometric Method for the Determination of Photoacid Generation Efficiencies Using Benzothiazole and Xanthene Dyes as Acid Sensors

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We report here on a new photometric method for acid quantification in nonaqueous media which has been developed to facilitate quantification for photoacid generators (PAGs) employed in resist compositions for microlithography, but may find application in other fields. The method employs laser excitation of the PAG and is based on the acid-induced bathochromic shift in the absorption spectra of a selected organic dye such as rhodamine B (**RB**), fluorescein (**Fl**), coumarin 6 (**C6**), and 2-[4-(3,4-dimethoxyphenyl)-1,3-butadienyl]-benzothiazole (**DB**). The differences in signal intensity of the protonated form of the sensor are used to evaluate the differences in acid generation efficiencies of the PAGs by relative actinometry. To test this methodology, we have determined the photoacid generation efficiencies of 2-methyl- (**1**), 2-(2′-furyl ethylidene)- (**2**), and 2-(4′-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine (**3**) in acetonitrile by laser flash photolysis, using direct 308 nm laser excitation for **2** and **3** and 355 nm excitation and various phenothiazine derivatives as sensitizers for **1**. The values determined this way for **2** and **3** using the four different dyes coincide fairly well, and the absolute values are in good agreement with those determined independently with an established technique earlier. Under sensitized conditions, the efficiency of acid generation seems to equal the combined quenching efficiencies of the S_1 and T_1 state of the sensitizers. Experiments in thin polymer films indicate that the same technique could be used to perform in situ acid analysis on coated quartz wafers. This approach has a set of advantages over existing methods and should be applicable to virtually every photoacid generating system by simply selecting the sensor that meets the specific requirements of the PAG under investigation.

Introduction

The rapid development of microelectronics has fueled an ever increasing demand for new materials and methods for microlithographic applications. It has become evident that the diazoquinone/novolac resist, the workhorse of the microelectronics industry today, will not be used in the fabrication of a 256 Mbit and 1 Gbit DRAM.[1] Therefore, a new class of photoresist systems has recently been developed[2−7] that works well at shorter wavelengths, notably 248 and 193 nm, thereby providing the spatial resolution required in the production of highest density components. A key element in all these systems is a so-called photoacid generator (PAG), i.e., a compound that yields an acid as one product of photolysis.[8] The achievable photospeed for these photoresist formulations depends strongly on the efficiency of acid generation Φ_{acid} upon photolysis of the PAG; therefore, it is a very important parameter when it comes to screening new compounds for the versatility as a PAG in these formulations.

Surprisingly, the methods used to determine Φ_{acid} values in a thin polymer film are rather cumbersome. Usually, this process involves the irradiation of several resist-coated wafers and subsequent dissolution of the films.[9,10] The acid concentration of this solution is then determined either by acid−base titration or colorimetric analysis. While these methods may be accurate, they are impractical as methods to screen new PAGs for efficiency, and it would be desirable to have an in situ method for acid analysis in polymer films. Even in solution, screening these materials is not straightforward.

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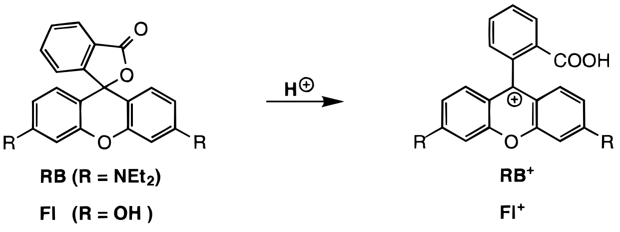
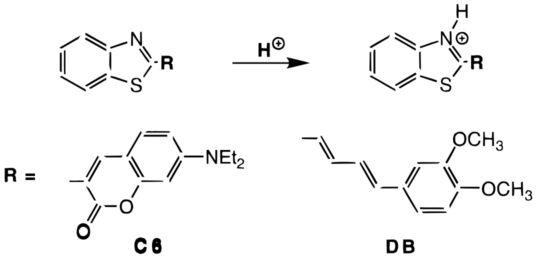
We are developing new methods in order to conveniently monitor the efficiency of photoacid generation in nonaqueous solutions and thin polymer films. For this purpose we employ organic molecules that show significant changes in the absorption characteristics upon protonation and monitor the changes by absorption spectroscopy. Two different classes of such acid sensors for nonaqueous systems are currently under investigation in our group. The first class comprises the xanthene dyes rhodamine B base (**RB**) and fluorescein (**Fl**) which exist in a colorless lactone form in aprotic solvents but undergo opening of the lactone ring upon protonation (reaction 1) or in protic solvents.[11,12]



reaction 1

The absorption spectra of the cations (**RB**$^+$ and **Fl**$^+$) of these dyes are markedly different from the lactone forms (Figure 1), and this large bathochromic shift upon protonation makes these compounds ideal acid sensors for the polymers used in microlithography.

While the solvatochromism of **RB** an **Fl** has been known for a long time, the acid–base properties of the second class of dyes that can be used as acid sensors for these nonaqueous media have not yet been reported nor have these compounds been used as acid sensors before. The two representative dyes used in this work are coumarin 6 (**C6**) and 2-[4-(3,4-dimethoxyphenyl)-1,3-butadienyl]benzothiazole (**DB**). These compounds show a significant red shift upon protonation of the ring nitrogen (reaction 2) yielding the cations **C6**$^+$ and **DB**$^+$.



reaction 2

The technique reported here should work with essentially any PAG; selection of the triazines **1**–**3** in Chart 1 simply reflects the convenience related to our recent work with these compounds. In a recent study[13] we have investigated mechanistic aspects of the direct and photosensitized PAG applications, and the results are summarized in Scheme 1. Direct excitation of **1**–**3** leads to photocleavage of one of the carbon–chlorine bonds as the primary photochemical step, and the subsequent hydrogen abstraction by the highly reactive chlorine atom generates HCl. Under sensitized conditions using phenothiazine derivatives (**PT-H**) as sensitizers, electron transfer from the sensitizer to the triazine yielding a radical ion pair has been established. The HCl generation quantum yields of **1**–**3** under direct excitation have been determined to be 0.45, 0.010, and 0.012 in diglyme under steady-state conditions, and for **1** the chlorine atom formation efficiency (which should

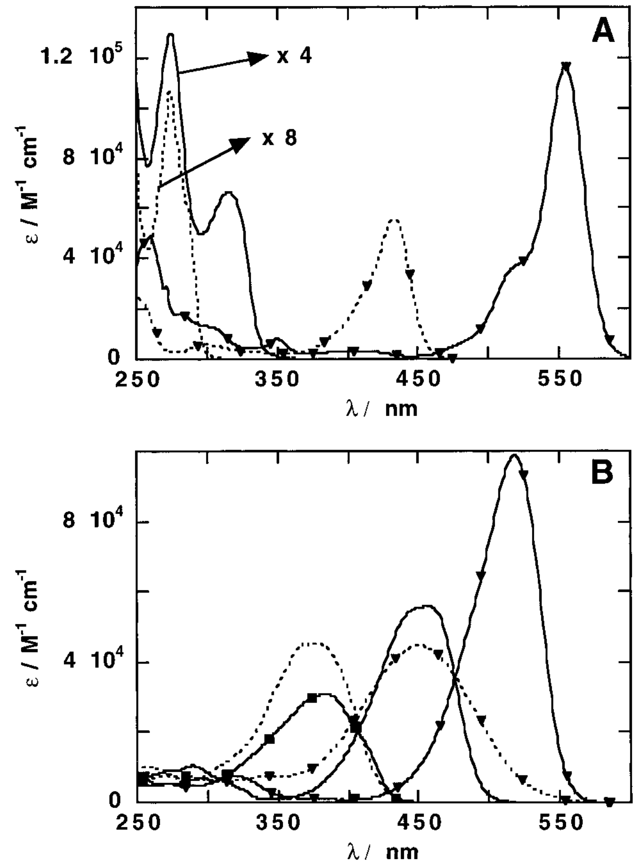
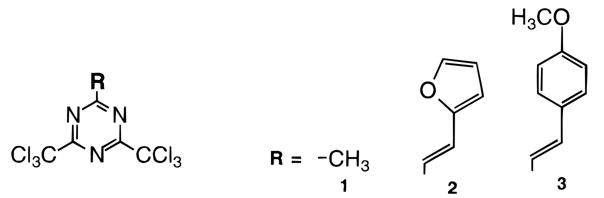


Figure 1. (A) Absorption spectra of rhodamine B base (—) and fluorescein (···) without and with (▼) 0.1M methanesulfonic acid in acetonitrile at room temperature. The spectra of the unprotonated forms have been magnified. (B) Same as A for Coumarin 6 and 2-[(3,4-dimethoxyphenyl)-1,3-butadienyl]benzothiazole, except that the acid concentration in the case of **C6** was 0.004 M (cation) and 2 M (dication, ■).

Chart 1



Scheme 1

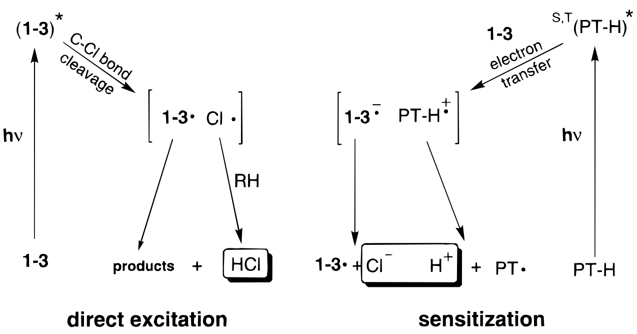


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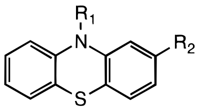
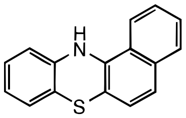
Chart 2





R_1 = H R_2 = H **PT**
R_1 = H R_2 = OCH_3 **MEPT**
R_1 = H R_2 = $COCH_3$ **ACPT**
R_1 = CH_3 R_2 = H **NMPT**

BAPT

equal the HCl generation efficiency in a good hydrogen donor solvent) was found to be 0.40 in acetonitrile under 308 nm laser excitation in an independent experiment.

In this paper we describe a novel method for the determination of photoacid generation quantum yields using the four different acid sensors and establish their versatility as acid sensors for nonaqueous media.

Experimental Section

Materials. Rhodamine B base and fluorescein were obtained from Aldrich. For purification, fluorescein was dissolved in dilute aqueous NaOH, filtered, precipitated by adding dilute HCl, and dried. This procedure was repeated twice. Rhodamine B base was purified by column chromatography on silica gel (230−400 mesh) using acetone as eluent. Coumarin 6 was obtained from Kodak and recrystallized once from cyclohexane/toluene. **DB** was synthesized by etherification of 4-hydroxy-3-methoxycinnamaldehyde (Aldrich) using iodomethane in acetone/K_2CO_3[14] and subsequent condensation of the aldehyde with 2-methylbenzothiazole using the procedure of Dryanska et al.[15] The crude product was purified by 4-fold recrystallization from methanol. The purity of the dyes was checked using fluorescence excitation spectroscopy.

The three PAGs **1**−**3** (Chart 1) were purchased from Panchim. Compound **1** was purified by recrystallization from methanol (2×) and subsequent sublimation, and **2** and **3** were recrystallized two times from ethanol.

Phenothiazine (**PT**) and 2-acetylphenothiazine (**ACPT**) (Chart 2) were obtained from Aldrich. **PT** was recrystallized from toluene in the presence of charcoal and sublimed. **ACPT** was recrystallized from toluene, sublimed, and then recrystallized from ethanol again. 2-Methoxyphenothiazine (**MEPT**) and *N*-methylphenothiazine (**NMPT**) were purchased from TCI and Kodak, respectively, and purified by sublimation. The 12*H*-benzo[a]phenothiazine (**BAPT**) was prepared by the method of Purnendu et al.[16] and the crude product sublimed and finally recrystallized from ethanol.

The purity of the phenothiazines was checked using fluorescence excitation spectroscopy and time-resolved fluorescence. All showed monoexponential fluorescence decays. Acetonitrile and diglyme (OmniSolv grade) were from BDH and used as received.

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. Suprasil quartz cells with a 10 mm optical path were employed in all these experiments.

For the nanosecond laser flash photolysis, a Lumonics EX-530 excimer laser (Xe/HCl, 308 nm, ~6 ns pulse width, 50−100 mJ/pulse) or the third harmonic of a Surelite Nd:YAG laser (355 nm, ~6 ns pulse width, $\leq$20 mJ/pulse) was used for excitation. The system is controlled by a Power Macintosh computer running LabVIEW 3.1.1 software (National Instruments). A Tektronix 2440 digital oscilloscope is used to capture and digitize the signal from the photomultiplier tube. Detailed descriptions of similar laser systems have been provided elsewhere.[17,18]

Experiments in Solution. The optical densities of the samples used in the experiments to determine the efficiency of photoacid generation were matched very carefully; the difference in absorbance at the excitation wavelength did not exceed 0.005. In all experiments a flow system (a 7 × 7 mm Suprasil quartz flow cell that is connected to a reservoir with Teflon tubing) was used. The flow technique was the method of choice in order to ensure that the laser always irradiates a fresh portion of the sample. This is a crucial point since both the photoproducts formed upon photolysis of the PAG and the indicator act as a UV/visible screen for the incident light if a static setup is used. The solutions were carefully protected from light all the time by wrapping the flasks and the reservoir of the flow system in aluminum foil. Unless stated otherwise, all samples were deaerated by bubbling with oxygen-free nitrogen for 15 min.

Experiments in Thin Polymer Films. Thin polymer films were spin coated at 3000 rpm for 20 s from 25% w/w coating solutions of poly(vinylphenol) (PVP) and poly(methyl methacrylate) (PMMA) in diglyme onto 10 cm quartz disks using an Integrated Technologies Inc. P-6000 spin coater. The films were baked at 100 °C for 10 min immediately after coating. Typical film thickness was ~1 μm for PVP and ~3.5 μm for PMMA. The disks could be mounted in a stepper-motor driven holder which moved the disk a determined distance between two laser pulses. This ensured that each laser pulse hit a fresh portion of the film. The concentrations of PAG and dye given are the concentrations of the respective coating solution used for spin coating.

Results

Experiments in Solution. Steady-State Absorption Spectra. To demonstrate the effect of acid on the absorption characteristics of the xanthene dyes, the spectra with and without methanesulfonic acid (MSA) in acetonitrile are shown in Figure 1A. In the absence of acid they exist in the lactone form and both spectra are dominated by the $\pi-\pi^*$ transition of the substituted benzene chromophores. The red shift of the long wavelength band observed for **RB** compared to **Fl** is characteristic for dialkylamino substitution (e.g. λ_{max} [phenol, methanol] = 273 nm, λ_{max} [*N*,*N*-dimethylaniline, ethanol] = 298 nm).[19] Protonation upon addition of MSA leads to lactone ring opening and formation of an extended conjugated π-system that causes the extreme bathochromic shift in the absorption spectrum with sharp, very intense peaks at 555 (**RB**$^+$, $\epsilon = 116000$ M^{-1} cm^{-1}) and 433 nm (**Fl**$^+$, $\epsilon = 55600$ M^{-1} cm^{-1}).

The spectra for the benzothiazole dyes with and without MSA are shown in Figure 1B. The long wavelength bands for the neutral compounds correspond to charge transfer (CT) transitions,[20−22] the charge transfer occurring from the electron-rich moiety of the molecules (i.e. the electron donor group substituted phenyl ring) to the electron-deficient benzothiazole moiety. Protonation of the heterocyclic nitrogen further increases the electron deficiency of the benzothiazole moiety, thereby decreasing the energy of the CT state,

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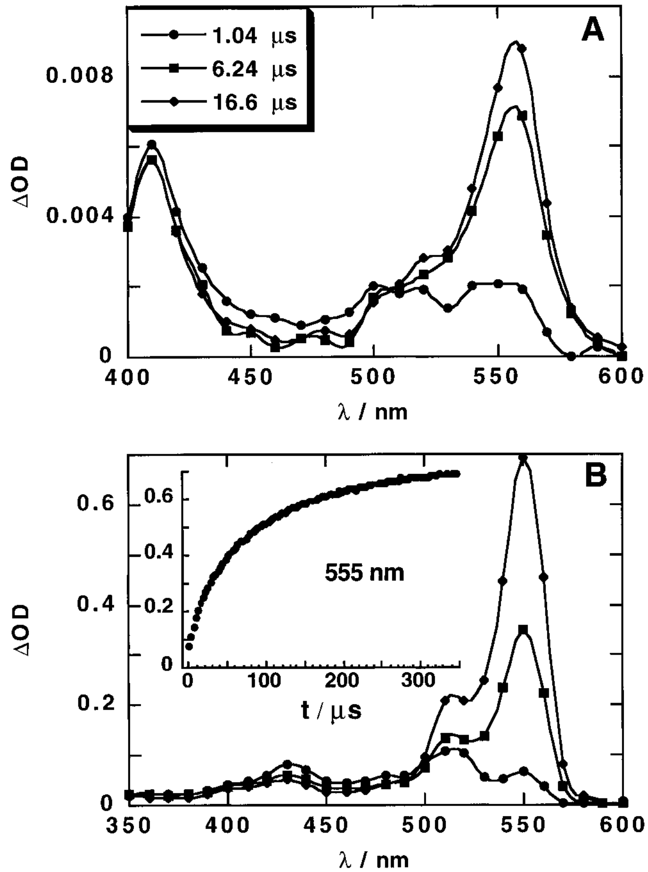

Figure 2. (A) Transient spectra recorded at different time intervals following 355-nm laser excitation of **2** (2×10^{-5} M) in the presence of 5×10^{-5} M^{-1} rhodamine B base in deaerated acetonitrile containing 0.5 M diglyme. (B) Transient spectrum recorded following 355-nm laser excitation of phenothiazine (7×10^{-4} M) in the presence of 0.001 M and 5×10^{-5} M^{-1} rhodamine B base in deaerated acetonitrile. The spectra were recorded at 3.2 (●), 32.8 (■) and 167 (◆) μs after the laser pulse. Both spectra were recorded under the same conditions and the absorbances of the samples at 355 nm had been matched. Inset: growth of the signal at 555 nm under the same conditions.

which manifests itself in the red shift of the CT band (ϵ = 100000 M^{-1} cm^{-1} at 519 nm).

In the case of **C6**, a further increase of the MSA concentration ultimately leads to protonation of the exocyclic nitrogen yielding the dication **C6**$^{2+}$. This species absorbs at considerably shorter wavelengths (λ_{max} = 385 nm, ϵ = 31000 M^{-1} cm^{-1}) than the monocation or even the neutral form since the second protonation destroys the donor ability of the diethylamino group and thereby the possibility for an effective charge transfer. The bathochromic shift observed for **C6**/**C6**$^{+}$ relative to **DB**/**DB**$^{+}$ is due to the better donor ability of the diethylamino group compared to the methoxy group.

Time-Resolved Absorption Spectra. Figure 2A shows the transient spectrum obtained after laser excitation (355 nm) of PAG **2** in deaerated acetonitrile in the presence of 5×10^{-5} M **RB**. The band at 555 nm exhibits growth kinetics in good agreement with that recorded independently for the authentic sample of **RB**$^{+}$ in a steady-state spectrometer (Figure 1A), thus indicating HCl formation due to PAG photolysis and subsequent protonation and opening of the lactone ring. The two additional peaks at 410 and 500 nm in Figure 2 are not related to the presence of **RB.** They are also observed in the absence of dye; the band at 410 nm is due a stable photoproduct of **2**, and the signal at 510 nm has been assigned to a complex between **2** and the chlorine atoms formed as a result of the C−Cl bond cleavage.[13]

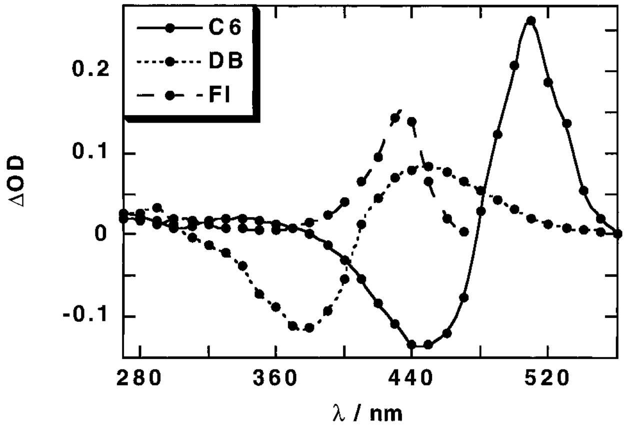

Figure 3. Transient spectra obtained following 308-nm laser excitation of **1** (3×10^{-3} M) in the presence of 5×10^{-5} M^{-1} **Fl**, **C6**, and **DB** in deaerated acetonitrile containing 0.5 M diglyme.

The transient absorption spectra under sensitized conditions, i.e., using phenothiazine in the presence of 0.001 M **1** and 5×10^{-5} M **RB** in acetonitrile after 355 nm laser excitation is shown in Figure 2B. As already observed for direct excitation using **2** as acid generator, the recorded spectrum is basically the superposition of the spectrum obtained without **RB** under the same conditions and the ground state absorption spectrum of the rhodamine B cation. Again the band at 555 nm shows a growth kinetics as illustrated in the inset in Figure 2B. In contrast, the bands at 430 and 515 nm belong clearly to a transient species and have been assigned in our earlier study[13] to the radical cation of **PT** formed as a result of the electron transfer from the sensitizer to the triazine (see Scheme 1).

It should be noted that the absorbance observed at 555 nm under sensitized conditions is approximately 80 times higher than in the experiment using direct excitation of **2** as PAG (Figure 2A). Since both the experiments above were recorded under the same conditions and both samples had the same optical density at the excitation wavelength, this difference in absorbance should reflect the different amounts of acid generated in both experiments, thereby providing a method of evaluating acid generation efficiencies (vide infra).

Basically the same observations were made for the other sensors, i.e., the spectra exhibit the growth signal due to the protonated dye and the transient signals generated upon photolysis of the respective PAG. For example, Figure 3 shows the transient spectra obtained for the other sensors after 308 nm laser excitation of **1** as PAG in deoxygenated acetonitrile. For the benzothiazole dyes, strong photobleaching due to the ground-state depletion of the neutral molecules by protonation is observed. The signal due to radical **1**$^{\bullet}$ (λ_{max} = 295 nm) formed as a result of C−Cl bond homolysis[13] is not observable in these spectra since they were recorded at relatively long time intervals times after the laser pulse, i.e., at a point where most of **1**$^{\bullet}$ had already decayed.

For all dyes and PAGs we ensured that the formation of the protonated sensor was only due to the photolysis

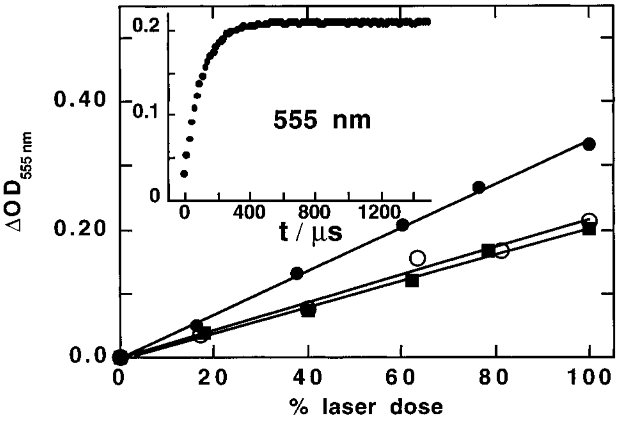

Figure 4. Maximum absorbance signal due to the rhodamine B cation at 555 nm for PAGs **1** (●), **2** (○) and **3** (■) upon 308 nm laser excitation as a function of laser dose in deaerated acetonitrile containing 0.5 M diglyme at room temperature. The data of **2** and **3** have been expanded by a factor of 20. Inset: Representative trace showing the buildup of **RB**$^+$.

of the PAG, i.e., irradiating the dye alone or selective excitation of the dye in the presence of the PAGs did not lead to protonation.

For a given dye concentration, the kinetics observed for the growth of the signal due to the protonated sensor ranges from clean first order to second order, high laser power, i.e., high proton concentrations, favoring the latter. A detailed analysis of the kinetic behavior and the rate constants for protonation will be reported elsewhere.

Quantum Yields. To evaluate the quantum yields of photoacid generation upon both direct excitation and sensitized conditions, the method of relative actinometry was used, employing **1** as actinometer. We choose **1** for this purpose because both its Φ_{HCl} and Φ_{Cl} value have been determined independently by two different methods yielding approximately the same result.[13] As mentioned above, acid analysis can be done by simply monitoring the signal intensity of the protonated acid sensor for the PAG with the unknown quantum yield and the PAG used as actinometer.

Thus, in a typical experiment the top OD values monitored at the λ_{max} of the protonated form of the respective dye were recorded for various laser doses for **2** and **3** and the actinometer. The measurements were taken from the plateau region of traces such as that shown for **RB** in the inset in Figure 4. The optical densities at the excitation wavelength had been carefully matched for all these samples. Generally, in all the experiments where **1**−**3** were excited directly the samples contained 0.5 M diglyme as hydrogen donor to ensure the quantitative trapping of the chlorine atoms. In Figure 4 results are exemplary shown for **RB** as acid sensor in acetonitrile and 308 nm laser excitation. The data for **2** and **3** have been expanded to be accommodated in the same plot as the actinometer. The quantum yields of **2** and **3** have been calculated according to eq 1. where *S* is the slope obtained from plots

$$\phi^{\mathbf{X}}_{\mathrm{HCl}} = \phi^{\mathbf{1}}_{\mathrm{HCl}} \frac{S^{\mathbf{X}}}{S^{\mathbf{1}}} \qquad (1)$$

such as that shown in Figure 4, and the indices **1** and X denote PAG **1** used as actinometer and the PAGs with the unknown quantum yield, respectively.

Table 1. Quantum Yields for Chlorine Atom ($\Phi_{Cl^\bullet}$) and HCl (Φ_{HCl}) Photogeneration of the Triazines 1−3 at Room Temperature. The Superscripts Refer to the Different Dyes Used

triazine	$^{RB}\Phi_{HCl}{}^{a,b}$	$^{Fl}\Phi_{HCl}{}^{a,b}$	$^{C6}\Phi_{HCl}{}^{a,b}$	$^{DB}\Phi_{HCl}{}^{a,b}$	$\Phi_{Cl^\bullet}{}^{a}$	$\Phi_{HCl}{}^{c}$
1	*d*	*d*	*d*	*d*	0.40	0.45
2	0.013	0.010	0.010	0.009	−	0.010
3	0.013	0.010	0.010	0.009	−	0.012

[a] In acetonitrile upon laser excitation (308 nm). [b] samples contained 0.5 M diglyme. [c] In dearated diglyme under steady-state conditions from ref 13. [d] **1** was used as actinometer in these experiments.

The results obtained for **2** and **3** upon direct excitation at 308 nm using the different dyes are shown in Table 1 and can be summarized as follows:

1. The results obtained for a given PAG using the four dyes coincide fairly well, ranging from 0.009 for **DB** to 0.013 for **RB**, especially if one considers the low absolute value.

2. The absolute values are in good agreement with those determined earlier[13] under steady-state conditions in diglyme by acid−base titration; this demonstrates the applicability of this new method.

The excellent linearity observed for all the plots reflects that the formation of the monoprotonated dye occurs long after the completion of the laser pulse. This can be seen in the insets in Figures 2 and 4 for where the growth of the rhodamine B absorption is shown under sensitized conditions and upon direct excitation of PAG **1**, respectively. In both cases the complete buildup of the monocation absorption occurs over several hundred microseconds. Thus, while the protonated form could behave as a UV−visible screen, virtually none of this form is produced during the 6 ns long laser pulse. Thus, acid generation is effectively determined at *zero conversion* for reaction 1.

After we had tested the applicability of this method as outlined above using systems with known quantum yields, i.e., **2** and **3**, we tried to determine the photoacid generation quantum yields using the various sensitizers in the presence of **1** as electron acceptor and 355 nm excitation, since these values had not been determined in our earlier study. We choose 355 nm for excitation because **1** is transparent at this wavelength, i.e., all monitored acid is due to the electron-transfer process, and contributions resulting from direct excitation of **1** can be ruled out. This excitation wavelength required calibration of another actinometer that could be used at 355 nm. We decided to use a molecule that absorbs at both wavelengths, i.e., 308 and 355 nm, and exhibits an intense triplet−triplet absorption. Coincidentally phenothiazine itself proved to be ideal for this purpose due to its combination of a high extinction coefficient for the T−T absorption (ϵ_T at 460 nm = 23000 M^{-1} cm^{-1})[23] and a high quantum yield of intersystem crossing (0.96).[23] Furthermore, its triplet state energy is high enough to avoid triplet sensitization by the lactone form of rhodamine B base which also absorbs at 308 nm. This was a problem with some aromatic compounds with low lying T$_1$-states tested for this purpose, e.g. anthracene and chrysene.

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Table 2. Rate Constants for Triplet State Quenching and Acid Generation Quantum Yields of the Phenothiazines Using 0.001 M 1 as Quencher. All Values in Deaerated Acetonitrile at Room Temperature

sensitizer	k_q (**1**) 10^9 M^{-1} s^{-1}	$^{RB}\Phi_{HCl}$	$^{C6}\Phi_{HCl}$
PT	9.0	1.04	0.97
MEPT	11.9	0.82	0.78
NMPT	6.7	<0.01	<0.01
BAPT	9.9	0.57/0.98[a]	0.60
ACPT	4.5	0.19	0.15

[a] Quencher concentration was 0.01 M.

To calibrate **PT** against **1**, we measured the change in absorbance of the phenothiazine T−T absorption signal at 460 nm and the ground-state absorption of the rhodamine B base cation as a function of laser dose in acetonitrile for a sample of **PT** and **1**, respectively, with matching optical densities at 308 nm and the same **RB** concentration (plots not shown). The same type of experiments as outlined above for **2** and **3** were then carried out for the sensitized systems (phenothiazine derivative/0.001 M **1**), now employing **PT** as actinometer. From the slopes of these plots (not shown), the quantum yields of acid generation were determined (Table 2) using eq 2, where (**xPT/1**) refers to the system phenothiazine derivative/0.001 M **1** as quencher and f_{cal} is the determined calibration factor, i.e., the ratio $S_{308}^{\mathbf{PT}}/S_{308}^{\mathbf{1}}$:

$$\phi_{HCl}^{(\mathbf{xPT/1})} = \phi_{HCl}^{\mathbf{1}} f_{cal} \frac{S_{355}^{(\mathbf{xPT/1})}}{S_{355}^{\mathbf{PT}}} \qquad (2)$$

Since the very long-lived signal of the phenothiazine cation radical interferes with the $\mathbf{DB}^+$ and the $\mathbf{Fl}^+$ signal at 435 and 450 nm, no Φ_{HCl} values under sensitized conditions could be determined with these dyes. Due to the bathochromic shift of the $\mathbf{RB}^+$ and $\mathbf{C6}^+$ ground-state absorption (λ_{max} = 555 and 520 nm) and the lower sensitizer concentration required (due to the higher sensitivity of these dyes), this was not a problem using rhodamine B base and Coumarin 6 as acid sensors.

Since all the relevant parameters for the electron-transfer process have been determined in our earlier study and its quantum yield of intersystem crossing is known, for **PT** as sensitizer the quality of the experimentally obtained $\Phi_{\mathbf{HCl}}$ values can be checked by comparing it to the theoretically expected value for $\phi_{\mathbf{HCl}}^{\mathbf{PT/1}}$ calculated as follows:

From the quencher concentration used (0.001 M), the rate constant for singlet quenching which has been shown to be close to the diffusional limit (~2 × 10^{10} M^{-1} s^{-1} in acetonitrile) and the fluorescence lifetime (0.84 ns) of **PT** in acetonitrile,[13] the quantum yield of singlet quenching of **PT** by **1** via electron transfer under these conditions is calculated to be 0.02. An analogous calculation for the T_1-state using the triplet lifetime (3.8 μs) and the rate constant for triplet quenching of **PT** in acetonitrile (9 × 10^9 M^{-1} s^{-1}, Table 2) yields 0.97. Given its intersystem crossing quantum yield of 0.96 which is reduced to 0.94 in the presence of quencher, the quantum yield of acid generation from the T_1-state of **PT** is expected to be 0.91 i.e., the overall photoacid generation efficiency from both states should be 0.93, which is in good agreement with the experimental values of 0.97 (using **C6**) and 1.04 (using **RB**).

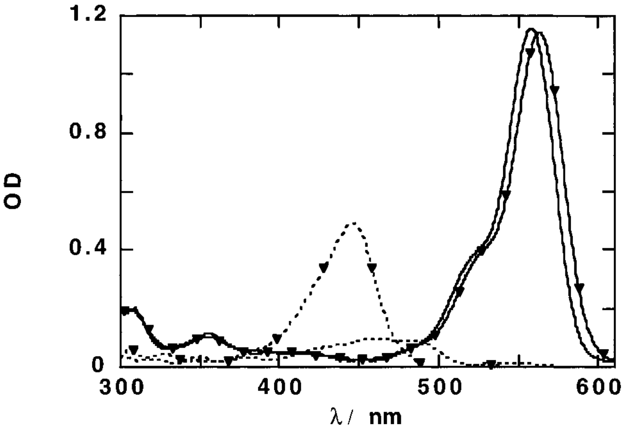

Figure 5. Absorption spectra of rhodamine B base (—) and fluorescein (···) without and with (▼) acid in a PVP film at room temperature. The acid was methanesulfonic acid for fluorescein (0.05 M in the coating solution), in the case of rhodamine B the acid (HBr) was generated photochemically (see text).

The difference in the acid generation quantum yields for **PT**, **MEPT**, and **ACPT** probably reflects predominantly the difference in the triplet formation efficiency since the triplet states of all these compounds are quenched very efficiently (≥97%) under these conditions (0.001 M **1**); in contrast, the singlet state is subject to only minor quenching (≤4%). In the case of **BAPT** on the other hand, the singlet state is quenched significantly (26%) by 0.001 M **1** due to its relatively long singlet lifetime of 26.43 ns.[13] In an experiment using a 10 times higher quencher concentration (0.01 M **1**) the quantum yield was determined as 0.98, indicating that the quantum yield reaches unity if both states are quenched effectively.

From the data for **NMPT**, it is clear that a high quenching rate constant does not necessarily equal a high acid generation efficiency. The reason for its low Φ_{acid} value is probably the pK_a of the radical cation which should be markedly higher compared to the other phenothiazine derivatives which possess a hydrogen bound directly to the nitrogen atom.

Experiments in Films. Steady-State Absorption Spectra. It would be clearly desirable to adapt the technique described for usage in resist polymer films. Therefore we carried out a set of experiments to find out whether the ability to monitor acid is preserved in PMMA and PVP films.

The absorption spectra of **Fl** in a PVP film with and without methanesulfonic acid are shown in Figure 5. In contrast to the spectrum in acetonitrile, fluorescein in PVP films exhibits some absorption at wavelengths > 300 nm where the lactone form does not absorb. This absorption is due to the zwitterion and quinone forms. However, in a PMMA film the spectrum (not shown) does not differ markedly from that observed in acetonitrile. From these observations, we conclude that the lactone ring is opened in PVP. By comparison with the results obtained by Sjoeback et al.[24] who report the absorption spectra of the various prototropic forms of fluorescein in water, we conclude that the band observed in PVP (λ_{max} 450 nm) is a superposition of the absorption due to the neutral form (λ_{max} = 434 nm/water) and the

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(24) Sjoeback, R.; Nygren, J.; Kubista, M. *Spectrochim. Acta, Part A* **1995**, *51A*, L7.

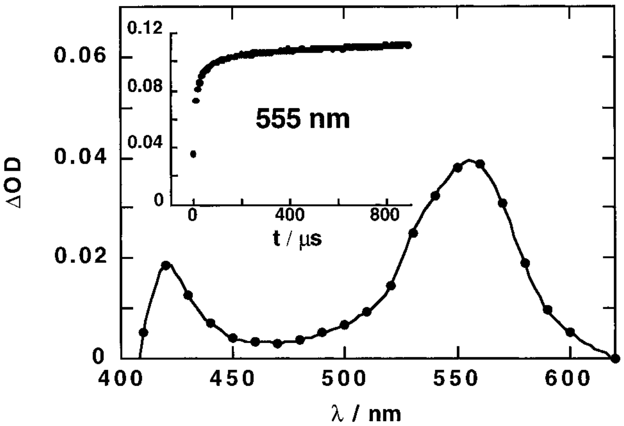

Figure 6. Transient spectrum recorded following 355-nm laser excitation of **2** (0.07M) in the presence of 0.01 M rhodamine B base in PMMA film. Inset: Formation of the signal at 555 nm due to $\mathbf{RB}^+$.

anion (λ_{max} = 472 nm/water).[24] It was not possible to decide from the absorption spectra whether there is still some of the lactone form, since at wavelengths < 300 nm the strong absorption of the PVP-based film makes spectral quantification very difficult. This makes the observation of any residual absorption due to the lactone form at 280 nm nearly impossible. The sample containing acid exhibits a similar band (λ_{max} = 446 nm) already observed for the cation in acetonitrile, except for a bathochromic shift of 13 nm.

In the case of **RB** we had to use a PAG (1,3,5-tris-(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione) and generate the acid (HBr) photochemically since addition of MSA leads to degradation of the dye during the baking process. The absorption spectra of **RB** in PVP are not markedly affected by the presence of acid, except for a bathochromic shift of 5 nm observed for the sample containing acid, whereas the spectra in a PMMA film are similar to those obtained in acetonitrile. This means that in PVP the lactone form is also not stable due to the presence of the phenolic groups, and the ring is opened as already observed for **Fl**. However, from the essentially identical spectra observed with and without acid it is inferred that in the case of **RB** the ring opening seems to be induced by protonation leading directly to the cation rather than the zwitterionic form. This is consistent with the higher sensitivity of **RB** toward acid already observed in solution. Furthermore, the zwitterionic form of **RB** is reported to have a significantly smaller extinction coefficient at the long wavelength band, but the presence of acid does not affect the intensity. This also means that there is no residual lactone form present in PVP since this would have lead to an increase in intensity for the acid sample due to complete ring opening induced by the HCl. The small bathochromic shift is probably induced by the chloride anion, this effect has been observed before for solutions of rhodamine B in alcohols containing LiCl.[25]

The absorption spectra of the benzothiazole dyes in a PVP film with and without MSA (not shown) do not differ substantially from those obtained in acetonitrile, except for a small bathochromic shift.

Time-Resolved Absorption Spectra. Figure 6 illustrates the transient spectrum obtained after laser excitation of PAG **2** (0.07 M) and 0.01 M **RB** in a PMMA film; it exhibits essentially the same features as the spectrum of **2** and **RB** in solution (Figure 2A). The signal at 555 nm corresponds well with the steady-state absorption spectrum of $\mathbf{RB}^+$ in a PVP film, indicating the formation of acid and subsequent ring opening. The additional band at 420 nm is due to the PAG again (vide supra). Analogous results were obtained for the other dyes, i.e., the spectra in film and solution are essentially the same.

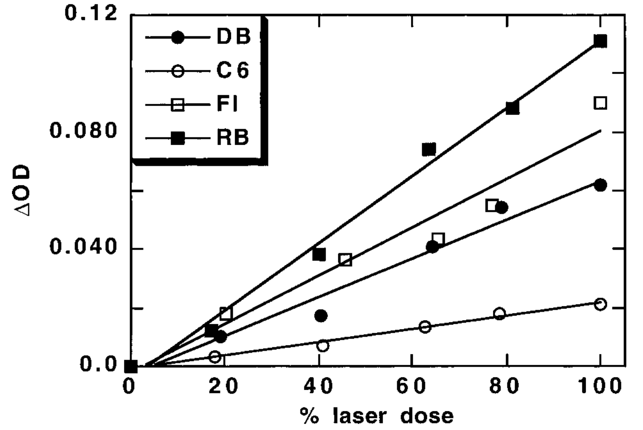

Figure 7. Maximum absorbance monitored at the λ_{max} of the respective protonated sensor for the four dyes as a function of laser dose in PVP (**Fl**, **C6**, **DB**) and PMMA (**RB**) films. PAG **2** and 355 nm laser excitation were used to generate the acid. The data of **DB** and **Fl** have been expanded by a factor of 5 and 15, respectively.

Finally, Figure 7 shows the maximum transient absorbance values monitored at the λ_{max} of the protonated forms as a function of laser dose. Again, these were taken from the plateau region of traces such as shown in the inset in Figure 6, but the optical densities of these samples were not matched, and the purpose of these experiments was merely to demonstrate that a correlation between the amount of photogenerated acid and the signal intensity of the protonated sensor exists. As already observed in solution, the plots show excellent linearity, indicating that the same methodology that has been developed for solution studies could also be used in thin polymer films.

Discussion

The method developed here combines the advantages of two other methods based on relative actinometry that have been used before to determine quantum yields of acid generation. The first method has been employed for HX generating PAGs (X = Br, Cl) using a laser flash system.[13,26] This method monitors the transient absorption due to a complex $X_2^{\bullet-}$ formed between the generated halogen atoms and the respective halogen anion added to the solution. A molecule that yields an intense, well characterized T−T absorption signal such as benzophenone usually serves as an actinometer. The use of a laser flash system is advantageous since it ensures monochromatic excitation and, in combination with a flow system, eliminates problems arising from changes in absorption characteristics of the sample due to conversion of the starting material. However, this

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(25) Faraggi, M.; Peretz, P.; Rosenthal, I.; Weinraub, D. *Chem. Phys. Lett.* **1984**, *103*, 310.

(26) Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. *J. Am. Chem. Soc.* **1993**, *115*, 8340.

method yields the efficiency of halogen atom generation and not the acid generation efficiency, i.e., great care should be taken to ensure that all the halogen atoms are trapped by the halogen anion, especially in the case of the highly reactive chlorine atoms. Further, even in the case of HX-generating PAGs it works only if halogen *atoms* are generated; i.e., it cannot be used if the reaction involves halogen *anions* as it is the case for the system phenothiazine/triazine. Finally, the relatively short monitoring wavelength for the $X_2^{\bullet-}$ complexes (<400 nm) is disadvantageous, e.g. the Φ_{HCl} values of **2** and **3** could not be determined by this method because the weak complex signal was masked by photobleaching caused by ground-state depletion of **2** and **3** ($\lambda_{max} = 368$ and 370 nm, respectively).[13]

The second method is applicable to basically all types of PAGs and involves the irradiation of PAG and actinometer (e.g. Norrish II reaction of valerophenone) under steady-state conditions in a photoreactor.[13,27] The chemical changes in the actinometer solution are monitored using GC (or another analytical technique), and the acid concentration of the PAG solution is determined by acid−base titration using an indicator. This method yields the actual quantum yield of acid generation, but the determination of the concentrations of test solution and actinometer by two different analytical techniques makes this method less accurate and more time-consuming. Furthermore, visual recognition of the transition interval of the acid−base indicator might be difficult if the solutions are colored as it is the case for the phenothiazine/triazine system.

Our new approach combines the use of an "acid−base indicator" to monitor directly the proton (without determining the absolute acid concentration) and the convenience and advantages of a laser flash system in combination with a flow system as outlined above. To evaluate the versatility of the four dyes studied, three main criteria have been taken into consideration:

1. Dye sensitivity toward acids, which depends both on the pK_a value of the unprotonated form and the extinction coefficient of the protonated species. The sensitivity of the dye largely determines the lower limit of the quantum yield that can be determined by this method.

2. The protonated sensor form can be monitored more in the long wavelength spectral region where interference with other signals is less likely to occur. Thus, the monitoring wavelength for the protonated form is a very important parameter.

3. It is important to select dyes applicability in a wide range of media.

The relative sensitivity of the four dyes used in this study was checked by preparing solutions (2.5×10^{-5} M) in the same stock solution of PAG **1** in acetonitrile and monitoring the absorbance at the maximum of the absorption spectrum of the protonated sensor form using 308 nm laser excitation. The relative signal intensity was found to be 1(**RB**):0.19(**C6**):0.06(**DB**):0.03 (**Fl**), indicating that in terms of sensitivity **RB** is superior to the other three dyes, and moreover its protonated form can be monitored at 555 nm. However, its serious drawback is that its usage is limited to aprotic media due to the ring opening in protic environment. Although the same behavior is found for fluorescein, the difference in the absorption spectra of the cation and the anion/neutral form are large enough to monitor the changes upon protonation. However, it exhibits the lowest sensitivity and the most undesirable absorption characteristics (λ_{max} [**Fl**$^+$] = 433 nm) of the four dyes. The benzothiazole dyes, especially **C6**, combine a higher sensitivity and a more favorable monitoring wavelength for the cation with its applicability virtually not limited by the solvent. Taking this into account, **C6** is clearly the most versatile acid sensor tested in this study in terms of overall performance. The set of dyes investigated in this work should make it possible to meet the specific requirements for nearly any PAG and medium.

Two other dyes that have been used earlier in the photometric determination of photoacid generation deserve comment. *McKean et al.*[9] employed 1-octadecyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (OOED), a merocyanine dye that shows a remarkable blue shift upon protonation and had first been introduced by Gaines[28] as an acid sensor for nonaqueous systems and determined PAG-efficiencies in solution and polymer films. However, OOED exists partly as its conjugate acid form even in a extremely weak acid such as ethanol and its likely that this equilibrium is shifted almost completely toward the protonated form in a PVP film as already observed for **RB**, i.e. the usage of this dye is limited to solvents or polymers with extremely low acidity.

The second indicator that has first been used by Buhr et al.[29] for the photometric determination of PAG-efficiencies and since then by several other groups[10,30,31] is the sodium salt of tetrabromophenol blue (TBPB). The drawback of this dye is that the TBPB itself generates HBr upon irradiation. Further, the purity of the commercially available material varies significantly from batch to batch and it exhibits solution instability. The benzothiazole dyes **C6** and **DB** used in this study do not have these problems. Another important advantage of this class of dyes over OOED or TBPB is that they are highly fluorescent in organic polymers including PVP. This enables the detection of acid via fluorescence spectroscopy which is far more sensitive than absorption spectroscopy. This combination of properties makes these new indicators superior to TBPB or OOED for the monitoring of acid in nonaqueous systems.

Although photometric determinations have been used to determine PAG-efficiencies as outlined above, the use of laser excitation in combination with a flow system is clearly advantageous compared to the steady-state irradiation used before,[9] where the dye is added after the PAG solution has been irradiated. The experiment has to be repeated several times to get a reliable value by averaging the data obtained this way. With the laser system, irradiating the sample and monitoring the indicator absorbance is virtually simultaneous. Further, by just varying the laser power it is possible to obtain several values taken under otherwise the same conditions; i.e., one single data point in Figure 4

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(27) Barra, M.; Scaiano, J. C.; Calabrese, G. S.; Sinta, R.; Thackeray, J. *Chem. Mater.* **1994**, *6*, 724.

(28) Gaines, G. L. *Anal. Chem.* **1976**, *48*, 450.

(29) Buhr, G.; Dammel, R.; Lindley, C. R. *Polym. Mater. Sci. Eng.* **1989**, *61*, 269.

(30) Asakawa, K.; Ushirogouchi, T.; Nakase, M. *Proc. SPIE-Int. Soc. opt. Eng.* **1995**, *2438*, 563.

(31) Kihara, N.; Saito, S.; Ushirogouchi, T.; Nakase, M. *J. Photopolym. Sci. Technol.* **1995**, *8*, 561.

corresponds to a experiment using the steady-state method.

From the results presented it is clear that the same technique can be used in thin polymer films; this in situ technique would considerably simplify the cumbersome current method of acid analysis in films. Given that exact matching of absorbances in a polymer film is difficult, the use of samples with high absorbance ($\geqslant 2$) at the irradiation wavelength should be preferred. This would ensure that different samples absorb approximately the same number of photons.

Conclusion

Rhodamine B base, fluorescein, coumarin 6 and 2-[4-(3,4-dimethoxyphenyl)-1,3-butadienyl]benzothiazole can be used as acid sensors in nonaqueous media due to the large bathochromic shift induced upon protonation. In the case of the xanthene dyes this is caused by the opening of the lactone ring. Both *direct* laser irradiation of the three PAGs and *sensitization* of PAG **1** using phenothiazine derivatives in the presence of the four investigated dyes leads to photoacid generation and subsequent protonation of the dye. The intensity of the growth signal due to the protonated dye is a linear function of the acid concentration. This allows the determination of photoacid generation of PAGs relative to a PAG with a known quantum yield.

Using this method, we have found that the differences in the efficiency using the various sensitizers seem to be a function of quencher concentration, i.e., for quencher concentrations high enough to ensure quantitative quenching of both the T_1 and S_1 state of the phenothiazines the quantum yield should reach unity, as exemplary shown for 12*H*-benzo[*a*]phenothiazine. From the experiments in PMMA and PVP films we conclude that it should be possible to employ the same technique as an in situ method in thin polymer films. However, in PVP films the lactone ring of rhodamine B base and fluorescein is opened even in the absence of acid which makes the benzothiazole dye a better candidate for this type of application. This new technique has several advantages over existing techniques and should be applicable to virtually any photoacid generation system.

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