Highly Efficient Bicolor (Green−Blue) Fluorescence Imaging in Polymeric Films

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A novel approach for photochemical definition of distinct, basic color, emission areas in thin polymeric films is introduced. Two-color, blue and green, fluorescence imaging is demonstrated using an amino diphenylhexatriene derivative that upon protonation shows sizable shifts in both absorbance and fluorescence spectra. Protons are generated photochemically in selected areas of the thin polymeric films containing the probe by a typical onium salt photoacid generator. Significant "flow" of transferred electronic energy from a typical aromatic polymer, epoxy novolac, to the mentioned dye was manifested permitting amplification and color tunability of fluorescent signals.

Introduction

Patterning using films of photosensitive polymeric materials, photoresists, is one of the most critical areas in modern semiconductor industry where the capability for IC dimension shrinkage still defines the level of the whole technology. Advanced photoresist materials capable of manufacturing sub-0.2 micron images with optical lithography are already in the market, while the research efforts in this area target these days to the sub-tenth micron regime. The most successful strategy adopted in the development of new photoresists during the last 15 years is based on "chemical amplification", where a photoacid generator (PAG) usually provides protons upon optical e-beam or X-ray exposure inside the resist film, which then catalyze or initiate the necessary for solubility change chemical reactions.[1] In addition to the development of new photoresist materials capable for exposure at deep, and lately vacuum, UV spectral regions, increased interest has also arisen in the development of suitable metrology tools and methodolologies to monitor and control physicochemical changes occurring inside the resist films. One of the areas where intense activity is reported lately is related with the introduction of suitable probes, including fluorescence probes, for the study of photogenerated acid formation and diffusion aiming at the optimization of lithographic materials and processes.[2−4]

On the other hand, the investigation of fluorescence patterning possibilities in thin polymeric films emerges as an important topic of research in the area of plastic materials suitable for image recording and display applications.[5−7] The exploration of novel strategies for the formation of full color displays—by defining blue, green, and red emissive pixels—is in particular a very hot subject nowadays.[8]

Fluorescent organic dyes dispersed in the polymer film or moieties pending to the polymer itself have been used so far in fluorescence imaging, either in the area of lithographic processing or in one of the organic displays, including fluoresceins,[2] acridins,[3] cumarins,[4] anthracene derivatives,[7] quinizarins,[6] and recently pyridylbenzoxazoles.[5] The acid-induced changes of emission properties in all these cases result in production of fluorescent and nonfluorescent areas (acid-induced dye quenching).

In this paper, we introduce a new approach for the fluorescence patterning of thin films on the basis of the photochemical definition of *distinguishable* green and blue fluorescent areas. This new approach results to *photochemically activated color-changing media (PACCM*) by using an appropriate luminescent probe and offers new opportunities both for fluorescence probing of acid generation and diffusion inside photoresists and for full-color display applications in the area of organic light-emitting diodes (OLEDs).

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Experimental Section

Materials and Instrumentation. 1-(4′-dimethyl-aminophenyl)-6-phenyl-1,3,5-hexatriene (DMA-DPH) was purchased from Lambda Probes and Diagnostics. The parent molecule, *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) was purchased from Fluka. The PMMA polymer used is Elvacite 2041 purchased from DuPont, whereas the epoxy novolac was obtained after fractionation of Shell Epikote 164.[9]For absorption spectra, the Perkin−Elmer Lambda-16 spectrophotometer was employed. Fluorescence and excitation spectra were recorded on a Perkin−Elmer LS-50B fluorometer. Steady-state and time-resolved fluorescence anisotropy measurements were determined using the time-correlated single-photon counter FL900 of Edinburgh Instruments equipped with Glan−Thompson polarizing prisms. The steady-state, $\langle r \rangle$, and time-dependent fluorescence anisotropy, $r(t)$, were calculated by using the expressions 1 and 2, respectively:

$$\langle r \rangle = \frac{GI_{VV} - I_{VH}}{GI_{VV} + 2I_{VH}} \quad (1)$$

and

$$r(t) = \frac{GR_{VV}(t) - R_{VH}(t)}{GR_{VV}(t) + 2R_{VH}(t)} \quad (2)$$

where I and R stand for the integrated spectrum intensity and time-resolved decays, the symbols VV and VH correspond to parallel and perpendicular plane of the analyzer with respect to that of excited light, while the plane of the polarizer is fixed to that of incidence. Finally, G, also called G-factor, is a correction factor dependent on the emission wavelength and is given by $G = I_{HH}/I_{HV}$ and $G = R_{HH}(t)/R_{HV}(t)$ for static and time-dependent anisotropy expressions, respectively.

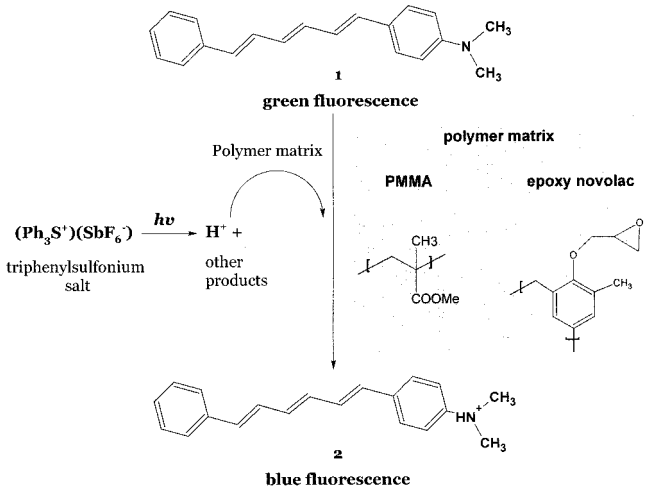
Polymeric Film Preparation and Processing. Solutions containing either the polymer poly(methyl methacrylate) (PMMA) (7% w/w) or the epoxy novolac (EPNOV) (22% w/w), a photoacid generator triphenylsulfonium hexafluoroantimonate (TPSHFA), in various contents (2%, 3%, and 10% w/w) and the fluorescence probe DMA-DPH (1% w/w) were prepared using propylene glycol methyl ether acetate PGMEA as the solvent. Films were spin coated at 4000 rpm and then baked on a hot plate at 110 °C for 1 min. Film thicknesses were measured with a Dektak profilometer (typical film thickness 0.53 μm). Photoacid generation was induced by exposing films with a 500 W Oriel Hg−Xe exposure tool through a 248 nm narrow-band filter (6.5 nm half-bandwidth) for assessed times (see text). The incident power was 0.21 ± 0.02 mJ/s.

Fluorescence Imaging. Solutions similar to the ones described above were used for fluorescence imaging. Solutions after spin coating and baking as above were exposed to 248 nm UV light for 15 min through a patterned photomask. The fluorescence image pattern was photographed using a Nikon Microphot-FXA fluorescence microscope.

Results and Discussion

Recently, we have reported an extensive spectroscopic study[10] of a derivative of the fluorescence probe 1,6-diphenyl-1,3,5-hexatriene (DPH) which carries the electron donating *para*-dimethyl-amino group on one of the phenyl rings, namely 1-[4-(dimethylamino)phenyl]-6-phenylhexa-1,3,5,-triene (DMA-DPH) (compound **1**). Briefly, it was found that in contrast to the parent molecule DPH, the emission wavelength of DMA-DPH is very sensitive to the micropolarity of its immediate environment. The observed sizable spectral shifts of DMA-DPH arise from charge delocalization in the extended conjugated system of the molecule induced by the electron-donating effect of the *p*-dimethylamino group. By keeping this in mind, we made the hypothesis that photoinduced protonation of the dimethylamino group in DMA-DPH may disrupt the conjugation effect and as a consequence could hypsochromically shift the DMA-DPH absorption and emission maxima toward those of the parent DPH molecule (Scheme 1). As a result, information concerning the photogeneration of acid in thin polymeric films can be suitably transmitted to us via intense light signals. Moreover, if photoinduced protonation of DMA-DPH into the polymer films is efficient, then by exposing selected areas through a photomask, patterned bicolor fluorescent images could be obtained.

Scheme 1



In an effort to verify this hypothesis, we examined the spectral changes of DMA-DPH (**1**) incorporated into selected polymer matrixes. The formation of the protonated form (compound **2**) and the photoinduced color changes were tested by both UV−vis and fluorescence spectroscopy. Two representative polymer matrixes were employed in this study: poly(methyl methacrylate) (PMMA), an almost transparent matrix in the tested wavelength range (248 ± 7 nm) which is also chemically inert toward photogenerated acid, and an epoxy novolac polymer (EPNOV), which *absorbs significantly* in the mentioned wavelength range and *emits fluorescence* in the ultraviolet-near-visible region. It is also well documented that photoacid generated by a sulfonium salt in this epoxy matrix causes cross-linking reactions.[9]

I. UV−Vis Absorption Spectroscopy. The UV−vis absorption spectrum of a thin (0.53 μm) film prepared by spin coating a propylene glycol methyl ether acetate (PGMEA) solution of PMMA containing DMA-DPH (1% w/w) and a photoacid generator, triphenyl sulfonium hexafluoroantimonate (3% w/w), on quartz substrate is shown in Figure 1a (curve 1). The *para* substitution effect in the DMA-DPH molecule induces broadening of the absorption spectrum and shifts the wavelength maximum to ca. 400 nm. This maximum is shifted 24 nm hypsochromically with respect to that of DPH (see Figure 1a dotted line). Upon subsequent irradiation with 248 nm light (curves 2, 3, and 4), photoacid generation is triggered and the absorption at the

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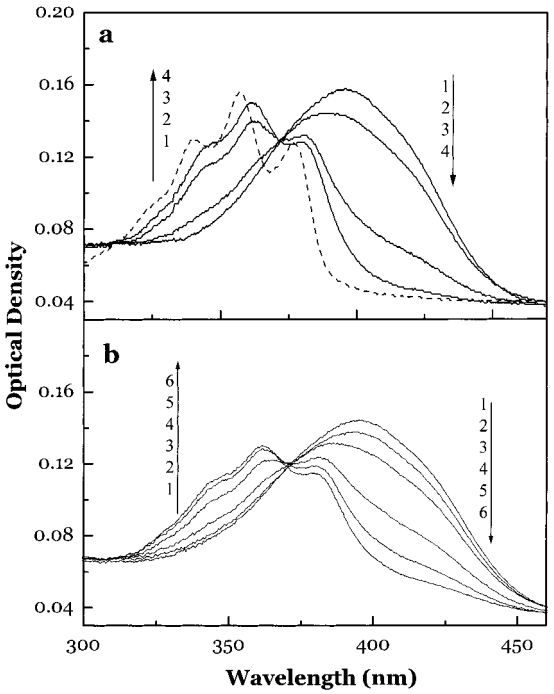

Figure 1. (a) UV−vis spectra of compound **1** in poly(methyl methacrylate) plus TPSHFA (3 wt %) after 248 nm UV irradiation; irradiation time: (1) 0, (2) 30 s, (3) 240 s, and (4) 600 s. Dotted line: Absorption spectrum of DPH in PMMA. (b) UV−vis spectra of a PMMA film containing equimolar quantities of compound **1** and TPSHFA; irradiation time: (1) 0 s, (2) 10 s, (3) 60 s, (4) 240 s, (5) 540 s, and (6) 1140 s.

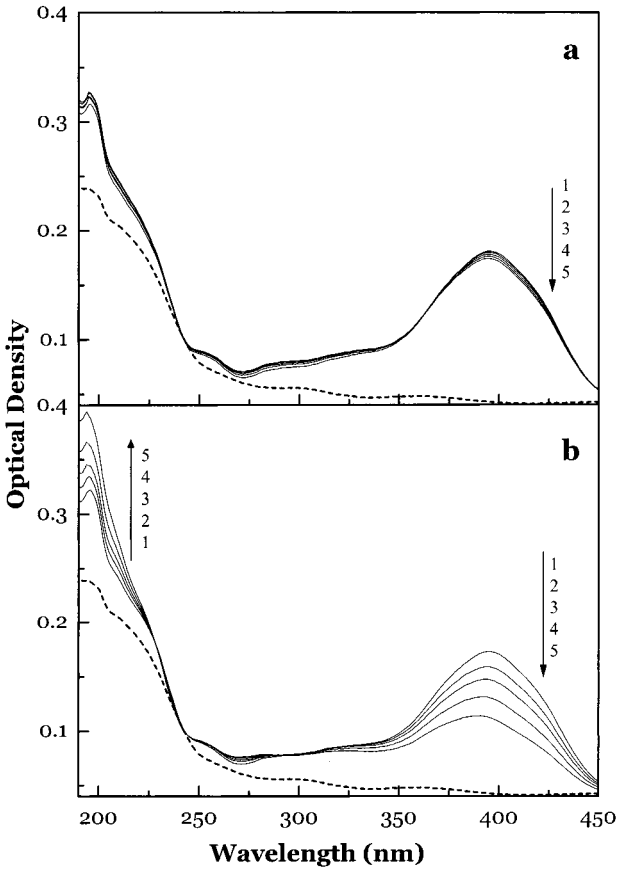

Figure 2. UV−vis spectra of compound **1** in PMMA after UV irradiation with (a) 248-nm narrow-band filter (6.5 nm half-bandwidth) and (b) 254-nm wide-band filter (50 nm half-bandwidth). *Dashed line* corresponds to absorption spectrum of PMMA alone. Assessed times are as hereupon: (1) 0 s, (2) 180 s, (3) 360 s, (4) 660 s, and (5) 1080 s.

wavelength maximum (400 nm) of the neutral DMA-DPH form (compound **1**) progressively decreases, whereas a new structured band appears with a maximum at 361 nm. The new absorption features resemble very closely those of DPH in accordance to our hypothesis. On the other hand, the evident isosbestic point occurring at 374 nm strongly supports a mechanism that proceeds between two distinguishable species involving no intermediates. Furthermore, fluorescence excitation spectra (Figure 3, inset) of compound **1** and compound **2** agree satisfactorily with the corresponding absorption spectra of the same compounds. It is also documented that 1-[4-(trimethylamino)phenyl]-6-phenylhexa-1,3,5,-triene (TMA-DPH), an analogous cation to compound **2**, which is also a derivative of DPH with a cationic moiety (trimethylamino) affixed to the *para* position of one of the phenyl rings, has photophysical properties that are generally very similar to those of DPH.[11]

Even though the polymer film contains TPSHFA and DMA-DPH in near 1:1 molar ratio, the yield of photoprotonation approaches 100% even in such highly stiff matrixes as those under investigation (see section III). In fact, in a PMMA film containing equimolar concentrations of each component, namely, compound **1** and TPSHFA, ([compound **1**] ≈ [TPSHFA] ≅ 2×10^{-2} mol/l), the conversion of compound **1** to the protonated form (compound **2**) proceeded quantitatively after irradiation for 15 min as manifested by absorption and fluorescence spectra (Figure 1b).

One could argue that the absorption spectral change observed after UV exposure is not related to photoacid generation but is rather due either to photooxidation products, since aromatic amines are easily oxidized by air, or most likely to the well-known photoisomerization that polyenes undergo after exposure to light even when they are enclosed in well-defined molecular cavities.[12] In an effort to clarify this point and safely eliminate the possibility of such artifacts, we performed control experiments having exposed the polymeric film to UV irradiation without using the photoacid generator. Two filters were employed in this part of study; the first one was the narrow-band filter which we had used in the experiments where the spectrum shift was noticed (248 nm, 6.5 nm half-bandwidth), and the second was a broad-band filter (254 nm, 50 nm half-bandwidth) that permits direct irradiation into the short- and near long-wave absorption band of the DMA-DPH molecule. As can be seen in Figure 2a, irradiation using the narrow filter did not induce any significant change in the UV−vis spectrum of the DMA-DPH molecule even after a prolonged illumination time period of about 20 min.

On the contrary, under irradiation with the broad-band filter, the fundamental all-trans absorption band of compound **1**, centered at 395 nm, gradually decreased to 65% of the original value, after a lapse of 18 min and,

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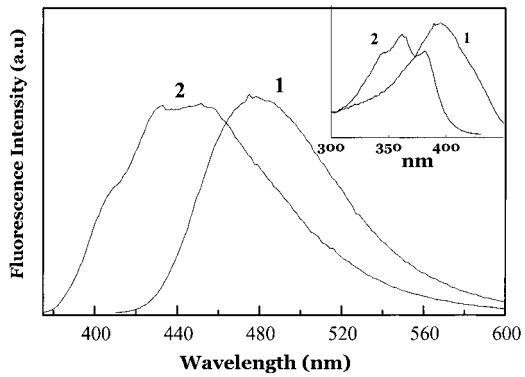

Figure 3. Fluorescence spectra of neutral (compound **1**) and fully protonated form of DMA-DPH (compound **2**). Excitation spectra of both forms are given in inset

simultaneously, an increase in absorbance at around 200 nm was observed as shown in Figure 2b. At the same time several isosbestic points were detected at 295, 240, and 228 nm, the initial maximum of all-trans conformer of compound **1**, located at 395 nm, progressively shifted toward the short-wavelengths spectral region. Clearly, these spectroscopic observations demonstrate the existence of structural rearrangement(s) occurring after illumination of the dye just with the broad-band filter. Although the verification of the identity of those new species is out of the scope of the present work, however, taking into account the similarity of our spectroscopic data with those concerning photoisomerization of the parent molecule DPH (Diphenylhexatriene) or related diphenylpolyenes in fluid media [13], it can be speculated that the primary photoproducts *cis-trans-trans* andr *trans-cis-trans* are responsible for the observed spectral changes. Photochemical destruction, however, should not be excluded as an additional factor to the aforementioned changes, under conditions of direct probe illumination.

Therefore, when triphenylsulfonium hexafluoroantimonate (TPSHFA) sensitizer is present in the film, as in the case of film illumination through the narrow 248 nm filter, the shifts in DMA-DPH absorbance spectra clearly indicate that the photogenerated protons attack the *para*-dimethylamino group of compound **1**.

II. Fluorescence Spectra and Imaging. On going to fluorescence spectral changes, the results are even more interesting. As can be seen in Figure 3 (curve 1), the initial neutral form of DMA-DPH (compound **1**) fluoresces strongly in the green spectral region. After irradiation for 10 min, green fluorescence totally disappeared and, by exciting the film into the new absorption band of the protonated form (compound **2**), blue fluorescence is observed as the single component (curve 2). The quantum yields of both forms are identical whereas further illumination does not induce changes on electronic spectra.

Having established effective signaling of photoacid generation in the above system, our next effort focused on the demonstration of the capability for the definition of bicolor fluorescence patterns. A thin film (0.53 μm)

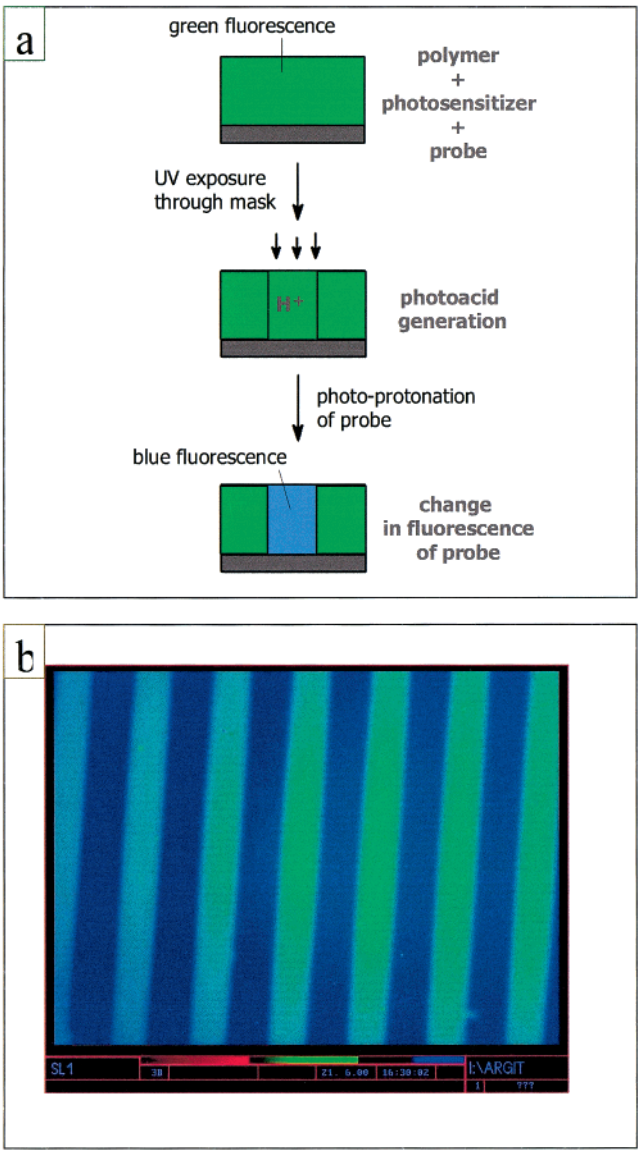

Figure 4. (a) Illustration of color patterning process. (b) Fluorescence patterns obtained with a PMMA thin film containing compound **1** (1 wt %) and the photoacid generator TPSHFA (3 wt %). The green areas are the regions exposed through the photomask. The actual colors may differ somewhat because of computer image process and printing quality. (Film thickness: 0.53 μm. Line width: 50 μm)

containing the polymer (PMMA), the photoacid generator (3% w/w), and the fluorescent compound **1** (1% w/w) was irradiated for 15 min in contact with a photomask at 248 nm (using the narrow-band filter mentioned above). The photograph shown in Figure 4b reveals two clearly resolved fluorescent regions under illumination with a 365-nm broad UV lamp adapted to a fluorescence microscope. As expected, the blue fluorescent areas are the regions exposed through the photomask.

The color patterning process is also illustrated schematically in Figure 4a. The exposure through a lithographic mask results in the generation of acid in selected film areas according to a well established microlithography process. Using the suitable fluorescence probe dispersed in the polymeric film, this photoacid generation leads to the definition of distinct color areas, in our example blue and green, in the polymeric film. Further extension of the technique for the defini-

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tion of red areas as well is conceivable. Nevertheless, suitable probes and ideas for the definition of three different color areas, possibly at the same level, are needed. In any case, the resolution capabilities of the technique are much higher and depend mostly on the lithographic equipment used for the patterning.

On the other hand, a reference to related techniques should be made at this point to facilitate further discussion on the potential of the presented methodology. In the area of OLEDs, the effect of protonation−deprotonation processes on tuning optical properties of a new type, PPV-like, conjugated polymer containing bipyridylene-vinylene subunits has been recently demonstrated by Y. Eichen et al.[14] They observed optical tunability both in concentrated solution of the above polymers in formic acid and in films saturated mainly by using different acid/base vapors in the atmosphere surrounding the film. According to the scheme presented here, however, color patterning using in situ photogeneration of acid in selected areas of the polymer matrix could be also effective upon suitable material modifications and the use of suitable probes. Analogous processes based on well-established processes adopted from semiconductor microlithography have been also proposed for the in situ modification of conductivity in polyaniline films and for the fabrication of polymer-based transistors.[15]

III. Fluorescence Depolarization in Polymeric Films. The definition of bicolor patterns according to the proposed scheme is based on the presence of protonated and unprotonated probe molecules in distinct film areas. Pattern stability issues, related to the probe diffusion, could prove important for the possible use of the technique in image recording or display applications. In a first attempt to study the motion of the unbound probe molecules in the typical polymer matrixes used in this investigation, we used the technique of fluorescence depolarization.

Fluorescence depolarization gives an estimation of the free volume inside the matrix if energy transfer from the originally excited dye molecule to a neighboring one is negligible. Figure 5a shows the effect of dilution upon the fluorescence anisotropy of the diphenylhexatriene (DPH) incorporated in PMMA matrix. The concentration region at which energy migration takes place and the region limit at which this is practically absent (below 2.7×10^{-3} M) are clearly seen. Figure 5b shows the linear dependence of $1/P$ (P is the fluorescence polarization) upon dye concentration as has been well verified for small molecules in viscous solvents.[16] The working eq 3 for the concentration range where intermolecular energy transfer between dye molecules is present is given by

$$\frac{1}{P} - \frac{1}{3} \cong \left(\frac{1}{P_0} - \frac{1}{3}\right)\left(1 + 1.68\left(\frac{R}{2a}\right)^6 C\right) \qquad (3)$$

where P and P_0 are the observed and maximum polarization, respectively, R is the critical distance between the two molecules such that the energy transfer probability equals the emission probability, a is the molecular radius, and C is the concentration in moles/l. By introducing a molecular radius of 8 Å for DPH in the above equation, a value of 26 Å for R is estimated from the line slope, which is in the typical range of 15−40 Å for small molecules in viscous solvents. A linear dependence of the fluorescence intensity versus concentration is also observed exactly below 2.7×10^{-3} M (Figure 5c), in perfect agreement with depolarization experiments.

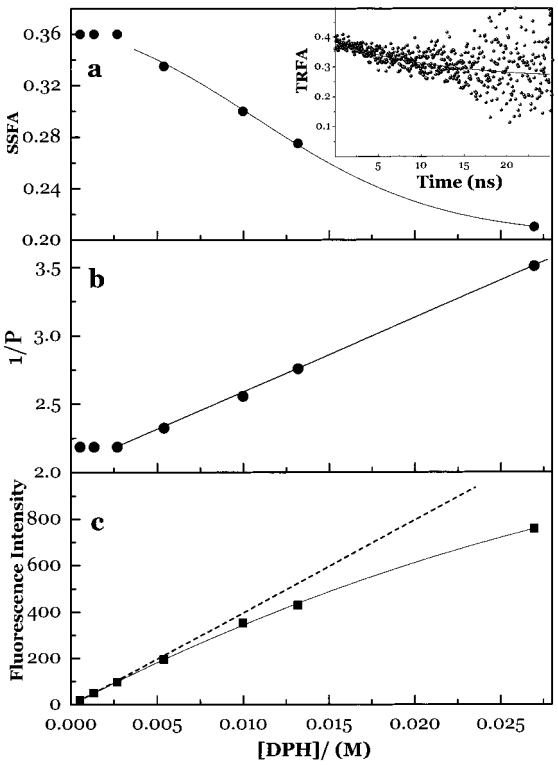

Figure 5. (a) Variation of steady-state fluorescence anisotropy (SSFA) on DPH concentration in a PMMA film. Inset: time-resolved fluorescence anisotropy (TRFA) trace. (b) A plot of $1/P$ vs concentration of DPH. Solid line indicates computer fit ($R^2 = 0.9999$) in the concentration region in which energy migration is present. (c) Dependence of fluorescence intensity on DPH concentration. Linearity was observed below critical concentration (2.7×10^{-3}M).

Under these conditions, steady-state anisotropy values $\langle r \rangle$ as high as 0.36 and 0.33 for DPH in PMMA and EPNOV, respectively, were found, whereas the DPH time-dependent anisotropy profiles decay before leveling off to residual anisotropy values of $r_\infty = 0.30$ and $r_\infty = 0.26$, respectively (see inset Figure 5a). The static $\langle r \rangle$ and limiting time-dependent anisotropy values (r_∞) for both matrixes are much larger than zero and close to the value measured in frozen solutions ($r_0 = 0.38$ [10]) demonstrating that diffusive and rotational motions of the dye are strongly hindered in the above matrixes.

Even though such stiff matrixes contain the dye and the photosensitizer at stoichiometry level, the photoprotonation yield approaches 100%.

IV. Energy Transfer in an Aromatic Polymer Matrix. The possibility for energy transfer to the probe in the typical aromatic polymer matrix (EPNOV) employed in the present contribution was investigated.

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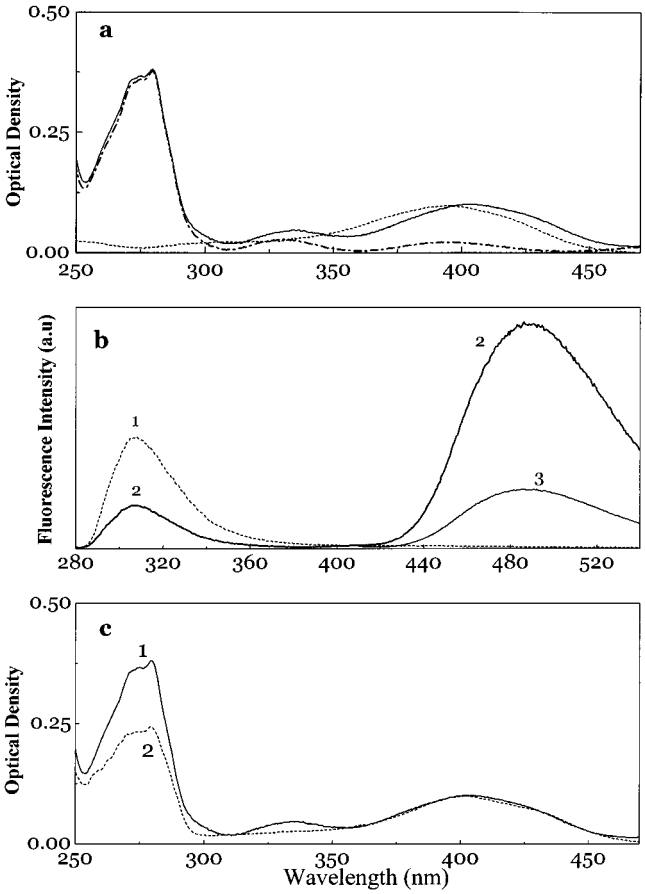

Figure 6. (a) UV−vis absorption spectra of various thin films. *Dash−dot line*: absorption spectrum of EPNOV. *Dash line*: absorption spectrum of compound **1** in PMMA matrix. *Solid line*: Absorption spectrum of compound **1** in EPNOV. (b) Fluorescence emission spectra of thin films: (*curve 1*) EPNOV alone, exc. at 275 nm; (*curve 2*) EPNOV + compound **1**, exc. at 275 nm; (*curve 3*) exc. at the absorption maximum (402 nm) of I. (c) Absorption (*curve 1*) and fluorescence excitation spectrum (*curve 2*) of compound **1** in EPNOV, recorded at the λ_{em} of the dispersed dye. Spectra have been normalized at the absorption maximum (402 nm) of the dye.

Transfer of energy in this system can be easily recognized because around 275 nm, where the polymer absorbs strongly, the absorption of the probe is negligible, as shown from the absorption spectra of thin films containing compound **1** dispersed in the EPNOV matrix on one hand and in an optically transparent matrix such as PMMA on the other (Figure 6a). An inspection of Figure 6b clearly shows that when the epoxy polymer units are excited at $\lambda_{exc} = 275$ nm, its own fluorescence ($\lambda_{em} = 310$ nm) is quenched and green fluorescence centered at 500 nm of compound 1 is observed, indicating energy transfer from the polymer backbone to the dispersed dye molecule. Upon excitation at $\lambda_{exc} = 275$ nm, no fluorescence was detected at 500 nm from the polymer backbone alone, whereas the fluorescence signal at 500 nm is amplified up to a nearly 400% higher value than the one obtained upon direct excitation of chromophore **1** at its maximum (402 nm).

The energy transfer efficiency was first determined by comparing the absorption and the fluorescence excitation spectrum recorded at the λ_{em} of the dispersed dye.[17] In fact, when these two spectra are normalized at the λ_{max} of the dye, any "loss" in intensity in the excitation spectrum relative to the absorption spectrum should reflect the energy lost during the transfer step. In our case, efficient intermolecular energy transfer through dipole−dipole interaction[18] of about 63% was manifested as seen in Figure 6c. The energy transfer efficiency was also estimated by the degree of the donor (polymer) emission quenching in the presence of the acceptor (dye). Figure 6b shows a comparison between the fluorescence spectrum of the epoxy novolac units, without and in the presence of compound **1**. It is roughly 62% at maximal loading, which is within experimental error in perfect agreement with the former method. In the matrixes consisting of the epoxy novolac polymer (EPNOV) plus the photosensitizer TPHSFA (3% w/w in our experiments), referred also in the literature as epoxy-resist (EPR),[9] the DMA-DPH probe shows similar absorption and fluorescence spectra shifts with those described in PMMA. Although the addition of the photosensitizer TPSHFA in the EPNOV polymer matrix induced a partial quenching of energy transfer, the transfer efficiency remained effectual and equally distributed in the two dye forms, the neutral (compound **1**) and the protonated (compound **2**)

The energy transfer observed in an aromatic polymer matrix, namely, EPNOV, as described above, permits excitation at the wavelength of the polymer absorption, that is, around 275 nm, resulting not only in fluorescent signal amplification but also in prevention of the chromophore photobleaching.[19] The results from the energy transfer experiments provide also further support for the potential of color patterning via in situ photoacid generation in the area of organic light-emitting devices (OLEDs), provided that similar results could be obtained in blue electroluminescent polymer matrixes using suitable color-shifting probes. Photochemical alteration of emission properties in selected film areas could greatly simplify the processes toward full color display microfabrication by reducing the necessary layers or even by totally eliminating the need for multilayer structures.

Summary

Photochemically induced color patterning in polymeric films has been demonstrated. In particular, the effectuality and applicability of the fluorescent dye DMA-DPH (compound **1**), in photoacid generation monitoring as well as in color and fluorescent imaging in polymer films was investigated. Well-resolved two-color fluorescent image patterns of high sensitivity were readily obtained.

Several advantages characterize the dye studied. First, it has a high extinction coefficient (≅70,000 M^{-1} cm^{-1}) and a high fluorescence quantum yield,[10] allowing effective signaling at low concentration levels in the polymer matrix so that the perturbation of the photoresist film properties is minimized. Second, the changes in electronic spectra of compound **1** that accompanied the photoacid generation procedure are very well dis-

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tinguishable permitting two-color imaging in fluorescence and "on to of" color in absorption. Third, the selectivity of the dimethylamino group of the probe toward photogenerated protons is as high as 100% even in such highly stiff matrixes as those under investigation, allowing also its use as an acid diffusion control additive at optimized concentrations in photoresist formulations. Fourth, in polymeric matrixes containing aromatic moieties that absorb and emit fluorescence in UV spectral region, for example, epoxy novolac polymer, significant "flow" of transferred energy from polymer to the probe was manifested, permitting amplification of fluorescent imaging signals as well as protection from dye photobleaching. Fifth, its absorption around 248 nm is negligible, and this allows the photosensitizer to absorb practically all incident light at exposure in this wavelength range.

This work is considered as the starting point in the investigation of photosensitive polymeric matrixes with DPH-DMA probe and other homologues. Fluorescence imaging by exposure at shorter wavelengths (e.g., 193, 157 nm and X-rays) and e-beam in suitable photoresist matrixes is conceivable. On the other hand, a similar strategy in electroluminescent polymer matrixes can lead to *photochemically activated color changing media* suitable for organic display applications.

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