Mapping Photogenerated Radicals in Thin Polymer Films: Fluorescence Imaging Using a Prefluorescent Radical Probe

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Photoinitiators, both free radical initiators and photoacid generators, are ubiquitous in imaging technologies which rely on polymerization reactions and chemically amplified processes in polymers.[1−4] Understanding the mechanism and efficiency of radical generation is key in their potential use in the design of more efficient photoinitiators. In microlithography, acid-sensitive fluorescent dyes have been employed extensively in the study of both photoacid-generating efficiencies and acid diffusion in polymer films.[5−8] Fluorescent images of acid generated in this way are actual maps of the spatial distribution of acid in polymer films. Although images of this type have been used primarily to gain insight into the development of physical images from latent images of acid, similar techniques, also relying on acid-sensitive fluorescent dyes, have been employed for the purpose of generating functional fluorescent images in polymer films.[9−11]

A novel approach to fluorescence imaging involving a prefluorescent radical probe has been developed and can be employed with free radical photoinitiators in much the same manner as acid-sensitive dyes have been used with photoacid generators. The technique makes use of two properties of nitroxides: their behavior as free radical scavengers and as quenchers of excited states. Molecules which contain a nitroxide tethered to a fluorophore via a short covalent link show dramatically reduced fluorescence due to intramolecular quenching of the fluorophore's excited state.[12−14] Free radical trapping by the nitroxide moiety yields a diamagnetic alkoxyamine, thus restoring the emission from the fluorophore. Similar chemistry occurs in living radical polymerization.[15] This behavior of fluorophore−nitroxide adducts has allowed their use as highly sensitive optical probes for free radical species.[16−22]

In this report, fluorophore−nitroxide adducts **1**[23] and **2** are employed in polymer films as probes for photogenerated free radicals from both α-hydroxy ketone, **3**, and diaryl-α-disulfone, **4**, thereby forming a fluorescence imaging system based on photoinitiated radical generation. Additionally, **2** serves as a dual probe for both photogenerated acid and free radicals from **4**. The use of **3** as a free radical photoinitiator is well-established, and it serves as an efficient source of a benzoyl-dimethyl ketyl radical pair.[24] The photodecomposition of diaryl-α-disulfones, such as **4**, to yield arylsulfonyl radicals as precursors to protic acids has been noted.[25−29] However, unlike α-hydroxy ketones, diaryl-α-disulfones are not widely used as photoinitiators; hence, most insight into their behavior has come from studies performed in solution as opposed to polymeric matrices.

Thin polymer films of poly(methyl methacrylate) (PMMA) containing **1** (0.5 wt %) and **3** (5 wt %) were prepared on quartz disks by spin-coating. Irradiation of these films resulted in a dramatic increase in the fluorescence of the film, consistent with photogeneration of free radicals by **3** and subsequent trapping by **1** (Figure 1A). These results are consistent with those obtained in solution studies using 2,2′-azobisisobutyronitrile and dibenzyl ketone as photoinitiators (results not shown). Similar increases in
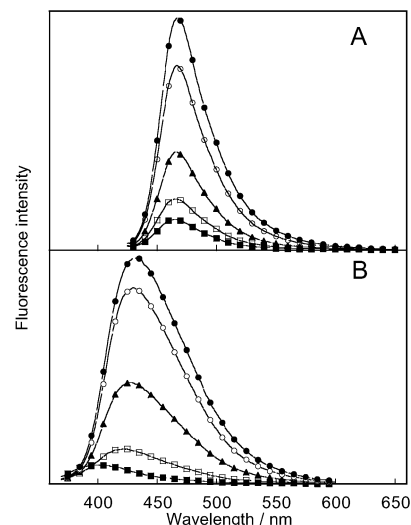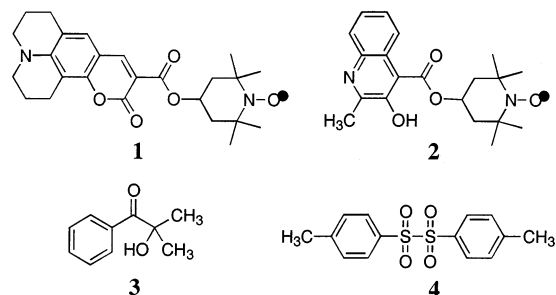

Figure 1. Fluorescence spectra of a 2.3-μm thick PMMA film containing **1** (0.5 wt %) and **3** (5 wt %) at 0 s (■), 15 s (□), 30 s (▲), 45 s (○), and 60 s (●) of exposure, obtained by excitation at 410 nm (A) and a 20-μm thick PMMA film containing **2** (0.5 wt %) and **4** (3.5 wt %) at 0 s (■), 30 s (□), 90 s (▲), 330 s (○), and 1000 s (●) of exposure, obtained by excitation at 360 nm (B).

fluorescence intensity were obtained with films containing **1** and **4**, demonstrating the intermediacy of free radicals in the photodecomposition of **4** within PMMA films.

It should be noted that PMMA films containing **1**, but without any photoinitiator also experience a slight increase in fluorescence intensity upon irradiation. Under the conditions shown in Figure 1A, a 40% increase in intensity is observed as compared to the 750% increase observed in the presence of **3**. This is a general result with fluorophore−nitroxide adducts and is likely due to hydrogen abstraction from the polymer by an excited state of the nitroxide, a well-known reaction.[30] In the presence of photoinitiators, the importance of this side reaction is greatly minimized and is expected to be unimportant due to shielding of the fluorophore-nitroxide adduct from the photolysis light.

Irradiation of PMMA films of **1** and **3** through a mask with 10-μm features produced finely resolved fluorescent images in which
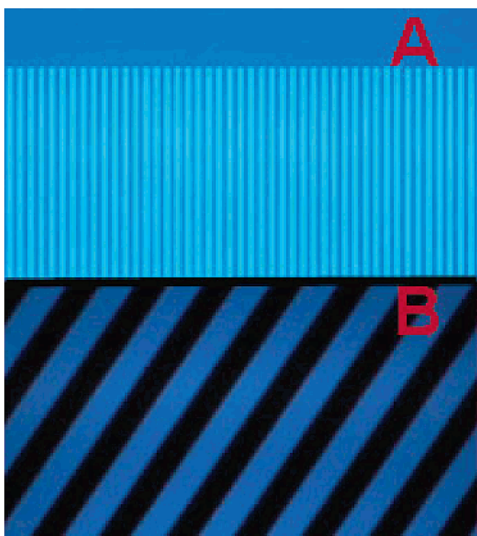
Figure 2. Fluorescent images (real color) of a 2.3-μm thick PMMA film containing **1** (0.5 wt %) and **3** (5 wt %) obtained by exposing through a mask with 10-μm line spacing for 90 s (A) and a 20-μm thick PMMA film containing **2** (0.5 wt %) and **4** (3.5 wt %) obtained by exposing through a mask with 55-μm line spacing for 200 s (B).

the highly fluorescent regions are those in which radicals have been photochemically generated and trapped by **1** (Figure 2A). In this way, mapping of the photogenerated radicals within the polymer films was achieved.

To further investigate the behavior of **4** as a photoacid generator in PMMA films, **2** was employed as a probe for both acid and free radicals. Aromatic monoazines have been employed as pH-probes in polymer films due to shifts in their wavelengths of maximum fluorescence (λ_{max}) which occur upon protonation.[5] The usefulness of **2** as a probe for acid was confirmed by the shift in λ_{max} from 395 to 450 nm upon addition of p-toluenesulfonic acid to an acetonitrile solution of **2** (data not shown). This behavior, in conjunction with that previously shown by fluorophore−nitroxide adducts, allows for the use of **2** as a sensor with independent output signals for acid (shift in the λ_{max}), and for free radicals (increase in fluorescence intensity).

Polymer films of PMMA containing **2** (0.5 wt %) and **4** (3.5 wt %) were prepared on glass microscope slides using the extensor technique, in which a calibrated rod is used to coat the substrate with the polymer solution. This technique was used for preparing thicker films of **2** because it allows for the creation of thicker films than the spin-coating technique. The longer path length provided by a thick film is required for performing fluorescence measurements with **2** due to its lower quantum yield of fluorescence than that for **1**. Irradiation of these films resulted in both an increase in the λ_{max} and an increase in the overall intensity of fluorescence from the film shortly after the onset of photolysis (Figure 1B). This behavior is consistent with photodecomposition of **4** to yield arylsulfonyl radicals which react via two competitive pathways, trapping by **2** and oxidative acid generation, which is not completely suppressed under the conditions employed.

Irradiation of PMMA films of **2** and **4** through a mask with 55 μm features produced finely resolved fluorescent images (Figure 2B) in which the highly fluorescent regions are those in which both acid and free radicals have been photochemically generated and trapped by **2** (Figure 1B, note red-shift due to protonation). When dibenzyl ketone (that generates radicals but no acid) is used as the initiator, the growth of fluorescence (at ~400 nm) is not accompanied by a spectral shift. We anticipate that future applications

of this method may allow the quantification of acid and radicals, and the sequence for their formation.

Prefluorescent radical probes and photoinitiators were used to detect free radical generation in polymer films using fluorescence spectroscopy and microscopy. In this way, prefluorescent radical probes are the foundation of a fluorescence imaging system for polymer films which is based on photoinitiated radical generation and does not require any postexposure baking or wet development of the film to obtain an image. This system may serve both as a mechanistic tool in the study of photoinitiated radical processes in polymer films and in the preparation of functional fluorescent images. Additionally, a pH-sensitive prefluorescent radical probe was employed as a dual probe for both photogenerated acid and free radicals and may prove useful in the study of photoacid-generator behavior in polymer films.

Supporting Information Available: Experimental details of the synthesis of compound **1**, UV/vis absorption spectra for compounds **1**−**4** as well as details on polymer film preparation and fluorescent image acquisition (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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