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Mono- and Multicolor FL Image Patterning Based on Highly Luminous Diphenylacetylene Polymer Derivative by Facile Photobleaching

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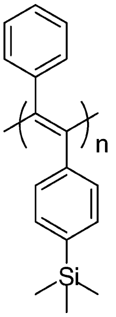
ABSTRACT: The fluorescence quenching behavior of thin films of poly[1-(trimethylsilyl)phenyl-2-phenylacetylene] (**PTMSDPA**) was investigated for the purpose of application of this polymer to mono- and multicolor FL imaging. When the film was exposed to 365-nm UV light with a power of 18.6 mW/cm^2 in air at room temperature, the fluorescence band with a maximum at 530 nm rapidly decreased, and then finely resolved fluorescent images were easily obtained using photomasks. After a prolonged irradiation time of 30 min, the **PTMSDPA** film exhibited an IR absorption peak at 1650 cm^{-1} due to the carbonyl group. On this basis, we presumed that the fluorescence quenching reaction was due to a small amount of diradical formed initially upon UV irradiation. The fluorescence of the **PTMSDPA** film was little quenched under an irradiance less than 1.15 mW/cm^2 even for tens of minutes, whereas the fluorescence of a highly photosensitive dye, such as Nile red, was readily quenched because of the high polarity in the excited state. As a result, the Nile-red-dispersed **PTMSDPA** film provided multicolor fluorescent images upon an irradiance of 1.15 mW/cm^2. The portions exposed through the photomask appeared the yellowish-green color of **PTMSDPA**, whereas the protected portions were the reddish-orange color of Nile red.

Introduction

The fluorescence (FL) imaging photolithography technique for potential application in photonic/electronic devices and biosensor chips was first explored by Kim et al.[1,2] Current related R&D efforts are directed toward novel strategies for the synthesis of functional materials, such as acid-sensitive fluorescent dyes and prefluorescent radical probes that are dispersed in polymer matrices or directly incorporated into the side chain of the polymers.[1−5] Very recently, another approach for attaining patterned FL imaging by using functional conjugated polymers was developed.[6−10] As demonstrated by Ohshita et al., photooxidation of such photosensitive polymers as silicon−π-conjugating polymer with a pendant fluorophor successfully led to patterned FL imaging in the pure film.[6] This type of polymer is expected to be precisely suited for the preparation of finely patterned FL imaging without significant phase separation and aggregation in the film. Meanwhile, the syntheses, photophysical properties, and application of fluorescent conjugated polymers such as polyacetylenes, polyfluorenes, poly(phenylenevinylene)s, and poly(phenyleneethynylene)s have been well described to date, and of course, they do not need any further reaction that attaches the pendant fluorophor into the polymer chain. Very recently, Tang et al. succeeded in FL image patterning through photooxidation and photo-cross-linking using substituted acetylene polymers.[9,10] Thus, these polymers could be more promising for the development of a synthetically simpler process for FL imaging if they show remarkable quenching behaviors upon simple photoirradiation.

Chart 1. Chemical Structure of PTMSDPA



Most disubstituted polyacetylenes exhibit very intense fluorescence, whereas the corresponding monosubstituted polyacetylenes usually do not, except for some polymers[9,11] containing appropriate chromophoric pendants.[12−17] Notably, some substituted acetylene polymers with extremely high fluorescence quantum yields of up to 98% have been developed by Tang et al.[15,18] Among the disubstituted polyacetylenes previously synthesized by us, on the other hand, the aromatic polyacetylene, poly[1-(trimethylsilyl)phenyl-2-phenylacetylene] (**PTMSDPA** in Chart 1), has been recognized as a very useful conjugated polymeric material in the areas of PL/EL device materials,[19,20] highly gas-permeable membranes,[21] and optical sensors.[22] The polymer obtained with $TaCl_5$−n-Bu_4Sn catalyst exhibts a high molecular weight of up to 1.0×10^6, is intensively fluorescent (quantum yield: $\Phi = 0.25$ in toluene), is quite soluble in organic solvents such as chloroform and toluene, and also provides a free-standing membrane with excellent mechanical strength and thermal stability.[23,24] It was previously reported that certain substituted polyacetylenes appear to be unstable in air because of oxidative cleavage of the C═C double bonds of the main chain upon prolonged heating or intense light irradiation, although they are markedly improved compared to the significant photo/thermal instability and insolubility of unsubstituted polyacetylene.[25−27] Although the degrees of degradation differ depending on the bulkiness of the substituents, oxidative

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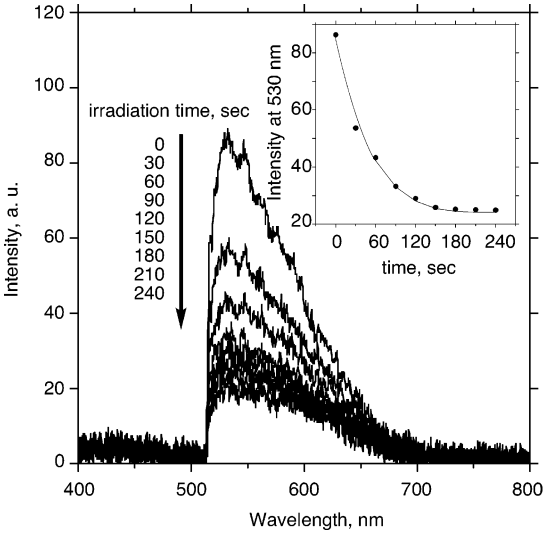


Figure 1. Change in florescence spectra of a 1.0-μm-thick **PTMSDPA** film upon UV irradiation (365 nm, 18.6 mW/cm^2). The inset shows a plot of the fluorescence intensity as a function of irradiation time.

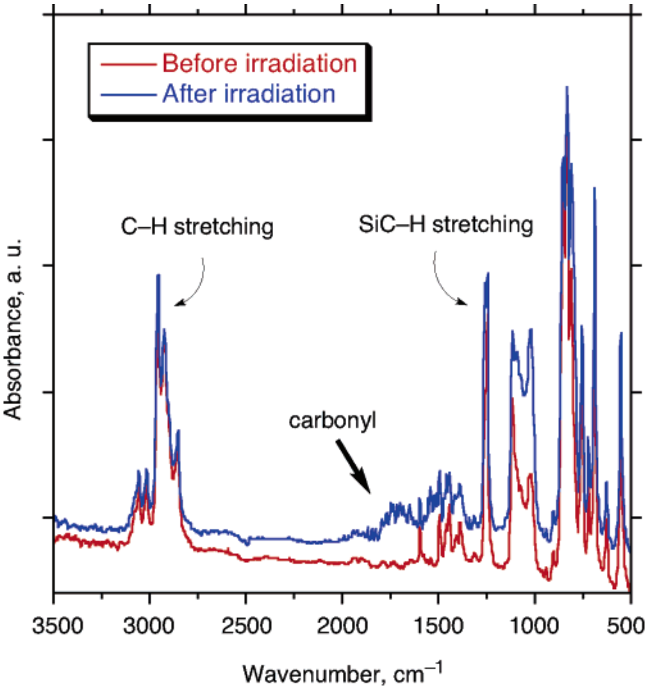


Figure 2. Change in IR spectra of a 1.0-μm-thick **PTMSDPA** film upon UV irradiation (365 nm, 18.6 mW/cm^2) for 30 min.

cleavage is essentially unavoidable. In aromatic polyacetylenes, however, the diradicals formed by irradiation or compression are stable as a result of delocalization of the energy absorbed, and the resulting mobile unpaired electrons, called solitons, do not have the ability to abstract hydrogen from the aryl groups because of the high bonding energy of aromatic hydrogen.[25,28,29] This implies that aromatic polyacetylenes are able to effectively afford radicals in the main chain upon light irradiation, while avoiding, as much as possible, fatal damages such as a significant decrease in molecular weight and a change in characteristics upon degradation. The photophysical properties of aromatic polyacetylenes can also significantly change upon photoirradiation as a result of the stabilized diradical formed in the main chain, because such a conjugated polymer usually exhibits collective properties that are sensitive to very minor electronic perturbations.[30] In particular, in the case of a fluorescent conjugated polymer, such cooperativity could be amplified by efficient energy migration, leading to significant fluorescence quenching. As mentioned above, **PTMSDPA** is strongly fluorescent and contains two phenyl groups in the side chain. On the basis of the advantages of its optical properties and chemical structure, we reasoned that **PTMSDPA** could be a promising material for FL imaging.

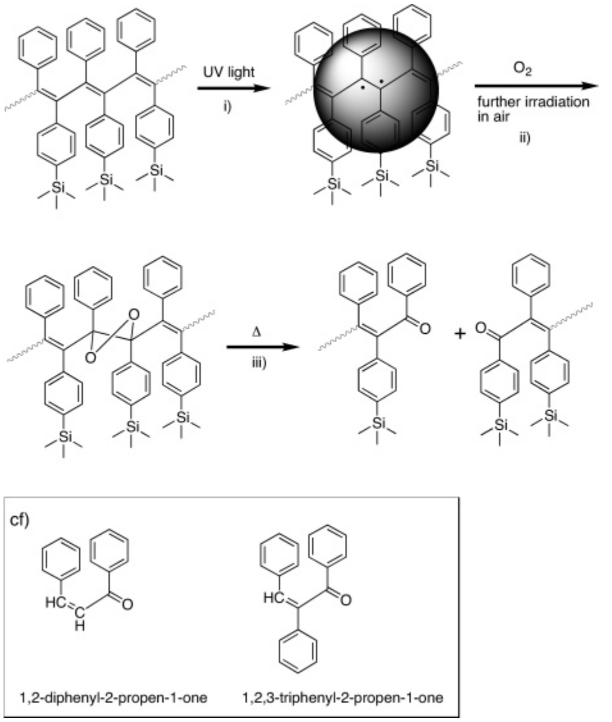
Results and Discussion

PTMSDPA was prepared according to a literature procedure.[23,24] The polymer had a weight-average molecular weight (M_w) of 1.3×10^5 with a polydispersity index of 4.2. To investigate the degree of quenching upon irradiation with UV light, a thin film (thickness $= 1$ μm) was prepared by spin-coating a toluene solution on a slide glass. Figure 1 shows the fluorescence spectra of the **PTMSDPA** film. The virgin film exhibited a fluorescence band with a maximum at 530 nm, and the stiff cutoff of the band around 510 nm might be due to a self-absorption ascribed to the thickness of the film. When the film was irradiated with UV light (365 nm, 18.6 mW/cm^2) in air at room temperature, the fluorescence band significantly decreased during the initial period of 120 s, and the quenching reaction reached equilibrium approximately 4 min later.

To examine the mechanism of the fluorescence quenching reaction, we measured the IR spectrum of the film upon UV irradiation. In contrast to the complete fluorescence quenching 120 s later, there was no detectable change in the IR spectrum. Also, the fluorescence quenching occurred not only in air but also under a pure nitrogen (99.995%) flow. A small amount of stabilized diradical presumably formed in the main chain upon UV irradiation with or without air during the initial period, and it quenched the fluorescence effectively, because such radicals intrinsically show a forbidden transition and may act as a fluorescence-energy-trapping site in such a conjugated polymer. In other words, the quenching is ascribed to an effective energy transfer between the radical formed and the polymer backbone. Notably, when the irradiation time was prolonged to about 30 min in air, a broad IR absorption peak newly appeared around 1650 cm^{-1}, as shown in Figure 2. Similarly, carbonyl absorption peaks of such unsaturated carbonyl aromatic compounds as 1,2-diphenyl-2-propen-1-one and 1,2,3-triphenyl-2-propen-1-one apparently appear at 1666 and 1645 cm^{-1}, respectively (see the structures in Scheme 1),[31] whereas saturated carbonyl compounds usually exhibit such characteristic carbonyl peaks at frequencies above 1700 cm^{-1}. Thus, the new peak is probably due to certain unsaturated carbonyl products. Presumably, the diradicals form initially in the **PTMSDPA** film and are stabilized through electron delocalization into the aromatic side groups, whereas further UV irradiation causes the diradicals to react with oxygen gradually in air to produce a dioxetane that decomposes thermally to excited triplet carbonyl products.[32−36] Accordingly, the most probable photobleaching mechanism of **PTMSDPA** should be that proposed in Scheme 1. At the same time, one can notice that the chemical structure of the unsaturated carbonyl terminal moiety in the degraded **PTMSDPA** is quite similar to those of 1,2-diphenyl-2-propen-1-one and 1,2,3-triphenyl-2-propen-1-one.

Figure 3 shows the finely resolved fluorescent images obtained by the photobleaching of the **PTMSDPA** thin film. Even using a photomask with 5-μm features, a finely resolved fluorescent image pattern was readily obtained. The portions exposed through the photomask appeared dark under fluorescent microscopy. Generally, the absorption behavior of a conjugated polymer is much less sensitive to minor electronic perturbations

Scheme 1. Proposed Reaction Mechanism for the Quenching of PTMSDPA[a]



[a] (i) Diradical forms upon initial UV irradiation (<90 s in Figure 1) and acts as a fluorescence quencher (the black circle signifies delocalization of the energy absorbed by the radical) and (ii) further irradiation makes the radicals react with oxygen in air to produce a dioxetane, (iii) which decomposes thermally to two carbonyl products.

induced by impurities and structural defects than its fluorescence behavior, which depends on energy transfer.[30] In fact, the fluorescence of **PTMSDPA** was almost completely quenched after the UV irradiation, whereas there was no detectable change in the UV−vis absorption spectrum or the color of the film. Furthermore, the refractive index of the **PTMSDPA** film, which was 1.62 at 530 nm, hardly changed after the UV irradiation. The **PTMSDPA** also essentially maintained its high molecular weight after the UV irradiation. M_w was still high as 1.1×10^5 ($M_w/M_n = 4.2$) even after the prolonged irradiation time of 30 min. This indicates that the UV irradiation efficiently induces fluorescence quenching without any marked changes in other properties.

In the photobleaching of **PTMSDPA** thin film, the reaction rate was significantly dependent on the UV irradiation power. As shown in Figure 4, no detectable change in fluorescence was seen under an irradiance of less than 1.15 mW/cm^2 for tens of minutes, whereas the fluorescence was immediately quenched with an irradiance of 18.6 mW/cm^2. In contrast, fluorescent dyes such as Nile red, DCM, and coumarin are polar in the excited state because of their intramolecular charge-separation character, and hence, they can be readily decomposed with a relatively low irradiation power, leading to fluorescence quenching. This finding led to the idea that it could be possible to quench only the fluorescence of the dye dispersed in a thin film of **PTMSDPA** to obtain a multicolor fluorescent image pattern.

Nile red was chosen for this purpose. Figure 5 shows (a) the optical properties of Nile red in a PMMA thin film and (b) the fluorescence quenching behavior. Nile red exhibits absorption and fluorescence bands with maxima at 530 and 596 nm, respectively, and its fluorescence is relatively readily quenched under an irradiance of 1.15 mW/cm^2, probably because of the high polarity (dipole moment = 14.4 D)[37] in the excited state.

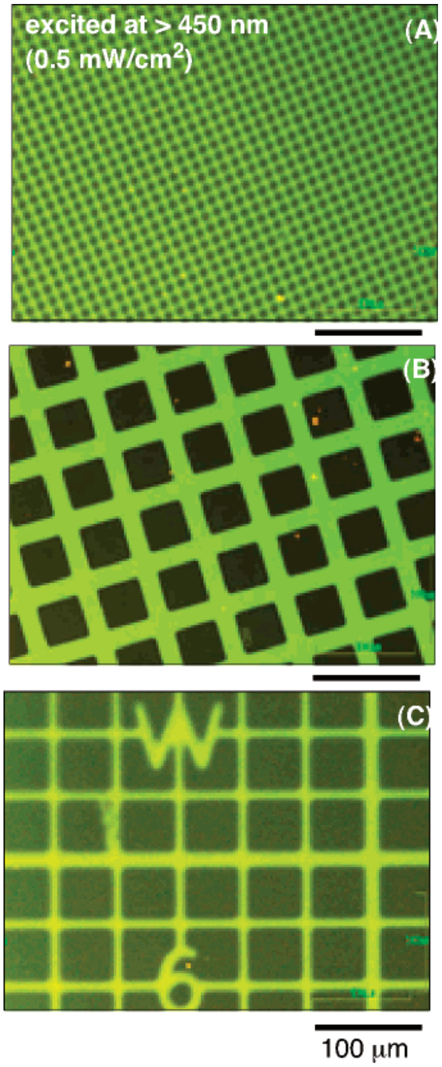


Figure 3. Fluorescent image patterns obtained with a 1.0-μm-thick film of **PTMSDPA** on a slide glass after UV irradiation (365 nm, 18.6 mW/cm^2) for 4 min through various photomasks with (A) 5-, (B) 20-, and (C) 10-μm-thick lines.

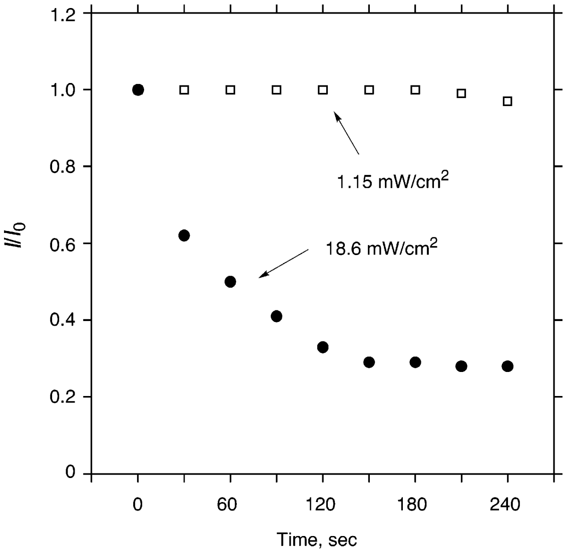


Figure 4. Plots of fluorescence quenching of a 1-μm-thick **PTMSDPA** film as a function of time under different irradiances (●, 18.6; □, 1.15 mW/cm^2). I_0 and I are the intensities of fluorescence at 530 nm before and after irradiation, respectively.

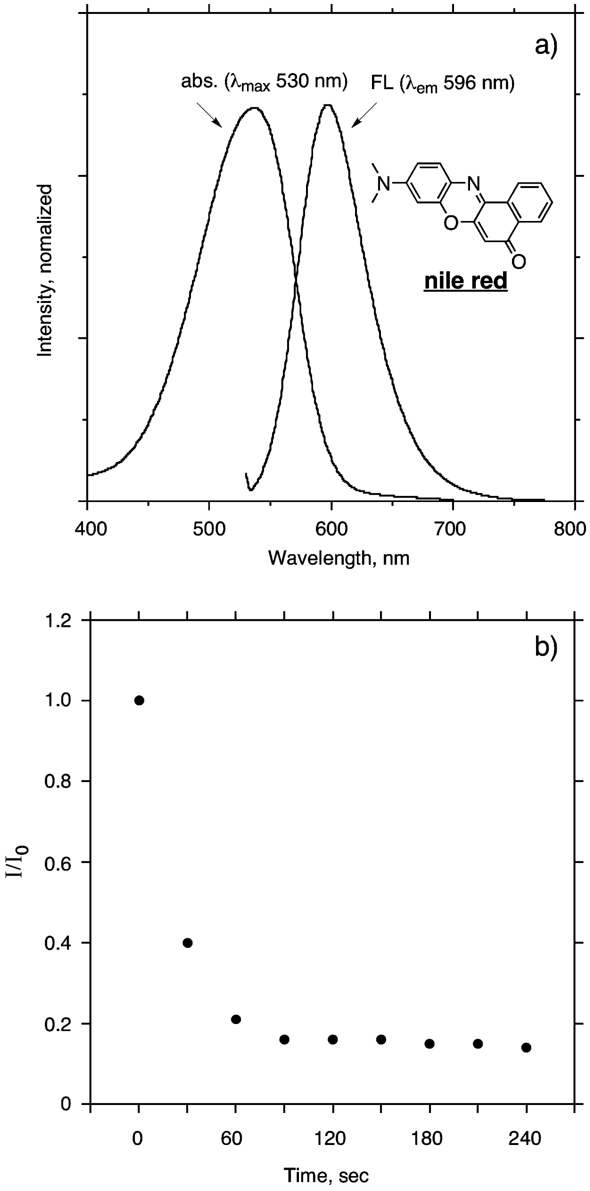


Figure 5. (a) UV absorption and fluorescence spectra of Nile red in a 1-μm-thick PMMA film (Nile red concentration = 5 wt %). (b) Plots of fluorescence quenching of Nile red dispersed in a PMMA film as a function of time under an irradiance of 1.15 mW/ cm^2. I_0 and I are the intensities of fluorescence at 596 nm before and after irradiation, respectively.

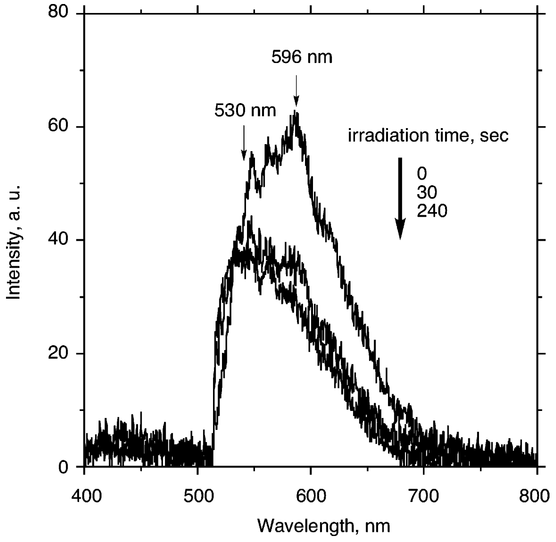


Figure 6. Change in florescence spectra of 1.0-μm-thick Nile-red-dispersed **PTMSDPA** film (Nile red concentration = 5 wt %) upon UV irradiation (365 nm, 1.15 mW/cm^2).

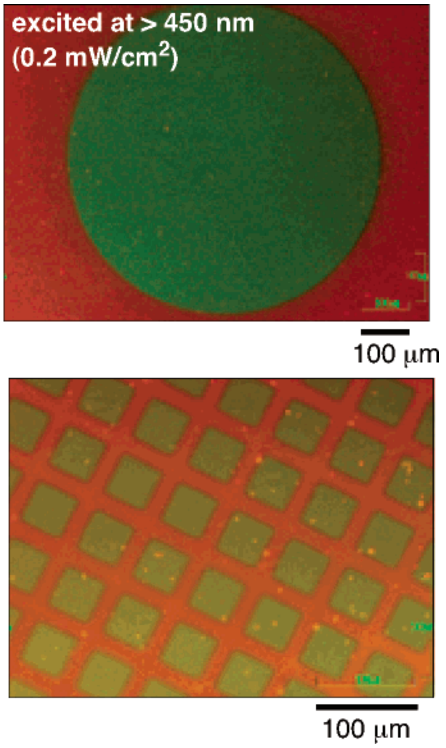


Figure 7. Fluorescent image patterns obtained with a 1.0-μm-thick film of Nile-red-dispersed **PTMSDPA** (Nile red concentration = 5 wt %) on a slide glass after UV irradiation (365 nm, 1.15 mW/cm^2) for 240 s through photomasks.

It should be noted that the absorption band of Nile red well overlaps the fluorescence band of PTMSDPA. This indicates the possibility of effective Förster-type energy transfer from **PTMSDPA** to the dye. Actually, when excited at the absorption wavelength of **PTMSDPA** in the range of 450−490 nm, the Nile-red-dispersed **PTMSDPA** film exhibits a fluorescence band located at 596 nm due to the intramolecular charge transfer of Nile red in addition to the 530-nm band. Figure 6 shows the change in fluorescence of the Nile-red-dispersed **PTMSDPA** film under an irradiance of 1.15 mW/cm^2. As expected, only the 530-nm band remains, whereas the 596-nm band immediately disappears In accordance with the spectral change, the fluorescence changes in color from reddish-orange to yellowish-green. As a result, a finely resolved multicolor fluorescent image was successfully obtained, as shown Figure 7.

In conclusion, we demonstrated that the fluorescence of thin films of **PTMSDPA** is significantly quenched by UV irradiation and finely resolved fluorescent images are easily obtained by exposure through photomasks. Also, the combination of **PTMSDPA** and a highly photosensitive dye such as Nile red can be used to obtain a multicolor fluorescent image simply by controlling the irradiation power. Further experiments concerning the possible fluorescence quenching of other luminous conjugated polymers, including polyfluorenes, poly(phenylenevinylene)s, poly(phenyleneethynylene)s, and polyesters,[38] are currently underway in our laboratory. This photobleaching technique using **PTMSDPA** as a photopolymer is applicable to optical data storage system with write-once read-many (WORM) capability. Furthermore, the combination of **PTMSDPA** with fluorescent dyes or other polymers in multilayer film might make it possible to develop a new type of high-density, three-dimensional optical data storage system. [39−42]

Experimental Section

Preparation and Photoimaging of PTMSDPA Thin Films. One-micrometer-thick pure and Nile-red-dispersed **PTMSDPA** films were prepared by spin-coating toluene and THF solutions (concentration = 2.5 wt %), respectively, on a glass slide (Matsunami) using a Mikasa 1H-D7 spin coater (500−3000 rpm). The films were exposed to 365-nm UV light amplified by an object lens from a super-high-pressure 100-W Hg lamp (OSRAM, HBO103W/2). The irradiation power was controlled using several neutral-density (ND) filters and was monitored by UV-light meter (Lutron, YK-34UV). For the purpose of FL imaging, several metal sheet meshes (Nisshin EM, G2000HS, F-400, H-7 type grids, thickness = 4−10 μm) were used as photomasks.

Measurements. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymer were evaluated using gel permeation chromatography [Shimadzu A10 instruments, Polymer Laboratories, PLgel Mixed-B (300 mm in length) as a column, and HPLC-grade tetrahydrofuran as the eluent at 40 °C], based on a calibration with polystyrene standards. UV−vis and IR spectra were measured on Jasco UV-550 and Horiba FT-730 spectrophotometers, respectively. CCD images were recorded on a Nikon Eclipse E400 fluorescence microscope equipped with a Nikon DL-5M digital camera. Fluorescence spectra were measured on an Ocean Optics HR4000 UV−NIR high-resolution spectrophotometer attached to the fluorescence microscope. The refractive indices of the polymer film were determined using a variable-angle spectroscopic ellipsometer (Unisel, Horiba-Jobin Yvon, Japan) using the wavelength range of 300−800 nm in air at room temperature.

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