Photochemically-Induced Refractive Index and Fluoresence Patterning on Polymer Films

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Summary: The molecular design for large photo-induced refractive index changes in transparent visible light region was proposed and realized with norbornadiene polymers and poly(vinyl cinnamate). The patterning of pure refractive-index contract on their transparent films was made with near-field scanning optical microscopy (NSOM). Reversible fluorescence patterning on polymer films is also presented by using controlled energy transfer from a fluorescent pyromethene to a photochromic diarylethene.

Keywords: refractive index; fluorescence; patterning; photochromic dye; NSOM

Introduction

Photoreactive substances such as photochromic compounds, when they are molecularly doped in polymer films, show various photoresponsive functions and have potential applications to optical memories, switches, and other photonics devices. Refractive index patterning is a key technology in waveguides and photonics devices. We have developed several materials with norbornadiene derivatives which show large refractive index changes in nonresonant visible light regions keeping transparency both before and after photochromic reactions[1]. Recently pure patterning of refractive index contrast on a transparent polymer film has been realized by using near-field scanning optical microscopy (NSOM) with He-Cd laser and norbornadiene derivatives[2,3].

Another kind of patterning on polymer films with the use of photochromic reactions would be carried out by the combination of a photochromic compound with fluorescent dyes. Fluorescence is very sensitive for detection and widely used as probes for microanalysis, dynamic studies on biological and polymer systems, and single molecule spectroscopy. Fluorescence has a possibility to be used also for nanoscale patterning with NSOM. The combination of a

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fluorescent dye with a photochromic compound provides wide possibility of photochemically-induced fluorescence patterning of polymer films.[4]

Molecular Design of Photochemically-Induced Large Refractive Index Changes

The refractive index, n, of a compound can be related to the molar refraction, R, the molar mass, M, and the density, ρ, by the Lorentz-Lorenz equation, (1) by[5]

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} \qquad (1)$$

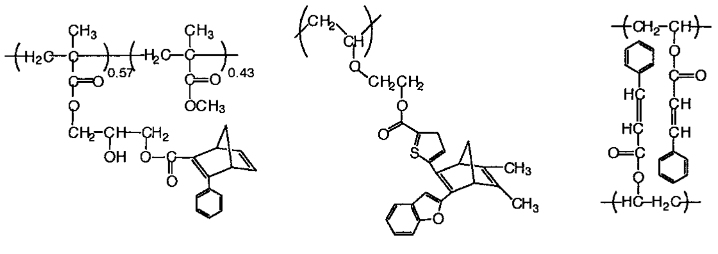
Photoinduced refractive index changes of polymer films containing various photochromic compounds were reported by several authors,[6-9] and they obtained refractive index changes of 10^{-3}~10^{-2} during photoreaction. However, photochromic dyes usually have absorption bands in the longer wavelength visible region.

In order to achieve both large refractive index change by photochemical reaction and large transparency in the wide wavelength regions especially in the visible region both before and after the photoreaction, the molecular design of dividing a large delocalized π-conjugation of a photoreactive compound into two small conjugation moieties by photochemical single bond formation at its central part has been proposed.[1, 10, 11]

Norbornadiene (NBD) is famous as a photochromic dye, and in past years the photoisomerization of NBD to quadricyclane (QC)[12] has attracted much attention for solar energy storage. NBD shows a large change in electronic distribution during the photoisomerization, only a small change in molecular volume with the ability to set up a high concentration in film, large transparency in the wide wavelength region especially in the visible region, and a high quantum yield of the photoisomerization.[1] We bound NBD moieties to the polymer chains due to easier film preparation with a high NBD concentration and high uniformity. Refractive index change of NBD during photoisomerization was found to be about -0.01 at 633 nm for P(MMA-co-GMA-PNCA) films,[1] where PNCA denotes phenyl-substituted norbornadiene carboxylic acid bound to glycidyl methacrylate (GMA), and −0.06 for a polymer film bearing thiophenyl- and benzofuryl-substituted norbornadiene groups (PolyTBFNBD). [3]

The photodimerization of poly(vinyl cinnamate) (PVCm) film [10] and photobleaching of (4-*N*,*N*-dimethylaminophenyl)-*N*-phenyl nitrone (DNAPN) doped in PMMA films[13, 14] realized irreversible large refractive index changes of −0.037 and −0.026 ~0.028, respectively, at 633 nm. These values are sufficient to make efficient channel waveguides, holography microlenses, and other optical devices by photoreactions. The chemical structures of these polymes are summarized in Figure 1, and the wavelength dependence of refractive index, *n*, of polyTBFNBD before and after Xe lamp irradiation are shown in Figure 2. The refractive indices and film thickness were measured by using a *m*-line method.[9]

The isolation of aryl and ester (esterthiophenyl) groups and the disappearance of delocalized π-conjugation between them would be the reason of providing large refractive index changes of these polymers in nonresonant regions induced by photoreactions.



P(MMA-co-GMA-PNCA) Poly(TBFNBD) PVCm

Figure 1. chemical structures of polymers realizing large photoinduced refractive index changes.

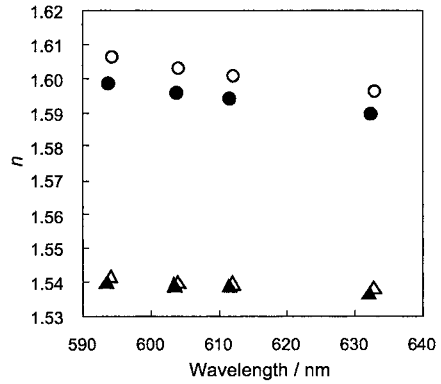


Figure 2. Refractive indices, *n*, of PolyTBFNBD film before (circle) and after 60 min (triangle) Xe lamp irradiation with a Y44 filter. Open symbols are for *n* in TE mode; filled ones are for *n* in TM mode.

Refractive Index Patterning Using NSOM

Nanostructure formation on the surfaces of various kinds of materials is a basic technology of so called "nanotechnology" which has recently been extensively studied. Pattern formation based on refractive index is of great importance with respect to the optoelectronic integrated circuits. Near-field scanning optical microscopy (NSOM) is one of the super-resolution techniques which can circumvent the diffraction limit of light.[15] NSOM can be used as a tool to modify the sample surface in addition to the image acquisition and spectroscopy. Although there are several reports on such surface modification using NSOM,[16-20] the first report on creating a pure refractive-index pattern, i.e., refractive-index patterning without changing the surface morphology and the transparency of the sample has been presented by the present authors[1] by using a thin film of 3-phenyl-2,5-norbornadiene-2-carboxylic acid (PNCA) 35 wt% doped in PMMA.

The simultaneously obtained topographic image and corresponding NSOM image (taken at 442 nm) are presented in Figure 3. The UV (325 nm) -irradiated line is located vertically at the center of the image. The topographic image is almost flat in the irradiated region. In contrast to the topographic image, there is a dark band in the NSOM iamge observed around the irradiated region. This band was not observed before irradiation, indicating that this band has been fomed by the photochemical reaction of PNCA doped in PMMA.

It should be noted that this material is transparent at 442 nm, therefore, the optical contrast observed in Figure 3 does not originate from the increase in optical density. It is reported that in the near-field regime, a transparent sample with spatial variations in the refractive index may also show a transmission contrast.[21, 22] The apparent variations in the transmission intensity are related to the coupling efficiency of the optical near field (evanescent light) to the far field (propagating light), and the theory of the conventional Rayleigh scattering can be applied to the coupling efficiency of the optical near field to the far field. For PNCA-PMMA thin films, the refractive index of the UV-irradiated area decreased by approximately 0.006 suggesting the expected contrast in the taransmission NSOM image of about a 2.3 % decrease, which is comparable to the measured value (0.5 %).

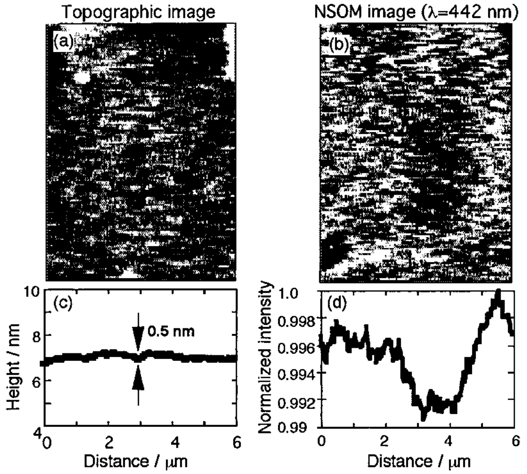


Figure 3. Topographic image (a) and corresponding transmission NSOM image (b) for the UV (325 nm)-irradiated PMMA-PNCA thin film (3 μm thick). The wavelength for obtaining the NSOM image was 442 nm. The irradiated area was a vertical line with length of 4 μm located at the center of the image. The averaged cross sections for (a) and (b) are displayed in (c) and (d), respectively.

Refractive-index patterning on PolyTBFNBD films was also carried out with NSOM. [3] A PolyTBFNBD film with the thickness of about 50 nm was irradiated with evanescent light from the NSOM probe coupled with 442 nm He-Cd laser, and simultaneous topographic and corresponding NSOM images were taken at 633 nm (He-Ne laser) before and after 442 nm irradiation. Before the 442 nm irradiation, no image was observed with either topographic or NSOM detection. After 20 second scanning irradiation of 442 nm light, the topographic image is almost flat in the irradiated region, but a dark band in the NSOM image appeared in the irradiated region, owing to the photochemical reaction of NBD groups in the film.

Photochemically-Induced Fluoresence Patterning by Combination of a Fluorescent Dye with a Photochromic Dye

Control of chemical and physical properties of photochromic compounds by photoirradiation has been widely studied because of their potential fabrication of reversible optical data storage and memory devices.[23, 24] However simple photochromic system has a problem that the readout process brings about partial erasure of the stored information.

To realize a non-destructive readout system, we can use some method including changes in refractive index,[8] luminescence[25-28] and optical rotation.[29] Among them, changes in luminescence properties are one of the most attractive candidates for the non-destructive systems because of its excellent properties such as high sensitivity, high resolution and high contrast. The system where luminescence is reversibly controlled can be effectively applied to a polymer film system because a polymer film provides some advantage of its processability and reasonable cost performance.

One effective approach to make luminescence patterns on a polymer film is that both a photochromic compound and a fluorescent dye are molecularly dispersed in a polymer film where fluorescence intensity of the fluorescent dye can be reversibly controlled by photoisomerization of the photochromic compound.[4] In this system, the fluorescence properties can be controlled as follows; the fluorescent dye fluoresces if there is no interaction between the excited state of the fluorescent dye and the photochromic compound. The fluorescent dye can not fluoresce if there is some interaction such as energy transfer or exciplex formation between the excited state of the fluorescent dye and a photoisomerized state of the photochromic compound. By choosing suitable combination of a fluorescent dye and a photochromic compound, complete on-off of fluorescence can be realized.

cis-1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE) as a photochromic compound and coumarin 540A (C540A) or pyrromethene 546 (PM546) as a fluorescent dye were molecularly dispersed in PMMA films in the present system (Figure 4). The absorption spectra of CMTE before and after photoirradiation together with the absorption and fluorescence spectra of PM546 are shown in Figure 5.[4] The overlap of fluorescence spectrum of PM546 with absorption spectrum of closed ring form of CMTE assures rapid excitation energy transfer between them and complete quenching of PM546 fluorescence. It should be noted that the light exciting the fluorescent dye (496 nm) is not absorbed at all by the open ring form of CMTE. A typical example of the change in fluorescence spectra before and after the photochromic reaction of CMTE is shown in Figure 6 for PM546 and CMTE in a PMMA film. The film shows strong fluorescence of PM546 before the photochromic reaction of CMTE (a), but the closed-ring form of CMTE after the photochromic reaction induced by a high-pressure mercury lamp irradiation quenched the PM546 fluorescence due to excitation energy transfer from PM546 to the closed-ring form of CMTE (b). The backward photochromic reaction by visible light irradiation on the sample provided the fluorescence emission again of the film (c).

Excitation energy transfer in a solid film is usually analized by using Perrin equation[30]

$$\ln (I_0/I) = C/C_0 \qquad (2)$$

where I_0 and I are the luminescent intensities of donor in the absence and presence of acceptor, respectively, C_0 is the critical concentration of quenching, and C is the comcentration of acceptor. A plot of ln (I_0/I) versus C gave straight lines for PM546/CMTE doped in PMMA films, with C_0 of 7.25 and 2.28 wt% before and after photoisomerization of CMTE, respectively. Recovery of fluorescence patterning during repeated writing and erasing has been ascertained for more than 20 times, which is limited mainly by the stability of the phtochromic compound.

The present system with CMTE and PM546 provides a reversible photochemically-induced fluorescence patterning with high contrast.

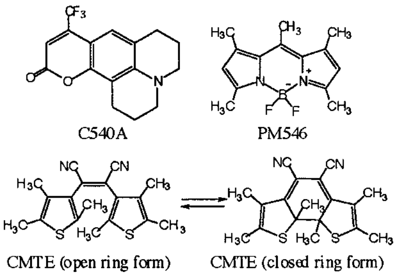


Figure 4. Fluorescent dyes and a photochromic dye for photochemical control of fluorescence patterning.

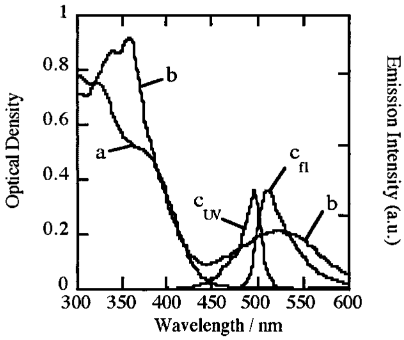


Figure 5. Absorption spectra for CMTE open ring form (a), CMTE closed ring form (b), and absorption and fluorescence spectra of PM546 (c).

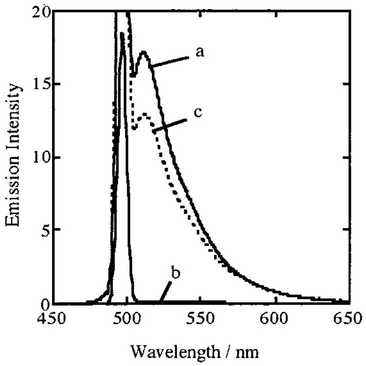


Figure 6. Change in fluorescence spectra (Excitation: 496 nm) of a PM546 (0.25 wt%) + CMTE (9.97 wt%)/PMMA film before (a) and after (b) photochromic reaction and after backward photochromic reaction (c) of CMTE.

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