

Large Photoinduced Refractive Index Change of Polymer Films Containing and Bearing Norbornadiene Groups and Its Application to Submicron-Scale Refractive-Index Patterning

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ABSTRACT: We measured photoinduced refractive index changes of polymer films containing various norbornadiene compounds. Poly(methyl methacrylate) (PMMA) films containing 51.6 wt% of 5,6-(2-benzofuryl)-2,3-di-(trifluoromethyl)-1,4,7,7-tetramethyl-2,5-norbornadiene (NBD4) showed refractive index changes of 0.037 during photoisomerization. A polymer film bearing thiophenyl- and benzofuryl- substituted norbornadiene groups (PolyTBFNBD) showed a refractive index change of 0.05–0.06 for 594–632.8 nm during photoisomerization. This value is the largest value of refractive index change so far in a nonresonant region induced by photochemical reactions. Submicron-scale patterning of pure refractive-index contrast on the PolyTBFNBD film was also demonstrated by using near-field scanning optical microscopy (NSOM).

KEY WORDS Refractive Index Change / Photoisomerization / Norbornadiene Compounds / M-Line Method / Conjugation / Near-Field Scanning Optical Microscopy (NSOM) / Refractive-Index Patterning /

Recently, organic polymers have received considerable attention as materials for various optical devices such as holographic image records, optical memories, optical waveguides, and other optical elements, because of their advantages in processability, a large variety of molecular design, and easy incorporation of functional groups inside.

A number of researches have been carried out on photoinduced refractive index changes of polymer films doped with various chromophores.^{1–12} Photochemical reactions can be categorized into two types of reactions, reversible ones and irreversible ones. Photochromic dyes are well known to induce reversible photoisomerization^{2–8} and have been studied for application to optical switching and recording devices. In contrast to reversible photochromic reactions, photopolymerization, photolocking, and other irreversible photochemical reactions^{9–12} are applicable to holography, microlenses, integrated optical interconnects, and waveguide lithography.^{13–16} Thus, for these both applications, large refractive index changes induced by photochemical reactions in polymer films should be achieved, and transparency in a wide visible region is also desired.

Norbornadiene (NBD) is also famous as a photochromic dye, and in past years the photoisomerization of NBD to quadricyclane (QC)^{17,18} 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, a large transparency in the wide wavelength region especially in the visible region, and a high quantum yield of the photoisomerization.⁸ We bound NBD moieties to the polymer chains due to an easier film preparation with a high NBD concentration and high uniformity. Refractive index change of NBD during photoisomerization was reported to be about 0.01 in our previous letter for P(MMA_{0.43-co}-GMA_{0.57}-PNCA) films,⁸ where PNCA denotes phenyl-substituted norbornadiene carboxylic acid bound to glycidyl methacrylate (GMA). Recently Nagai *et al.*¹⁹ reported a series of trifluoromethyl-substituted norbornadienes with large aromatic substituents.

Nanostructure formation on the surfaces of various kinds of materials is a basic technology of so called “nanotechnology” which has recently been extensively

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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.²⁰ In our previous papers,²¹ a pure refractive index patterning, *i.e.*, refractive-index patterning without changing the surface morphology and the transparency of the sample, was first realized with NSOM on a transparent film of PMMA doped with 35 wt% PNCA which shows the refractive-index change of 0.006. The use of films showing larger refractive-index change caused by a photochemical reaction has been desired for better patterning.

In the present study, we prepared a polymer bearing thiophenyl- and benzofuryl-substituted NBD (Poly-TBFNBD) and various NBD derivatives with anisyl or benzofuryl substituents, and measured photoinduced refractive index changes in polymer films containing norbornadiene compounds. Submicron-scale patterning of pure refractive index contrast on a PolyTBFNBD film was also realized by using NSOM.

EXPERIMENTAL

Materials

We used five norbornadiene compounds, 5-anisyl-1,4,6,7,7-pentamethyl-2,5-norbornadiene-2,3-dicarboxylic acid dimethyl ester (NBD1), 5-anisyl-2,3-dicyano-1,4,6,7,7-pentamethyl-2,5-norbornadiene (NBD2), 5,6-anisyl-2,3-di(trifluoromethyl)-1,4,7,7-tetramethyl-2,5-norbornadiene (NBD3), 5,6-(2-benzofuryl)-2,3-di(trifluoromethyl)-1,4,7,7-tetramethyl-2,5-norbornadiene (NBD4) and a polymer bearing thiophenyl- and benzofuryl-substituted norbornadiene groups (Poly-TBFNBD). Chemical structures are shown in Figure 1. NBD1–4 were synthesized as described in the literature.¹⁹ PolyTBFNBD was prepared through the cationic polymerization of 2-chloroethylvinyl ether with BF_3OEt_2 , followed by the quantitative reaction of 5-(2-benzofuryl)-2,3-trifluoromethyl-7,7-dimethyl-6-(4'-carboxy-2'-thiophenyl)-2,5-norbornadiene with chloroethyl groups in the polymer. This polymer with $M_n = 5.3 \times 10^4$ and $M_w/M_n = 1.9$ contains NBD moieties in side chains.

Absorption Spectrum and Refractive Index Measurements

The photoreaction was carried out using a 450 W high-pressure mercury lamp or xenon lamp with an appropriate filter (NBD1:UV27, NBD2:UV29, NBD3:UV39, NBD4:L42, Poly TBFNBD:Y44). The absorption spectra of NBD1–4 before and after pho-

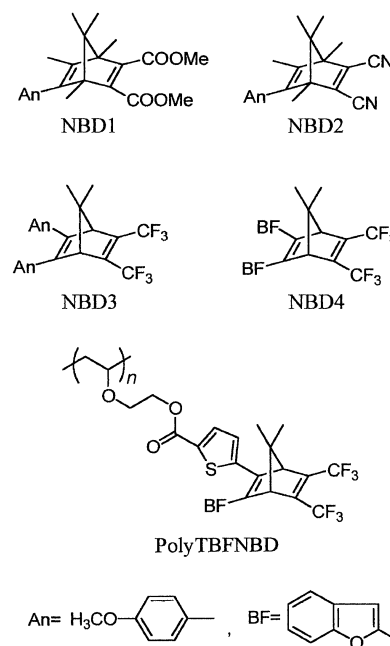


Figure 1. Chemical structures of norbornadiene derivatives and PolyTBFNBD.

toirradiation were measured in poly(methyl methacrylate) (PMMA) films. A film of PolyTBFNBD for absorption spectrum measurements was spin coated from about 5 wt% solution in chloroform onto a silica substrate (thickness: about 0.6 μm). The refractive indices of the polymer films were measured with an inline method.⁵ The probe beam used for refractive index measurements is a tunable He–Ne laser (LSTP-1010, Research Electro-Optics). Films for refractive index measurements with a thickness of approximately 4 μm were prepared with a barcoater method onto fused silica substrates from approximately 10 wt% solutions of PMMA in chloroform containing NBD1–4 with various weight fractions for PMMA. Films of PolyTBFNBD for refractive index measurements were cast from about 10 wt% solutions of the polymer in chloroform by using a barcoater onto a fused silica substrate (thickness: about 2 μm). We measured the refractive indices of the polymer films before and after irradiation in both TE (in-plane) and TM (out-of-plane) modes (NBD1–4: at 632.8 nm, PolyTBFNBD: at 632.8, 612, 604, 594 nm).

Refractive-Index Patterning by NSOM

The NSOM apparatus built in our laboratory is based on an illumination mode with a shear-force tip/sample distance regulation. Details of our NSOM apparatus were given elsewhere.²² A thin film for the NSOM measurements (about 50 nm thick) was prepared by spin coating a chloroform solution of PolyTBFNBD (0.7 wt%) onto a glass coverslip. For photochemical patterning the sample was irradiated by the NSOM

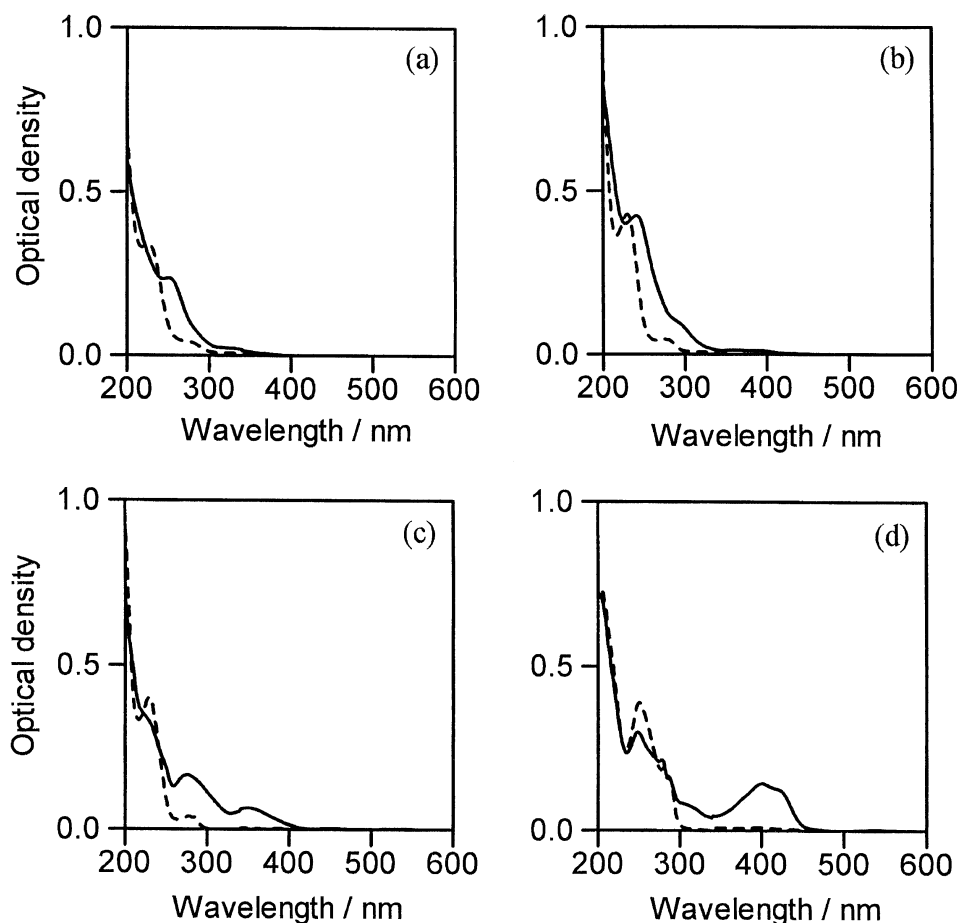


Figure 2. Absorption spectra of norbornadiene derivatives in PMMA film before (solid line) and after 1 min photoirradiation (dashed line): (a) NBD1 (5 wt%) / PMMA; (b) NBD2 (5 wt%) / PMMA; (c) NBD3 (5 wt%) / PMMA; (d) NBD4 (5 wt%) / PMMA.

probe (aperture: about 200 nm) coupled with 442 nm light from a He–Cd laser scanning a single line with a length of 2.9 μm on the sample. For image acquisition the NSOM probe was coupled with 633 nm light from He–Ne laser, then the intensity of transmitted light was monitored with a photomultiplier tube and a lock-in amplifier and mapped to a relevant region of the sample surface so as to obtain its NSOM image.

RESULTS AND DISCUSSION

Photoinduced Refractive Index Changes of PMMA Films with Norbornadiene Derivatives

The changes in absorption spectra of NBD1–4 are shown in Figure 2. The absorbance of NBD1 decreased around 250 nm ($\epsilon = 1.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and shifted to 226 nm after UV irradiation (Figure 2a). The absorbance of NBD2 decreased around 241 nm ($\epsilon = 1.9 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and shifted to 230 nm after UV irradiation (Figure 2b). The absorbance of NBD3 decreased around 350 nm ($\epsilon = 5.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) and 275 nm ($\epsilon = 1.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and shifted to 229 nm after UV irradiation (Figure 2c). The absorbance of NBD4 decreased around 400 nm ($\epsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and

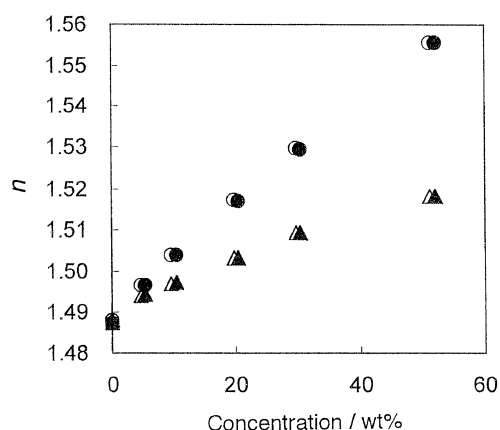
shifted to 251 nm after light irradiation below 420 nm (Figure 2d).

Accompanied by the change in absorption, the refractive indices of doped PMMA films decreased. The comparison in refractive index changes of various norbornadiene derivatives in PMMA are summarized in Table I. We can see that the refractive index changes are affected by their substituents very much. NBD4 has much longer π -conjugation system than other norbornadiene derivatives, which becomes localized during photoisomerization. So its refractive index change is much larger than those for other norbornadiene derivatives. From these results, we suggest that the disappearance of long π -conjugation system contributes to the refractive index changes of norbornadiene derivatives. Figure 3 shows the relationship between weight fractions of NBD4 in PMMA films and the refractive indices before and after photoirradiation. Up to about 50 wt% doping transparent films were obtained, and the refractive indices of PMMA films increase linearly with the increase in weight fractions of NBD4 in PMMA. Eventually we obtained large changes in refractive index of -0.038 (from $n_{\text{TE}} = 1.556$ to 1.518 and from $n_{\text{TM}} = 1.556$ to 1.518) by photoirradiation of

Table I. Refractive Indices and Their Changes for PMMA Films Containing Various Norbornadiene Derivatives (5 wt%) before and after Photoirradiation at 632.8 nm

	$n_b(\text{TE})$	$n_a(\text{TE})$	$-\Delta n(\text{TE})$	$n_b(\text{TM})$	$n_a(\text{TM})$	$-\Delta n(\text{TM})$
NBD1 / PMMA	1.4951	1.4949	0.0002	1.4954	1.4951	0.0003
NBD2 / PMMA	1.4965	1.4959	0.0006	1.4969	1.4960	0.0009
NBD3 / PMMA	1.4936	1.4925	0.0011	1.4940	1.4930	0.0010
NBD4 / PMMA	1.4965	1.4939	0.0026	1.4967	1.4942	0.0025

^a n_b = refractive index before irradiation; n_a = refractive index after irradiation, $\Delta n = n_a - n_b$. Film thickness: 4 μm . Irradiation time: 1 h.

**Figure 3.** Refractive indices, n , of PMMA films containing various weight fractions of NBD4 before (circle) and after photoirradiation (triangle). Open symbols are for n in TE mode; filled ones are for n in TM mode.

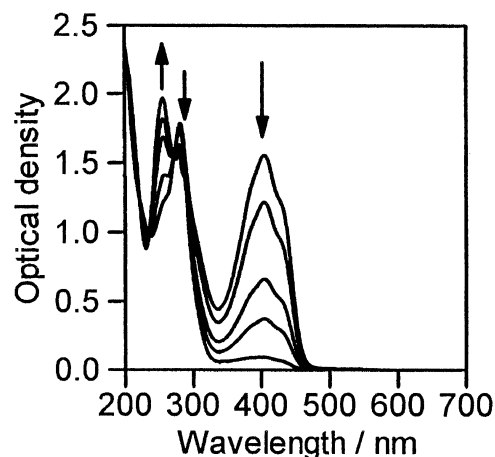
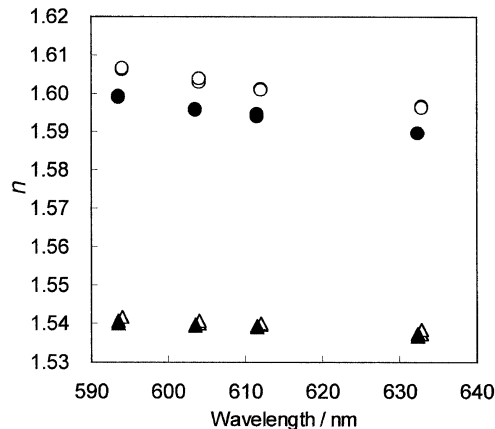
the PMMA film doped with 51.6 wt% of NBD4.

Photoinduced Refractive Index Changes of PolyTBFNBD Films

The changes in absorption spectra of PolyTBFNBD under high-pressure mercury lamp irradiation are shown in Figure 4. The absorbance of PolyTBFNBD decreased around 404 nm ($\epsilon = 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 281 nm ($\epsilon = 1.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and increased around 256 nm after photoirradiation. The quantum yield of photoisomerization of NBD to QC moieties for a PolyTBFNBD film at room temperature was determined from the first-order plot of the time-conversion curves. The light source was a high-pressure mercury lamp with UV39 filter. Actinometry for the incident light was carried out with a photometer (Model 840-C Newport). The quantum yield for photoisomerization was obtained from eq 1,

$$\ln\left(\frac{T}{1-T}\right) - \ln\left(\frac{T_0}{1-T_0}\right) = 2.3 \times 10^3 I_0 \epsilon \Phi t \quad (1)$$

where T is transmittance of NBD moieties at irradiation time, t , T_0 is the transmittance before irradiation, I_0 in einstein $\text{cm}^{-2} \text{ s}^{-1}$ is the incident light intensity, and $\epsilon = 1.5 \times 10^4 \text{ (M}^{-1} \text{ cm}^{-1})$ is the molar extinction coefficient of NBD moieties at 400 nm in chloroform solution. A straight line was observed for the plot of $\ln [T/(1-T)]$ against t for the first half of the photoisomerization in

**Figure 4.** Absorption spectra of PolyTBFNBD before and after irradiation by a high-pressure mercury lamp with Y44. Irradiation time is 0, 1, 3, 5, 10 min from top to bottom at 405 nm.**Figure 5.** Wavelength dependence of 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.

PolyTBFNBD film, from which the quantum yield for the photoisomerization of NBD moieties was found to be 0.83 at room temperature in the film. This value is very high, compared with those for other photochromic dyes.²³

Figure 5 shows the refractive indices of PolyTBFNBD films before and after photoirradiation in both TE and TM modes at several wavelengths (632.8, 612.0, 604.0, and 594.0 nm). We obtained the changes in refractive index of -0.058 (from $n_{\text{TE}} = 1.596$ to

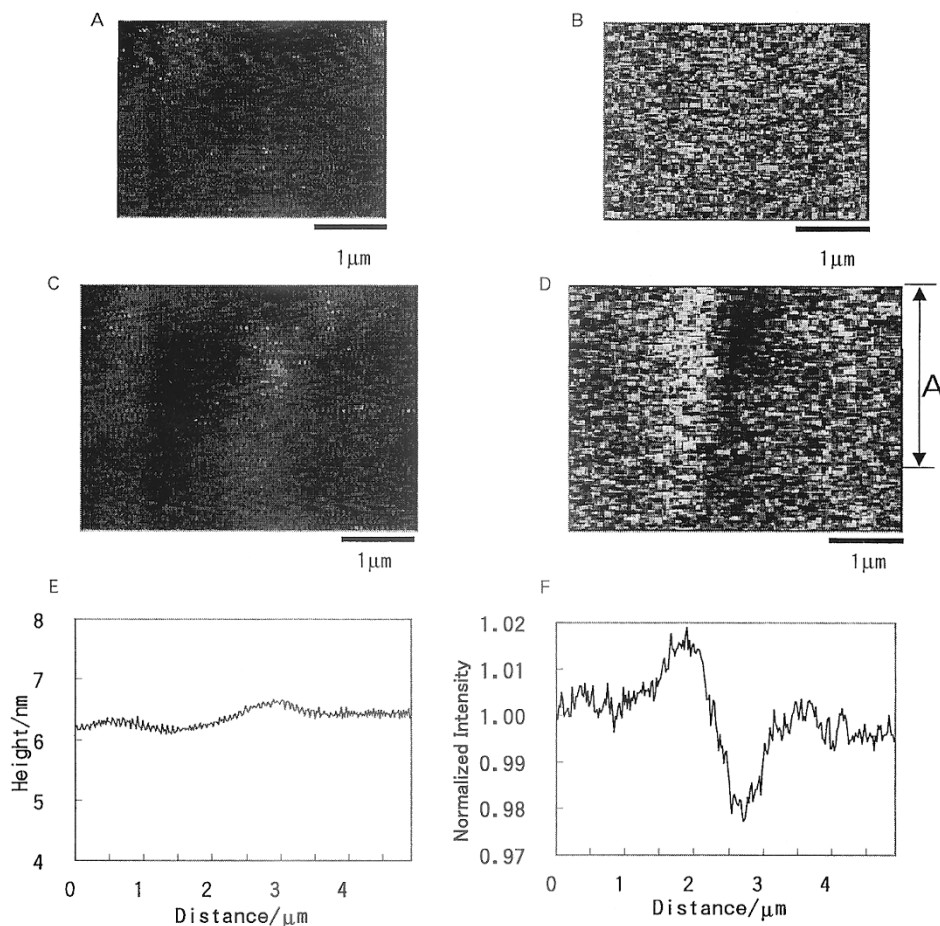


Figure 6. Topographic (A, C) and corresponding NSOM transmission (B, D) images at 633 nm of a PolyTBFNBD thin film (50 nm) before (A, B) and after (C, D) 442 nm irradiation with the NSOM probe. The irradiated area was a vertical line with length of 2.9 μm located at the center of the image. The average cross sections for C and D are shown in E and F, respectively. The averaging was taken over all horizontal scans covering the vertical range A.

1.538) at 632.8 nm for TE mode and -0.053 (from $n_{\text{TM}} = 1.590$ to 1.537) at 632.8 nm for TM mode. This refractive index change is the largest value so far obtained for polymer films containing photoreactive groups in nonresonant region. The large refractive index change is due to the disappearance of long π -conjugation caused by photoisomerization and resulting localization of aromatic groups and to the high concentration of NBD moieties in the film by their introduction into every side group of the polymers.

Refractive-Index Patterning on PolyTBFNBD Films with NSOM

A PolyTBFNBD film with the thickness of about 50 nm was irradiated by evanescent light from the NSOM probe coupled with 442 nm He–Cd laser. Simultaneously obtained topographic image and corresponding NSOM image taken at 633 nm (He–Ne laser) before and after 442 nm irradiation are presented in Figure 6. The irradiated line with the length of 2.9 μm is located vertically at the center of the image. Before the 442 nm irradiation, no image was observed with either

topographic or NSOM detection (Figure 6A, 6B). After 20 second scanning irradiation of 442 nm light, the topographic image (Figure 6C) is almost, but not completely, flat in the irradiated region. In contrast to the topographic image, a dark band in the NSOM image (Figure 6D) appears in the irradiated region, owing to the photochemical reaction of NBD groups in the film.

Average cross sections of the images were produced in order to evaluate the topographic and near-field optical contrasts more precisely. Figures 6E and 6F are the cross sections of averaged horizontal lines covering the vertical range A for Figures 6C and 6D, respectively. The topographic change is smaller than 0.5 nm and almost negligible for characterizing the optical properties of the thin-film sample. This topographic change is much smaller than those reported for photoisomerization²⁴ and photobleaching²⁵ of azo-dye-containing polymer films.

The cross section of the NSOM image normalized with the level of non-irradiated part (Figure 6F) shows a clear optical contrast of 0.02 created by the 442 nm irradiation, which is much larger than we have previ-

ously obtained for the optical contrast of 0.005²¹ in the PNCA-doped PMMA film. The width of the band observed in Figure 6F (about 500 nm) and the sharpness of edges of the pattern system (about 200 nm) have been improved in the present system compared to the previous results (2 μ m and 300 nm, respectively²¹), mainly due to much larger refractive index change of Poly-TBFNBD ($\Delta n = -0.058$) than that of the PNCA-doped PMMA film ($\Delta n = -0.006$) under photoirradiation.

It should be noted that PolyTBFNBD is completely transparent at 633 nm, therefore, the optical contrast observed in Figure 6 does not originate from the increase in optical density. It is reported that in the near-field regime, a transparent sample with spatial variation in refractive index may also show a transmission contrast.^{26,27} The apparent variation in the transmission intensity is related to the coupling efficiency of the optical near field (evanescent field) to the far field (propagating light). As was suggested in our previous letter,²¹ the theory of conventional Rayleigh scattering can be applied in the first approximation to the coupling efficiency of the optical near field to the far field. Thus, when the change in refractive index is small compared to its absolute value, the variation in the transmission intensity would be proportional to that in refractive index, which is the case in the present results. The reason of a bright area on the left side of the dark line in Figure 6D is not clear yet, but it might be due to scattering of 633 nm evanescent light leaking from the photoisomerized area at the interface of refractive index contrast. The less marked bright area on the right side might be explained by a shape of the NSOM probe aperture we used, where 442 nm light inducing the reaction goes a little to the right side area.

CONCLUSION

Large photoinduced refractive index changes were observed for PMMA films containing NBD derivatives and for a polymer bearing NBD groups. PolyTBFNBD bearing NBD groups with thiophenyl- and benzofuryl-substituents showed the refractive index decrease of 0.05–0.06 at 594–633 nm, which is the largest value reported so far for the refractive index change in non-resonant region induced by photochemical reactions. Submicron-scale refractive index patterning on a Poly-TBFNBD thin film by 442 nm irradiation and 633 nm image mapping was realized without any change in surface topology and optical absorbance by using a illumination-mode NSOM with a resolution of 200 nm.

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