Efficient Coloration and Decoloration Reactions of Fast Photochromic 3*H*-Naphthopyrans in PMMA-*b*-PBA Block Copolymer

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ABSTRACT

Fast photochromic molecules have attractive potential to apply to the ophthalmic lenses and real-time dynamic holography. However, the thermal decoloration reaction rate and the photoconversion efficiency of the photochromic molecules largely depend on their surrounding medium. Herein, we investigated the thermal decoloration behavior of fast photochromic 3*H*-naphthopyrans in poly(methyl methacrylate)-*b*-poly(*n*-butylacrylate) (PMMA-*b*-PBA) block

copolymer. The fast photoswitching properties of the fast photochromic molecules were achieved by using the block copolymer as a host polymer matrix.

KEYWORDS

Photochromism, block copolymer, naphthopyrane, photofunctional material

Graphical Abstract

1. Introduction

Photochromic molecules have potential applications to ophthalmic lenses, magnetic and electric switches, fluorescence modulations and molecular actuators [1-8]. The reversible color modulation and the switch of electronic properties between the two structural isomers are effectively utilized for those applications. In particular, fast photochromic molecules, that change the solution color upon UV light irradiation and its color quickly fades away once UV light irradiation stops, have potential applications to photochromic lenses and real-time dynamic 3D holographic materials [9,10]. Recently, we designed and synthesized fast switchable photochromic 3*H*-naphtho[2,1-*b*]pyrans (3*H*-naphthopyrans) by the introduction of the bulky aromatic substituent on the C2-position of 3*H*-naphthopyrans [11]. The naphthopyran derivative shows excellent durability against the repeated irradiation of UV light. For the application to the

practical use as the ophthalmic lenses, the fast switchable photochromic properties should be maintained even in the polymer film. However, the switching speed of the photochromic molecules is generally affected by the viscosity of the surrounding medium because photochromic molecules show large structural changes accompanied with the photochromic reaction [12,13]. For example, the molecular structure of 3*H*-naphthopyran instantaneously changes upon UV light irradiation: the C–O bond of the closed ring form (CF, the initial colorless form) is cleaved upon UV light irradiation to isomerize into the colored *transoid-cis* (TC) and *transoid-trans* (TT) isomers (Scheme 1). This large structural change leads to the decrease in the rate of the thermal decoloration reaction and the photoconversion efficiency of the photochromic molecules in a rigid polymer matrix due to the small size in the free-volume around the photochromophores. One of the solutions to overcome this issue is to design a molecule whose photochromic reaction does not depend on the free-volume of its surrounding. Generally, the investigation of pressure effect on the rate of chemical reactions provides the important insights into the conformational changes during chemical reactions [14-16]. We previously demonstrated that the value of the activation free volume ($\Delta V^\ddagger$) for the thermal back reaction is an effective measure to evaluate the efficiency of the photochromic reaction in polymer matrix [17,18]. The other solution is to reduce the viscosity of a host polymer matrix [10,19-21]. By using the soft polymer matrix such as siloxane or using the plasticizer, the glass transition temperature (T_g) of a polymer matrix is reduced effectively for the use of the host polymer matrix of photochromic molecules [10]. However, the mechanical strength of the low T_g polymers is insufficient for the practical use of the materials. Therefore, the development of a polymer matrix with both low viscosity and high mechanical strength has been required.

Scheme 1. Photochromic Reaction Scheme of 3*H*-Naphthopyran Derivatives

The concept to solve the above described issue is to use a block copolymer composed of a high T_g block segment and a low T_g block segment as a host polymer matrix of the fast photochromic molecules. The high T_g block segment and the low T_g block segment ensure the mechanical strength for the industrial processing and the sufficient free-volume around the photochromic molecule, respectively [22]. In this study, a commercially available block copolymer (KURARITY LA2330, Kuraray Co., LTD.) was used as a host polymer matrix for fast photochromic molecules. LA2330 is a tri-block acrylic-based polymer composed of poly(methyl methacrylate) (PMMA) and poly(butyl acrylate) (PBA). We found that the fast photoswitching properties of the fast photochromic 3*H*-naphthopyrans could be retained in LA2330.

2. Experimental

2.1. General

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Wakogel® C-300). ¹H NMR spectra were recorded at 400 MHz on a Bruker AVANCE III 400 NanoBay. DMSO-*d*₆, CD₂Cl₂ and CDCl₃ were used as deuterated solvent. ESI-TOF-MS spectra

were recorded on a Bruker micrOTOF II-AGA1. All glassware was washed with distilled water and dried. Unless otherwise noted, all reagents and reaction solvents were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Co., Inc., Kanto Chemical Co., Inc. and ACROS Organics and were used without further purification.

2.2. Syntheses

2-Naphthyl-3*H*-naphthopyran (**2-Np-NP**), which has the naphthyl moiety on the C2-position of 3*H*-naphthopyran, was synthesized according to Scheme 2. **2-bromo-3,3-diphenyl-3*H*-benzo[*f*]chromene (2)** was synthesized according to a literature procedure [11].

Scheme 2. Synthetic Scheme of **2-Np-NP**

2.2.1. 4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (1)

2-Bromonaphthalene (299 mg, 1.14 mmol) KAcO (416 mg, 4.24 mmol) and bis(pinacolato)diboron (558 mg, 2.20×10^{-1} mmol) were dissolved in 50 mL of DME and the mixture was purged with N₂ gas. Pd(dppf)Cl₂·CH₂Cl₂ (49 mg, 5.94×10^{-2} mmol) was added to the resulting solution and refluxed for 4 h. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through phase separator paper. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:40) to give **S1** as a yellow solid (170 mg, yield: 47%). ¹H NMR (400 MHz,

CDCl₃): δ 8.37 (s, 1H), 7.89 (d, J = 7.6 Hz, 3H), 7.86–7.79 (m, 3H), 1.39 (s, 12H). HRMS (ESI-TOF) calculated for C₁₆H₁₉BO₂ [M+Na]⁺: 276.1421, found: 276.1407.

2.2.2. 3,3-diphenyl-2-(naphthalene-1-yl)-3H-benzo[f]chromene (2-Np-NP)

2-Bromo-3,3-diphenyl-3H-benzo[f]chromene (147 mg, 3.57×10^{-1} mmol) Na₂CO₃ 168 mg and 4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (133 mg, 5.26×10^{-1} mmol) were dissolved in 4.28 mL of DME and 0.71 mL H₂O and the mixture was purged with N₂ gas. Tetrakis(triphenylphosphine) (12 mg, 9.95×10^{-3} mmol) was added to the resulting solution and refluxed for 10 h. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through phase separator paper. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:40) to give **2-Np-NP** as a yellow solid (127 mg, yield: 77%). ¹H NMR (400 MHz, CDCl₃): δ 8.07 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.74–7.68 (m, 2H), 7.67–7.61 (m, 3H), 7.60–7.54 (m, 5H), 7.51–7.45 (m, 1H), 7.43–7.37 (m, 2H), 7.36–7.31 (m, 1H), 7.29 (dd, J = 8.6 Hz, J = 1.8 Hz, 1H), 7.25–7.19 (m, 6H), 7.17 (d, J = 8.9 Hz, 1H). HRMS (ESI-TOF) calculated for C₃₅H₂₄O [M+Na]⁺: 483.1719, found: 483.1722.

2.3. Experimental Details for Laser Flash Photolysis

The laser flash photolysis experiments were carried out with a TSP-1000 time resolved spectrophotometer (Unisoku). A 10 Hz Q-switched Nd:YAG laser (Continuum Minilite II) with the third harmonic at 355 nm (pulse width, 5 ns) was employed for the excitation light. A halogen lamp (OSRAM HLX64623) was used as the probe beam arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a photomultiplier

tube (Hamamatsu R2949) through a spectrometer (Unisoku MD200) for the time profile for the thermal isomerization. Optical grade solvents were used for all measurements. An inner-cell type high pressure optical measurement cell (light pass length, 4 mm; Syn-Corporation Ltd PCI-500) and a high pressure hand pump (Syn-Corporation Ltd HP-500) were used for the pressure effects on the thermal back reaction rates.

3. Results and Discussion

Fig. 1 shows the steady state and transient absorption spectrum of **2-Np-NP** in benzene. The transient absorption at 450 nm after the 355-nm light irradiation is similar with that of the reported previously *3H*-naphthopyran derivatives [11], which can be attributable to the colored TC isomer. The colored TC isomer thermally goes back to the initial CF with the half-life of 28 μ s at room temperature. While the decay of the transient absorbance of the conventional *3H*-naphthopyran consists of the fast and slow decay components which can be attributable to the TC and TT isomers, respectively, the decay of the transient absorbance of **2-Np-NP** almost follows the first-order reaction kinetics. It indicates that the generation of the TT isomer is suppressed by the large steric hindrance of the bulky 2-naphthyl moiety [11].

Fig. 1. (a) The absorption spectrum of **2-Np-NP** in benzene at 298 K (dash) and the transient absorption spectrum of **2-Np-NP** in benzene upon 355-nm light irradiation (7 mJ, 5 ns) at 298 K (solid). (b) Time profile of the transient absorbance of **2-Np-NP** at 450 nm in benzene excited

with a 355-nm laser pulse (7 mJ, 5 ns). Inset shows the first-order plot of the time profile of the transient absorbance of **2-Np-NP**.

It is well known that PMMA-*b*-PBA block copolymer shows the microphase separation due to the large difference in the T_g between the PMMA (ca. 120 °C) and PBA (ca. -40 °C) block segments [23]. The microphase separation of the thin film of LA2330 was confirmed by an atomic force microscopy (AFM, Bruker Multimode-8) equipped with a cantilever (Bruker TAP150A). The block copolymer films were prepared on the glass substrates by the spin-coating method (3000 rpm). Fig. S6 (Supplementary data) shows the phase-mode AFM images of the block copolymer films before and after annealing at 150 °C for 15 h. Although the PMMA and PBA domains are not clearly separated before annealing, the microphase separation of the annealed block copolymer film was observed in a few tens of nanometer scales. The PBA domain has lower viscoelasticity than the PMMA domain, which induces the phase retardation of the oscillating frequency of the cantilever, resulting in the dark images of the PBA domain in the phase-mode AFM. The PBA pores in the PMMA lamella are arranged in a regular hexagonal array on the glass substrate. The films of LA2330 doped with **2-Np-NP** (10 wt%) were prepared on glass substrates by spin coating method (3000 rpm) for the AFM measurement. The chloroform solution of the block copolymer and **2-Np-NP** (polymer/chloroform; 20 mg/1mL, **2-Np-NP**; 2 mg) was prepared for the spin-coating method. The AFM images of the annealed block copolymer film doped with **2-Np-NP** are shown in Fig. 2. The microphase separation of the PMMA and PBA domains is also observed in the LA2330 film doped with **2-Np-NP** with the concentration of 10 wt%. Therefore, LA2330 is suitable for the polymer matrix of the 3*H*-naphthopyran derivative.

Fig. 2. AFM phase images of the LA2330 film doped with **2-Np-NP** (a) before and (b) after annealing at 150 °C for 15 h. Full scale is 400 nm.

Fig. 3. Time profile of the transient absorbance of **2-Np-NP** excited with a 355-nm laser pulse (7 mJ, 5 ns) at 298 K and probed at 450 nm in (a) LA2330, (b) PMMA, and (c) PBA. (d) First-order plots for the time profile of the transient absorbance of **2-Np-NP** at 450 nm in LA2330 (red) and PBA (green) at 298 K.

Table 1. Reaction Kinetics Parameters for the Thermal Back Reaction of the Colored Species of **2-Np-NP** in the Polymer Film

Polymer	k_1 [s^{-1}]	k_2 [s^{-1}]	C
LA2330 (unannealed)	2.7×10^4 (32 %)	8.0×10^4 (68 %)	3.9×10^{-4}
LA2330 (annealed 3h)	3.6×10^4 (41 %)	8.1×10^4 (59 %)	3.5×10^{-4}
LA2330 (annealed 15h)	5.2×10^4 (45 %)	2.1×10^5 (55 %)	-
PBA	6.4×10^4 (65 %)	1.6×10^5 (35 %)	-
PMMA	2.8×10^4 (40 %)	4.7×10^4 (60 %)	6.1×10^{-4}

We investigated the photochromic properties of **2-Np-NP** in the block copolymer film. The film (10 wt%) was prepared by the casting method for the laser flash photolysis measurement. The decay curves for the thermal back reaction of the colored isomer of **2-Np-NP** ($\lambda_{ex.} = 355$ nm, 7 mJ, $\lambda_{obs.} = 450$ nm) in the block copolymer film before and after annealing were fitted by the double exponential function (eq. 1)

$$f(x) = A_1 e^{-k_1 x} + A_2 e^{-k_2 x} + C \quad (\text{eq. 1})$$

The decay curve before annealing consists of two decay components (Fig. 3a, $k_1 = 2.7 \times 10^4$ s^{-1} and $k_2 = 8.0 \times 10^4$ s^{-1} , respectively) and the other component which did not completely disappeared within a millisecond time scale (the constant, C). This behavior is similar to the thermal back reaction rates in the PMMA film (Fig. 3b) although the ΔOD value just after laser excitation was much higher in LA2330 than that in PMMA. This type of photochromic response is also observed in the high- T_g polymers [24,25]. The deviation from the first-order reaction

kinetics can be attributable to the inhomogeneous local free-volume around the photochromic molecules, indicating the high viscosity and the inhomogeneity of the non-annealed block copolymer film because the domains of PMMA and PBA segments were not separated. In contrast, the thermal back reaction rate is accelerated after annealing at 150 °C for 15 h (Fig. 3a) and the colored TC isomer completely goes back to the initial **2-Np-NP**. The rate constants for the thermal back reaction in the LA2330 film after annealing are similar with those in the PBA film (Fig. 3c and 3d, Table 1). That is, the PBA domain of the block copolymer provides high molecular mobility for the isomerization process by the phase separation of the PBA and PMMA segments. The photochromic reaction of **2-Np-NP** in the PBA domain of the block copolymer would be mainly observed by the laser flash photolysis measurement because the ΔOD value upon UV light irradiation is negligibly small in the PMMA domain. However, it was difficult to estimate the distribution of the doped compounds in each domain of the block copolymer. To predict the distribution of the doped compounds in the block copolymer, it will be required to use the super resolution microscopy [26] and transmission electron microscopy [27] which have been proposed as efficient tools to reveal the distribution in nanostructures. Notably, **2-Np-NP** maintains the fast photochromic property after annealing at high temperature (150 °C), which is the important feature for the industrial use. The efficiency of the coloration reaction of **2-Np-NP** in the block copolymer film was compared with that in benzene (Fig. S7, Supplementary data). The efficiency can be predicted from the ΔOD values just after laser excitation because the ΔOD values are normally proportional to the quantum yield of the photochromic reaction. The optical length of the benzene solution was adjusted to coincide with the thickness of the block copolymer cast film (ca. 15 μm). The ΔOD values after the 355-nm laser excitation (7 mJ) were normalized by dividing with each absorbance at 355 nm in the film and in benzene, respectively.

As a result, the efficiency of the coloration reaction in the block copolymer film was estimated to be 40 % as compared to that in benzene.

When the large structural change is induced by the photochromic reaction, the thermal back reaction rate crucially depends on the viscosity of the polymer matrix [10,19-21]. The $\Delta V^\ddagger$ is one of the effective measure to elucidate the structural change associated with chemical reactions because $\Delta V^\ddagger$ originates from the difference in the partial molar volumes between the initial state and the transition state. Therefore, it is important to reveal the suitable $\Delta V^\ddagger$ for the photochromism of *3H*-naphthopyran derivatives in the block copolymer film. In this study, the $\Delta V^\ddagger$ values for the thermal back reaction of **2-Np-NP** was compared with those of the previously reported *3H*-naphthopyran derivatives, **2-Py-NP**, and **2,10-Ph-NP**.¹¹ The $\Delta V^\ddagger$ values were determined from eq. 1–3 [14-16],

$$\Delta V^\ddagger = -RT \left(\frac{\partial \ln k_p}{\partial P} \right)_T \quad (1)$$

$$\ln(k_p / k_{0.1}) = aP + b \ln(1 + cP) \quad (2)$$

$$\Delta V^\ddagger = -(a + bc)RT \quad (3)$$

where k_p is the rate constant at pressure P . The $\Delta V^\ddagger$ values of **2-Np-NP**, **2-Py-NP**, and **2,10-Ph-NP** were estimated to be -6.0 , -6.2 , and $-9.0 \text{ cm}^3 \text{ mol}^{-1}$ in toluene at 298 K, respectively (Fig. S8–10, Supplementary Data). Fig. S11 (Supplementary Data) shows the time profiles of the transient absorbance of the fast photochromic *3H*-naphthopyran derivatives in benzene and in the block copolymer film at 298 K. The rates of the thermal back reactions of the colored species of **2-Py-NP** and **2,10-Ph-NP** in the block copolymer film are decelerated as compared to those in benzene. In particular, the decay kinetics of

the colored species of **2-Ph-NP** which shows the large $\Delta V^\ddagger$ value, distinctly shows the deceleration of the thermal back reaction. It indicates that the large structural change of **2-Ph-NP** expected from the $\Delta V^\ddagger$ is inhibited in the block copolymer film. On the other hand, the colored species of **2-Np-NP** in the block copolymer film shows the fast thermal back reaction as well as that in benzene. These results indicate that **2-Np-NP** has the appropriate $\Delta V^\ddagger$ value for the photochromic reaction in LA2330.

4. Conclusion

In conclusion, we demonstrated the efficient photochromic reaction of the fast switchable 3*H*-naphthopyran derivative, **2-Np-NP**, in the commercially available PMMA-*b*-PBA block copolymer. The thermal back reaction is accelerated after the microphase separation of the PMMA and PBA domains, indicating that the block copolymer of PMMA and PBA is an attractive host polymer matrix of the fast switchable photochromic molecules because the polymer has both high mechanical strength and free volume around the doped photochromic molecules. The use of the commercially available PMMA-*b*-PBA block copolymer prompts the practical application of the photochromic materials. Moreover, we revealed that the optimization of the host polymer and the $\Delta V^\ddagger$ value for the thermal decoloration reaction of the fast photochromic molecule leads to the efficient photoswitching in the polymer film. These results give an attractive insight into the functional photochromic materials for the practical use.

Supplementary Data.

Characterization data, Photochromic properties in the PMMA-*b*-PBA block copolymer film and Pressure dependence of the rate of the thermal back reaction can be found at <http://dx.doi.org/xx.xxxx/j.dyepig.xxxx.xx.xx>.

Notes

The authors declare no competing financial interests.

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