Photochromism of a spiroperimidine compound in polymer matrices

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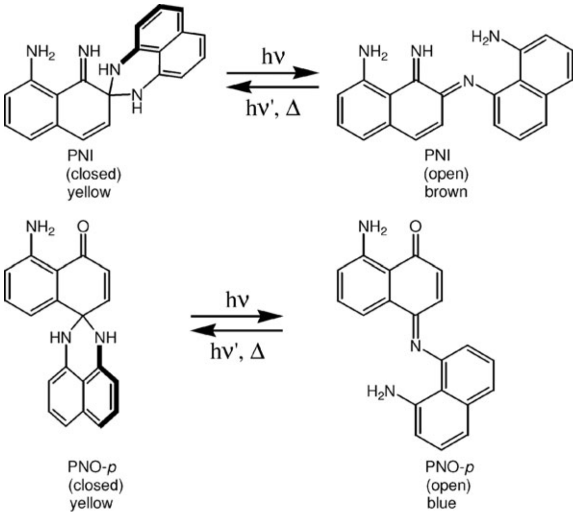
The photochromic behavior of a spiroperimidine compound, 2,3-dihydro-2-spiro-7′-(8′-imino-7′,8′-dihydronaphthalen-1′-amine)-perimidine (PNI), doped in various polymers has been studied. Upon irradiation with 405 nm light, PNI exhibits photochromism, and a color change (light yellow to brown) is observed. The initial (closed) and colored (open) forms exhibit absorption maxima (λ_{max}) around 400 and 500 nm, respectively. The open form possesses a wide absorption band, extending to ~750 nm. Little effect of the polymer matrix on the λ_{max} of either the closed or open forms was observed, and these values were also similar to those in solution. The lifetime of the open form depends mainly on the glass transition temperature (T_g) of the polymer, and ranges from, for example, 11 min to 5.4 d. This indicates that the lifetime of the open form can be readily tuned by simply choosing a suitable polymer matrix. Photochromism in different polymer substrates are demonstrated herein.

Photochromism is a reversible change in an absorption spectrum due to the transformation of a chemical species that is induced, at least in one direction, by irradiation with light. Numerous organic photochromic compounds and their derivatives have been reported, and they are potential candidates for diverse applications such as photochemical memories, molecular switches and light control materials.[1–8] One of the challenges of organic photochromic compounds in relation to these applications is their synthesis, as a multiple-step preparation from commercially available starting compounds is generally required. Complexity of synthesis raises the cost of compound production, which is a very important factor in commercial applications.

Recently, we have reported photochromic compounds (PNI and PNO-*p*) that can be synthesized *via* a one step reaction from inexpensive commercially available precursors.[9] They can be easily synthesized by stirring a toluene or benzene solution of 1,8-diaminonaphthalene in the presence of MnO_2 under ambient temperature for 3–4 h, although a subsequent separation on silica gel is required to obtain pure PNI (15%) and PNO-*p* (18%).[9,10] Upon irradiation with UV or blue light, the initial yellow color of solutions of PNI and PNO-*p* turn brown and deep blue, respectively. The photochromism of these molecules is attributable to photocleavage of the C–N bond at the spiro carbon, followed by the formation of an open form with extended π-conjugation (Scheme 1). Their colored open forms absorb across almost the entire visible light spectrum. These compounds exhibit so-called 'T-type' photochromism, where the reverse reaction proceeds thermally and photochemically. PNI and PNO-*p* possess primary amine groups, which enables their chemical modification and also coupling with other functional groups.[11]

The possibly significant advantages of PNI and PNO-*p* over other organic photochromic compounds are the low cost of their synthesis and color neutrality, and thus they are good candidates for photochromic materials. In particular, potential applications of these compounds are in the fields of photochromic lenses and light-controlling materials, where light irradiation (such as by sunlight) causes a deep coloration (preventing light transmission), which returns to the original color (enabling light transmission) in the dark. The color neutrality of photochromic glasses depends on the broadness of their visible light absorption spectrum, and is usually achieved by mixing compounds absorbing in different regions of the visible spectrum.[12,13] In the cases of PNI and PNO-*p*, it can be achieved by a single compound, due to the broad absorption of their open forms.[9,10]

In our previous papers, we have reported the photochromic properties of PNI and PNO-*p* in solutions.[9,10] It was revealed that the rate of the thermal back reaction (from open to closed form) of these molecules strongly depends on the nature of the solvent; the rate is greatly enhanced in protic solvents. The lifetime, defined as $\tau = 1/k$ (where k is the rate constant of the thermal back reaction),



Scheme 1

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of the open form of PNI is 600 μs in methanol, whereas it is 20 d in acetonitrile.[10] The –OH groups of alcohol solvents are understood to play an important role in catalyzing the thermal back reaction.[10] Therefore, the lifetime of the open form can be tuned by simply choosing the right solvent. The observations in our solution phase studies suggested that these lifetimes could also be controlled in polymer substrates by the rational design of an environment for the photochromic compound. Optimization of the photochromic reactions in polymer substrates, including the thermal back reaction, is essential and brings significant advancement in the application of PNI and PNO-*p* to photochromic lenses and light-controlling materials. The purpose of this study is to investigate the effect of a polymer matrix on photochromic reactions, especially the thermal back reaction, and to demonstrate the performance of photochromic films that suggest similar applications. The lifetime of the open form was dependent mainly on the glass transition temperature (T_g) of the polymer, and it was observed to range from 11 min to 5.4 d.

The absorption spectra of PNI in polymers (polycarbonate, HEMA and EVA) and in toluene are shown in Fig. 1, and the absorption maxima (λ_{max}) of its closed and open forms are listed in Table 1. The non-irradiated solutions exhibited a λ_{max} around 405 nm, which corresponds to that of the closed form. The λ_{max} values and shape of the absorption spectra of the closed form observed in polymers resemble those in solutions, as reported previously.[9,10] As can be seen in Fig. 1 and Table 1, the absorption spectra of the closed form is little affected by the polymer substrate. Similarly, in solutions, the absorption spectra were not affected significantly by the polar or protic nature of the solvents.

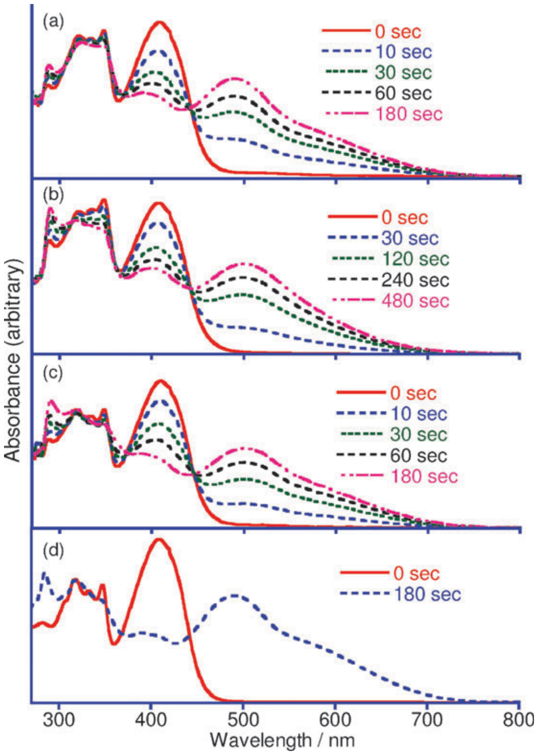

Fig. 1 The UV-vis absorption spectra of PNI in (a) polycarbonate, (b) HEMA, (c) EVA and (d) toluene upon irradiation with 405 nm light. The concentration of PNI in the polymer film is 3 wt%.

Upon irradiation of the polymer films using 405 nm light, the photochromic reaction was observed and the absorption band around 500 nm appeared, with a concomitant decrease in the absorption at 405 nm (Fig. 1). This absorption band at 500 nm, which is attributed to the open form, is significantly broad and extends to 750 nm. Together with this band, another band at around 590 nm appeared as a shoulder in most polymers. However, it was not observed in hydrophilic polymers such as PVA, HEMA and PVP. This shoulder was also prominent in toluene, but absent in alcoholic solvents, DMSO and acetonitrile.[9,10] Thus, we understand that this absorption band is dependent on the polarity of the medium. This band might be attributed to the existence of another chemical species that is in equilibrium with the open form. A possible candidate is the open isomer, a geometrical isomer of open form where the C=N bond of the imine moiety is inverted by 180°.[10] In this case, the thermal back reaction process consists of at least two events: the isomerization around the C=N bond and ring-closure. One might expect that spectral changes should deviate the isosbestic point. However, we did not observe a deviation of the isosbestic point during the thermal isomerization. The reason for this is a relatively faster equilibrium between *syn* and *anti* isomers (fast thermal isomerization around the C=N bond) than the ring-closure reaction. A shift of the transient absorption has been observed by transient absorption spectroscopy, and the shift is possibly attributed to isomerization around the C=N bond;[10] this event occurs on a microsecond timescale. Thus, a fast equilibrium should be established within a second. Although the transient absorption was measured in solution, we presume that a similar reaction takes place in polymer matrices. The existence of a similar species, in equilibrium with the open form, has been proposed in the case of photochromic spiroperimidines, which are derivatives of PNI.[11]

Although the photochromic reaction was observed in most polymers, no photochromic reaction was observed in PEG (MW ~ 3000) film, even with a transparent light yellow film on a glass substrate. This is probably due to crystallization of the PEG, thereby preventing molecular motion due to insufficient local free volume around the PNI molecules.

PNI exhibited a 'T-type' photochromism in polymers as well as in solution. When an irradiated polymer film (brown color) was kept in the dark, the original color (light yellow) returned. The lifetime, τ ($\tau = 1/k$, where k is the rate constant for the decay of the open form), varied with the polymer, as listed in Table 1. In polymers such as PMMA, polystyrene and polycarbonate, the lifetimes were as long as about 100 h. On the other hand, in PDMS, EVA and 1,2-polybutadiene, shorter lifetimes were observed, especially in the case of 1,2-polybutadiene, where the lifetime was as short as 11 min. Two rate constants for the thermal back reaction were observed for films of polycarbonate, HEMA and SBBC, whereas the other films of polymers displayed single rate constants. In general, the rate of the decoloration reaction of photochromic compounds is affected by several factors, such as residual strain in the photogenerated molecules, static distribution of local free volume and dynamic aspects of the molecular environment.[14–16] In addition, the volume required (sweeping volume) for isomerization often determines the

Table 1 Absorption maxima of the closed and open forms, reaction rates for the thermal back reaction, and the lifetime of the open form in polymers and solutions

Polymer	T_g/°C	Coating solvent	λ_{max} closed/nm	λ_{max} open/nm	k/s^{-1}	Lifetime (τ)
PMMA	82	Toluene	407	491	2.4×10^{-6}	130 h
Polyvinyl chloride		1,4-Dioxane	406	491, ~590 (sh)	3.3×10^{-6}	100 h
Polystyrene	100	Toluene	409	484, ~590 (sh)	2.9×10^{-6}	93 h
Polycarbonate	145–150	Chloroform	409	490, ~590 (sh)	3.4×10^{-6} (86%)	81 h
					7.7×10^{-5} (14%)	3.5 h
PVA	99	H_2O/ethanol	406	508	1.1×10^{-5}	26 h
HEMA	55	Methanol	407	500	1.1×10^{-5} (61%)	25 h
					1.1×10^{-4} (39%)	2.6 h
SIBC		Toluene	411	493, ~590 (sh)	3.0×10^{-4}	57 min
SBBC		Toluene	411	493, ~590 (sh)	1.1×10^{-5} (54%)	27 h
					9.1×10^{-4} (46%)	18 min
PVP	175	H_2O/ethanol	408	516	2.2×10^{-4}	78 min
PDMS		Toluene	400	480, ~590 (sh)	5×10^{-4}	33 min
EVA	~−35	Toluene	410	501, ~590 (sh)	6.7×10^{-4}	24 min
1,2-Polybutadiene	−95	Toluene	409	494, ~590 (sh)	1.5×10^{-3}	11 min
PEG		1,4-Dioxane	409			
Toluene[a,b]			410	490, 590 (sh)	6.3×10^{-5}	4.4 h
Acetonitrile[b]			403	489	5.2×10^{-7}	22 d
MeOH[b]			403	500[a]	1.7×10^{3}	600 μs

[a] Ref. 9. [b] Ref. 10.

reaction rate.[14] Due to these factors, the reaction rate deviates from single exponential kinetics. Although further studies remain to be completed to examine the matrix effect on PNI, it should be noted that this compound exhibits anomalously simple single- or double-exponential behaviors.

In solution, the lifetime strongly depends on the nature of the solvent.[10] For example, in toluene, the lifetime is 4.4 h. On the other hand, in alcoholic solvents, its lifetime decreases significantly (600 μs in methanol) as the size of the alkyl group of the solvent decreases. In polar aprotic solvents such as DMSO and acetonitrile, lifetimes are 10 and 22 d, respectively. Thus, in solution, the proton of the –OH group plays an important role in catalyzing the thermal back reaction. In line with previous observations, similar effects were expected in polymers, where polymers possessing –OH groups may facilitate the thermal back reaction. However, as can be seen in Table 1, the lifetime did not follow this trend. In PVA and HEMA, the lifetimes are both about 1 d, although these polymers have –OH groups. The decay profile of the open form in HEMA consists of another component with a relatively shorter lifetime of 2.6 h; however, the effect of the –OH group seems to be small compared to that in solutions.[10] On the other hand, it is noteworthy that shorter lifetimes were observed in PDMS, EVA and 1,2-polybutadiene. These polymers have elastic properties, and their T_g values are below room temperature. The lifetime is enhanced by about 700 times only by changing the polymer from 1,2-polybutadiene (11 min) to PMMA (130 h). Rigid polymers with higher T_g values seem to prevent the motion of the dispersed molecules, causing a slow thermal back reaction. Such effects of polymer matrices have been reported for the thermal back reaction of photochromic spirooxazines and spiropyranes.[8,17,18] Similar to these reports, the mobility of the photochromic molecules in the switching process is important, and it affects the rate of the thermal back reaction. However, the effect of T_g is very small when spirooxazine is dispersed in polystyrene and 1,2-polybutadiene,[17] which is in contrast to the case of PNI in this study.

The rate-determining step seems to be different in polymers and solutions for the thermal back reaction of PNI. In polymers, the rate depends on the rigidity of the medium. The ring-closure motion of the molecule, such as twisting and rotation of the bonds connecting the two aromatic rings, is the rate-determining step. Polymers having a low T_g value provide a larger free volume for the ring-closure reaction of the PNI molecules. The –OH groups of the polymer may facilitate the proton shift from the amine to the imine group for the ring-closure. However, the ring-closure molecular motion is significantly slow and thus may be considered the rate-determining step. In solutions, on the other hand, the rate-determining step is the proton shift from the amine nitrogen on the naphthalene group to the imine nitrogen. The –OH groups of alcoholic solvents assist the proton shift, and molecular motions involved in the ring-closure process occur easily and hence becomes relatively faster in solution.

Upon irradiation using 405 nm light through a photomask, polymer films of PNI dispersed in polycarbonate gave patterns with a good color contrast (Fig. 2). The irradiated area turned brown, while the non-irradiated regions remained light yellow. In addition, by using another photomask, we were able to write patterns onto a polystyrene film that depict high resolution imaging (Fig. 3). These images remained unchanged

Fig. 2 A photograph of a polymer film (22 mm × 22 mm) having PNI (3 wt%) dispersed in polycarbonate after 405 nm light irradiation through a photomask. The irradiated area turns to brown.

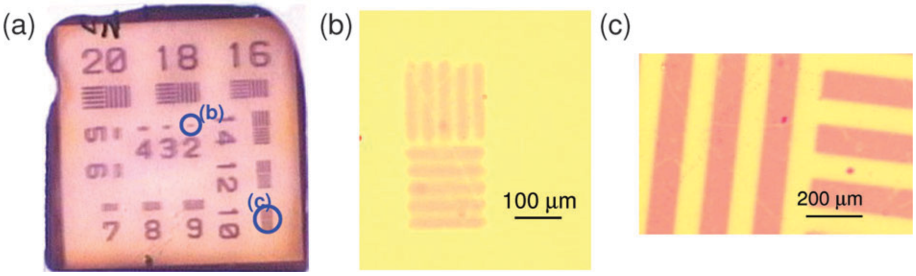

Fig. 3 (a) A photograph of a polymer film (22 mm × 22 mm) having PNI (3 wt%) dispersed in polystyrene after 405 nm light irradiation through a photomask. (b) and (c) Enlarged photographs of the indicated regions of the film.

for a week at room temperature in the dark. Similar results were also obtained using a PMMA film.

A demonstration of the 'fast' thermal back reaction in 1,2-polybutadiene is shown in Fig. 4. A film of PNI in 1,2-polybutadiene (1% w/w) was irradiated using 405 nm light with a photomask for 3 min. Immediately after the irradiation, the photomask was removed and the film exhibited a pattern with good color contrast. Leaving the film on the bench, it gradually lost its color contrast of the pattern and returned to the initial light yellow color within 1 h.

These polymers exhibit a photochromic reaction, even under sunlight (Fig. 5). Rapid photocoloration was observed within 1 min because the photochemical forward (ring-opening) reaction is more efficient than the photochemical back (ring-closure) reaction.[9] Thus, these polymers containing PNI can function as light-controlling materials triggered by sunlight.

In summary, the photochromic properties of PNI in polymers have been studied, and it has been revealed that the lifetime of its open form is sensitive to the polymer matrix, although its absorption spectrum is little affected. We have observed that the lifetime depends mainly on the T_g of the polymer, which is in contrast to the solvent effects reported previously, where –OH groups of alcoholic solvents play a significant role in catalyzing the thermal back reaction. Thus, in polymers, photochromic reactions depend on the available free volume in the medium, which affects the mobility of the photochromic molecule. As for applications leading to light-controlling materials, the optimization and tuning of the photochromic reactions are fundamental requirements. The tuning of the thermal back reaction rate can be achieved by simply selecting a suitable polymer substrate. PNI was stable upon photoirradiation for several hours in most of the polymer matrices studied. The fatigue resistance in polymer matrices is currently being studied and will be reported elsewhere.

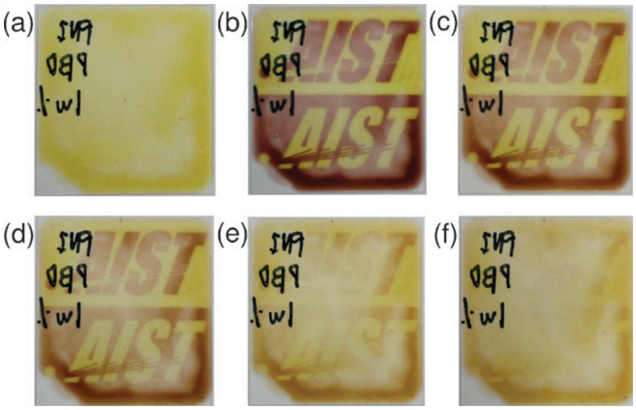

Fig. 4 Photographs of a polymer film (22 mm × 22 mm) having PNI (3 wt%) dispersed in 1,2-polybutadiene. (a) Before irradiation and (b) after 3 min of 405 nm irradiation. The film was then kept in the dark for (c) 5 min, (d) 10 min, (e) 30 min and (f) 50 min after the irradiation.

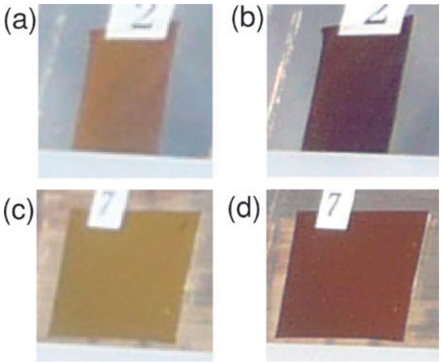

Fig. 5 Photographs of polymer films having PNI (1 wt%) dispersed in (a, b) 1,2-polybutadiene (10 mm × 17 mm) and (c, d) polycarbonate (14 mm × 14 mm). (a, c) Before exposure to light and (b, d) after 2 min exposure to sunlight.

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Experimental

PNI was synthesized as previously reported[9,10] and recrystallized from ethyl acetate. Polystyrene, polyvinyl alcohol (PVA), poly(2-hydroxyethyl methacrylate) (HEMA), styrene/isoprene ABA block copolymer (SIBC), styrene/butadiene ABA block copolymer (SBBC), ethylene/vinyl acetate copolymer (EVA) and 1,2-polybutadiene were purchased from Scientific Polymer Products, Inc. Poly(methyl methacrylate) (PMMA) was purchased from Lancaster. Polyvinyl chloride was purchased from the Wako Chemicals Co. Poly(bisphenol A carbonate) (Polycarbonate) was purchased from Aldrich. Polyvinyl pyrrolidone (PVP) was purchased from TCI. Polydimethylsiloxane (PDMS) was purchased from Dow Corning (Sylgard® 184 silicone elastomer kit). Polyethylene glycol (PEG) was purchased from the Kishida Chemical Co. Spectroscopic grade solvents were used for the preparation of polymer films.

The general procedure for the preparation of cast films was as follows. Solutions containing PNI and polymer were mixed at appropriate ratio to a final concentration of 1–3 wt% of PNI in the polymer substrate. Solvents used for sample preparation are listed in Table 1. The solution was drop-cast on a cover glass (22 mm × 22 mm), and the solvent was allowed to evaporate at room temperature under a continuous flow of dry nitrogen. After coarse removal of the solvent, the film was annealed in a vacuum oven at 100 °C for 1 h. After cooling to room temperature, the film was used for photochromic experiments.

UV-vis absorption spectroscopy was carried out using a JASCO V-570 spectrophotometer. Irradiation was carried out using a high pressure mercury lamp coupled with appropriate filters (405 nm, $\sim$1 mW cm^{-2}) or by LED (λ_{max} = 410 nm, 18 nm fwhm, $\sim$7 mW cm^{-2}). Rate constants for the thermal back reaction from open to closed forms were determined by monitoring the temporal change in absorption at 500 nm of the open form. These measurements were carried out at 295 K.

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