

# Photoinduced diffusive mass transfer in *o*-Cl-HABI amorphous thin films†

Azusa Kikuchi,\*<sup>a</sup> Yukari Harada,<sup>a</sup> Mikio Yagi,<sup>a</sup> Takashi Ubukata,<sup>a</sup> Yasushi Yokoyama<sup>a</sup> and Jiro Abe<sup>b</sup>

Received (in Cambridge, UK) 16th September 2009, Accepted 21st December 2009

First published as an Advance Article on the web 22nd January 2010

DOI: 10.1039/b919180a

**The first demonstration of photoinduced surface relief grating formation using amorphous thin films composed of a radical dissociative photochromic compound, 2,2'-di(*ortho*-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, show that mass transfer occurred from the UV-light-irradiated area to the shaded area by patterned light irradiation (365 nm).**

In the past decade, surface relief gratings (SRGs) have attracted attention from the viewpoint of mass transfer. SRGs formed on azobenzene-functionalized polymer films have attracted the interest of many researchers since the first reports by Natansohn *et al.* and Tripathy *et al.* in 1995.<sup>1</sup> SRGs formed on films composed of various amorphous polymers, liquid crystalline polymers and sol-gel matrices having azobenzene moieties, along with the origin of SRG formation, have also been described.<sup>2</sup> Recently, SRGs have also been formed on crystals and amorphous films composed of molecules containing azobenzene units.<sup>3</sup> SRG formation on photochromic materials other than azobenzene-based compounds has also been a topic of interest.<sup>4</sup>

Research on SRG formation on various photochromic materials is expected to provide a useful suggestion to design more suitable molecular structures for SRG formation. It has been reported a number of times that SRGs on azobenzene-functionalized polymer films are formed by efficient photoisomerization cycles and photoinduced reorientation of azobenzene moieties.<sup>2,3</sup> Reversible *trans* ↔ *cis* photoisomerization of azobenzene groups leads to mass transport processes upon irradiation with polarized light at an appropriate wavelength. The influence of polymer structures and properties, such as molecular weight, glass transition temperature  $T_g$  and azobenzene content, on the efficiency of SRG formation have also been investigated.<sup>5,6</sup> Although many experimental and theoretical studies have been reported in relation to SRG formation, the mechanism of its formation on photochromic materials is not yet fully understood.

In this study, we describe the first SRG formation on radical dissociative photochromic compounds in order to study the relationship between SRG formation and diffusive mass transfer caused by a chemical potential gradient arising from a difference in the amount of substance. The amount of substance is identical to the number of moles. Chemical potential plays a role in the discussion of material spontaneous diffusion, because it carries the information about how Gibbs energy ( $G$ ) changes as the amount of substance changes, and hence how  $G$  changes as the composition of a system changes.<sup>7</sup> 2,2'-Di(*ortho*-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole (*o*-Cl-HABI) can be useful for examining the relationship between SRG formation produced by diffusive mass transfer and the chemical potential gradient, because the amount of substance changes from 1 mol of *o*-Cl-HABI to 2 mol of *o*-Cl-TPIRs by radical dissociative photochromic reaction. Thus, the changes in chemical potential gradient would be considered to affect photoinduced mass transfer during SRG formation. A detailed study of the relationship between SRG formation and diffusion would help increase our understanding of the response to light.

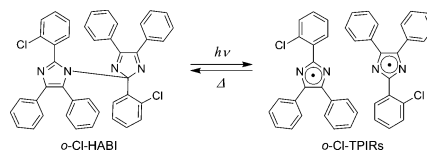
The photochromism of hexaarylbiimidazoles (HABIs) was discovered by Hayashi and Maeda in the 1960's. Several studies of the photochemical and photophysical properties of HABI and its derivatives have been reported.<sup>8</sup> We investigated SRG formation on amorphous thin films consisting of *o*-Cl-HABI. The photochromic behaviour of *o*-Cl-HABI can be attributed to photoinduced homolytic reversible cleavage of the C–N bond between the imidazole rings in an inert environment without other reactions (Scheme 1). Though photochromic properties of various HABI derivatives have been studied extensively, there are essentially no reports for the direct SRG formation on amorphous thin films of them to open up a new field of unique photoresponsive materials.

*o*-Cl-HABI (Wako Pure Chemical Industries, Ltd.) was recrystallized from a 1 : 1 mixture of dichloromethane and acetonitrile to yield pale-yellow block crystals. Dichloromethane and acetonitrile for recrystallization and benzene (Wako Super Special Grade) for film preparation were used without further purification.

<sup>a</sup> Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5, Tokiwadai, Hodogaya, Yokohama, 240-8501, Kanagawa, Japan. E-mail: akikuchi@ynu.ac.jp; Fax: +81 45 339 3948; Tel: +81 45 339 3944

<sup>b</sup> Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, 5-10-1, Fuchinobe, Sagami-hara, 229-8558, Kanagawa, Japan. Fax: +81 42 759 6225; Tel: +81 42 759 6225

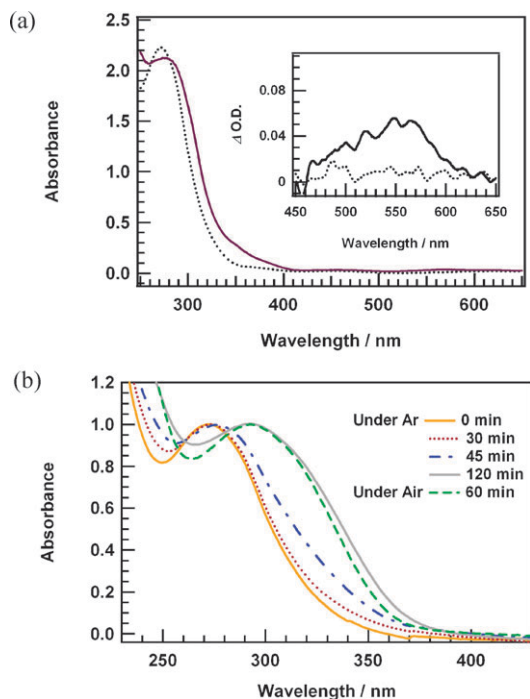
† Electronic supplementary information (ESI) available: Experimental details of *o*-Cl-HABI amorphous thin film, the time profile of the absorbance of *o*-Cl-TPIR in the amorphous thin film at 383 K. See DOI: 10.1039/b919180a



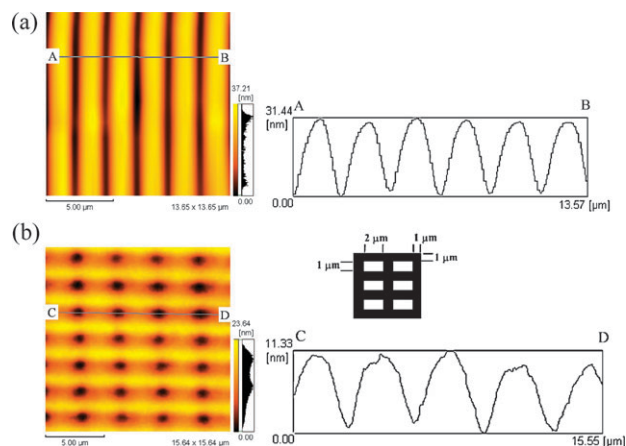
**Scheme 1** Reversible photodissociation reaction of *o*-Cl-HABI into two *o*-Cl-TPIRs.

Transparent amorphous thin films (*ca.* 120 nm thickness) were prepared by spin coating on a clean glass substrate from *o*-Cl-HABI benzene solution ( $16.3 \text{ mmol dm}^{-3}$ ). The thickness of the films was calculated from curve fitting of reflection fringe obtained from a UV-Vis-NIR spectrometer (JASCO, V-670) equipped with an absolute reflectance measurement unit (ARSN-733). The first differential scanning calorimetry (DSC) scan of *o*-Cl-HABI microcrystals displayed the melting point (462 K), whereas no peak due to amorphism was observed in cooling process. Therefore, the second DSC heating scan displayed no peak for the melting point of *o*-Cl-HABI microcrystals.  $T_g$  of *o*-Cl-HABI films was detected to be around 366 K by DSC (Fig. S1, ESI†).

Fig. 1(a) shows absorption spectra for a *o*-Cl-HABI amorphous thin film before and after UV light irradiation at 365 nm. Before irradiation, the main absorption band is at 270 nm. After irradiation, new bands appear at 350 and 550 nm, ascribed to the radical form of *o*-Cl-HABI, *o*-Cl-TPIR, produced by photoinduced homolytic dissociation. Then, under dark conditions, *o*-Cl-TPIRs thermally recombine at room temperature to reproduce the dimer form, *o*-Cl-HABI. *o*-Cl-TPIRs recombine within *ca.* 6–10 s in an amorphous film at 383 K (Fig. S3, ESI†). This photochromic behaviour is in good agreement with that observed in *o*-Cl-HABI acetonitrile solution. Fig. 1(b) shows UV-Vis absorption spectral change for *o*-Cl-HABI films during UV light irradiation. In order to reduce film decomposition, SRG formation was achieved within 30 min of irradiation under an Ar atmosphere. After film preparation, the glass substrate was maintained at 383 K



**Fig. 1** (a) UV-Vis absorption spectral change in the *o*-Cl-HABI film (*ca.* 500 nm thickness) at 300 K: (dotted line) before irradiation and (solid line) immediately after UV light irradiation (365 nm,  $11 \text{ mW cm}^{-2}$ , 5 s irradiation). (b) UV-vis absorption spectral change in the *o*-Cl-HABI film (*ca.* 200 nm thickness) after a variety of time periods of UV light irradiation (365 nm,  $22 \text{ mW cm}^{-2}$ , 383 K) under Ar and air atmospheres.

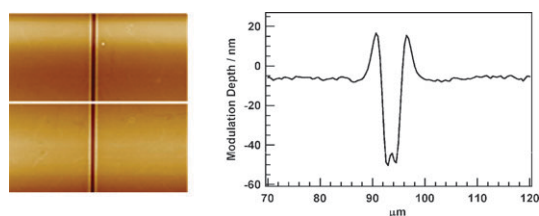


**Fig. 2** AFM images (left) and cross-sectional height profiles for the solid line (right) of surface relief structures produced by patterned UV light irradiation ( $365 \text{ nm}$ ,  $22 \text{ mW cm}^{-2}$ , 20 min, 383 K, under Ar atmosphere) on amorphous thin films of *o*-Cl-HABI (*ca.* 120 nm thickness) through different types of photomask: (a) through a stripe-type photomask with the period of  $2 \mu\text{m}$  and (b) through a grid-type photomask with transparent ( $2 \mu\text{m}$ ) and opaque ( $1 \mu\text{m}$ ) lines.

using a hotplate. This temperature is optimal for SRG formation of *o*-Cl-HABI. UV light irradiation was performed using a UV-LED lamp (Keyence UV-400 series, UV-50H type, 365 nm). Light was collimated to obtain an intensity of  $22 \text{ mW cm}^{-2}$  over the entire irradiation area. Patterned light irradiation was performed through a custom-made photomask (Toppa Printing Co.) composed of stripes with the  $2 \mu\text{m}$  widths of transparent and opaque lines, and orthogonal grids with transparent ( $2 \mu\text{m}$ ) and opaque ( $1 \mu\text{m}$ ) lines. After the films were irradiated for 20 min, the surface relief structures were observed through an AFM using a SHIMADZU SPM-9500 equipped with cantilever (OLYMPUS OMCL-TR800PSA-1).

Fig. 2 shows SRG structures formed by patterned UV light irradiation on the film through the photomask. Regular surface modulation was achieved with a spatial period of  $2 \mu\text{m}$ , in accordance with the photomask pattern, and observed peak-to-trough modulation depth of *ca.* 20–30 nm (Fig. 2(a)).

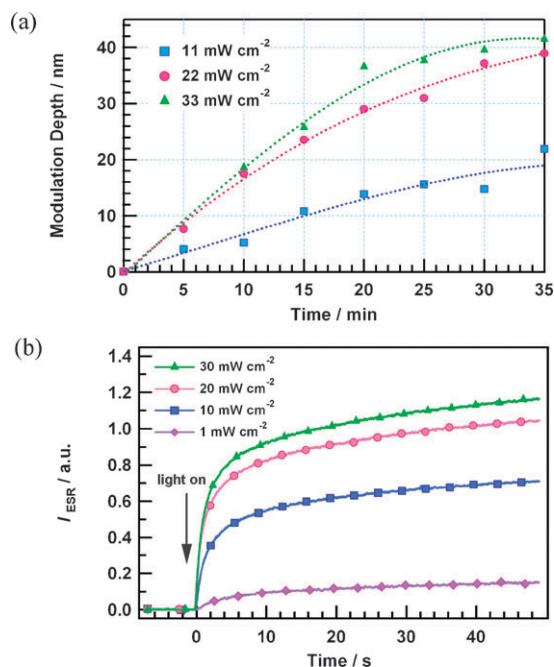
To investigate the direction of mass transfer, we irradiated the film through a photomask with just one slit line ( $4 \mu\text{m}$  wide; Fig. 3). The cross-sectional topography shows that the convex is higher and the concave is lower than the initial surface level, which clearly demonstrates that lateral mass transfer occurred on the film surface. On the surface of the irradiated areas, *o*-Cl-HABIs are readily cleaved photochemically into *o*-Cl-TPIRs; in contrast, on the surface of the shaded areas, almost all molecules are present in their dimer form, *o*-Cl-HABI. Mass transfer induced as a consequence of the radical dissociative photochromic reaction on the film surface can be explained as follows. Photochromic reaction of *o*-Cl-HABI increases the amount of *o*-Cl-TPIRs in the irradiated area, which causes the chemical potential of the irradiated area to differ from that of the shaded area and in turn drives the mass transfer. Molecular diffusion can be induced by chemical potential gradients. That is, the material moved from the irradiated areas to the shaded areas. We therefore propose that the chemical potential gradient may be a driving force for mass transfer.



**Fig. 3** AFM images of UV light irradiation ( $365\text{ nm}$ ,  $22\text{ mW cm}^{-2}$ ,  $20\text{ min}$ ,  $383\text{ K}$ , under Ar atmosphere) on amorphous thin films of *o*-Cl-HABI (ca.  $120\text{ nm}$  thickness) through a photomask (slit width  $4\text{ }\mu\text{m}$ ). The images on the right are cross-sectional height profiles for the solid lines shown in the AFM images.

Fig. 4a shows modulation depth of the recorded gratings as a function of irradiation time for various light intensities. Because the concentration of the radical form, *o*-Cl-TPIR, depends on light intensity (Fig. 4(b)). These results suggest that mass transfer is involved in the radical dissociative photochromic reaction, and is controlled by molecular diffusion driven by the chemical potential gradient.

In summary, SRGs are formed on the surface of amorphous thin films of *o*-Cl-HABI. The SRG structures are attributed to mass transfer resulting from the difference in the chemical potential between irradiated and shaded areas. Photochromic reaction of *o*-Cl-HABI increases the amount of *o*-Cl-TPIRs in the irradiated area. The chemical potential gradient thus formed by patterned UV light irradiation is reduced by mass transfer from irradiated to shaded area. Control of chemical potential might therefore be a key to mass transfer during SRG formation. Further detailed investigations, including studies on the reversibility of SRG formation, are in progress



**Fig. 4** (a) Modulation depth in the *o*-Cl-HABI film (ca.  $120\text{ nm}$  thickness) as a function of irradiation time with different  $365\text{-nm}$  UV light intensities at  $383\text{ K}$ . (b) Time profiles of ESR intensities (monitored at  $336.7\text{ mT}$ ) of *o*-Cl-TPIRs in *o*-Cl-HABI amorphous films ( $10\text{ mg}$ ) irradiated with different UV light intensities at  $300\text{ K}$ .

to elucidate the mechanism of SRG formation for HABI derivatives.

The authors wish to express their thanks to the Instrumental Analysis Center, Yokohama National University, for the use of the NMR spectrometer. They also thank Mr Yusuke Moriya for the help in the preliminary AFM measurement. This work was partly supported by a Grant-in-Aid Science Research in Priority Areas "New Frontiers in Photochromism (No. 471)" from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

## Notes and references

- (a) P. Rochon, E. Batalla and A. Natansohn, *Appl. Phys. Lett.*, 1995, **66**, 136; (b) D. Y. Kim, S. K. Tripathy, L. Li and J. Kumar, *Appl. Phys. Lett.*, 1995, **66**, 1166.
- (a) A. Natansohn and P. Rochon, *Chem. Rev.*, 2002, **102**, 4139; (b) O. N. Oliveira, Jr., J. Kumar, L. Li and S. K. Tripathy, in *Photoreactive Organic Thin Films*, ed. Z. Sekkat and W. Knoll, Academic Press, California, 2002, pp. 429–486; (c) J. A. Delaire and K. Nakatani, *Chem. Rev.*, 2000, **100**, 1817; (d) H. Yu, Y. Naka, A. Shishido and T. Ikeda, *Macromolecules*, 2008, **41**, 7959; (e) S. Yoneyama, T. Yamamoto, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *Macromolecules*, 2002, **35**, 8751; (f) T. Yamamoto, A. Ohashi, S. Yoneyama, M. Hasegawa, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *J. Phys. Chem. B*, 2001, **105**, 2308; (g) M. Hasegawa, T. Yamamoto, A. Kanazawa, T. Shiono and T. Ikeda, *Chem. Mater.*, 1999, **11**, 2764; (h) N. Zettsu, T. Ogasawara, N. Mizoshita, S. Nagano and T. Seki, *Adv. Mater.*, 2008, **20**, 516; (i) N. Zettsu, T. Ogasawara, R. Arakawa, S. Nagano, T. Ubukata and T. Seki, *Macromolecules*, 2007, **40**, 4607; (j) N. Zettsu and T. Seki, *Macromolecules*, 2004, **37**, 8692; (k) P. S. Ramanujam, N. C. R. Holme and S. Hvilsted, *Appl. Phys. Lett.*, 1996, **68**, 1329; (l) N. C. R. Holme, L. Nikolova, P. S. Ramanujam and S. Hvilsted, *Appl. Phys. Lett.*, 1997, **70**, 1518; (m) P. S. Ramanujam, M. Pederson and S. Hvilsted, *Appl. Phys. Lett.*, 1999, **74**, 3227; (n) N. Landraud, J. Peretti, F. Chaput, G. Lampel, J.-P. Boilot, K. Lahlil and V. I. Safarov, *Appl. Phys. Lett.*, 2001, **79**, 4562.
- (a) E. Ishow, B. Lebon, Y. He, X. Wang, L. Bouteiller, L. Galmiche and K. Nakatani, *Chem. Mater.*, 2006, **18**, 1261; (b) H. Nakano, *J. Phys. Chem. C*, 2008, **112**, 16042; (c) M.-J. Kim, E.-M. Soe, D. Vak and D.-Y. Kim, *Chem. Mater.*, 2003, **15**, 4021.
- (a) T. Ubukata, S. Fujii and Y. Yokoyama, *J. Mater. Chem.*, 2009, **19**, 3373; (b) T. Ubukata, S. Yamaguchi and Y. Yokoyama, *Chem. Lett.*, 2007, **36**, 1224; (c) T. Ubukata, K. Takahashi and Y. Yokoyama, *J. Phys. Org. Chem.*, 2007, **20**, 981.
- (a) C. J. Barrett, A. L. Natansohn and P. L. Rochon, *J. Phys. Chem.*, 1996, **100**, 8836; (b) J. Kumar, L. Li, X. L. Jiang, D.-Y. Kim, T. S. Lee and S. Tripathy, *Appl. Phys. Lett.*, 1998, **72**, 2096; (c) T. G. Pedersen, P. M. Johansen, N. C. R. Holme and P. S. Ramanujam, *Phys. Rev. Lett.*, 1998, **80**, 89; (d) K. Sumaru, T. Yamanaka, T. Fukuda and H. Matsuda, *Appl. Phys. Lett.*, 1999, **75**, 1878; (e) K. G. Yager and C. J. Barrent, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 487.
- (a) T. Yamamoto, M. Hasegawa, A. Kanazawa, T. Shiono and T. Ikeda, *J. Phys. Chem. B*, 1999, **103**, 9873; (b) O. Kulikovska, L. M. Goldenberg, L. Kulikovskiy and J. Stumpe, *Chem. Mater.*, 2008, **20**, 3528; (c) V. Börger, S. Pohle, O. Kulikovska, K. G-Hubmann, J. Stumpe and H. Menzel, *Macromol. Symp.*, 2009, **275–276**, 257.
- D. W. Ball, in *Physical Chemistry*, 2003, Books/Cole Pub. Co., Pacific Grove, CA, USA, ch. 6, pp. 141–165.
- (a) T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 565; (b) D. M. White and J. Sonnenberg, *J. Am. Chem. Soc.*, 1966, **88**, 3825; (c) M. A. J. Wilks and M. R. Willis, *Nature*, 1966, **212**, 500; (d) A. Kikuchi, T. Iyoda and J. Abe, *Chem. Commun.*, 2002, 1484; (e) A. Kikuchi, F. Iwahori and J. Abe, *J. Am. Chem. Soc.*, 2004, **126**, 6526; (f) I. Nakahara, A. Kikuchi, F. Iwahori and J. Abe, *Chem. Phys. Lett.*, 2005, **402**, 107; (g) Y. Kishimoto and J. Abe, *J. Am. Chem. Soc.*, 2009, **131**, 4227; (h) H. Miyasaka, Y. Satoh, Y. Ishibashi, S. Ito, Y. Nagasawa, S. Taniguchi, H. Chosrowjan, N. Mataga, D. Kato, A. Kikuchi and J. Abe, *J. Am. Chem. Soc.*, 2009, **131**, 7256; (i) B. M. Monroe and G. C. Weed, *Chem. Rev.*, 1993, **93**, 435.