ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 11891–11893

www.rsc.org/chemcomm

COMMUNICATION

Mass migration on a polymer surface caused by photoinduced molecular rotation†

Kunihiko Okano,*[a] Shohei Ogino,[a] Masuki Kawamoto[b] and Takashi Yamashita*[a]

Received 20th July 2011, Accepted 23rd September 2011
DOI: 10.1039/c1cc14375a

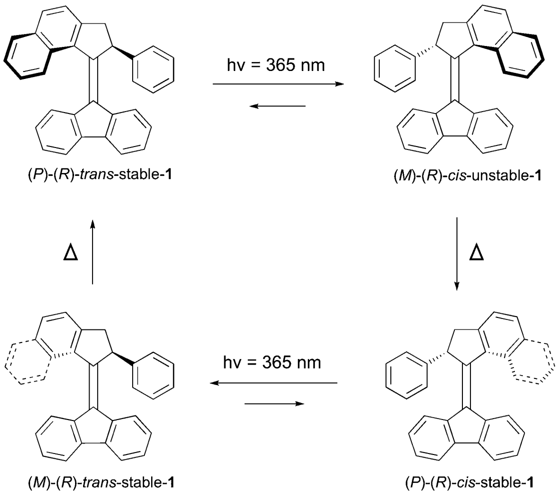
We demonstrated the formation of a photoinduced surface relief grating using thin films comprising a photochromic molecular motor, 9-(2-phenyl-2,3-dihydro-cyclopenta[*a*]naphthalen-1-ylidene)-9*H*-fluorene. Results show that mass migration occurred by patterned light irradiation prepared from interfered laser beams and a photomask.

Photochromism is a phenomenon in which exposure of a compound to light induces a change in its colour by photoisomerization. In recently developed advanced materials, photoisomerization changes the shapes of photochromic molecules and this can enhance to mechanical deformation in a broad size range from nm to cm.[1] For example, the designed photochromic liquid-crystalline elastomers show macroscopic deformation upon exposure to light.[2] In addition, nanostructures formed from liquid-crystalline block copolymers containing an azobenzene moiety can be controlled during the process of photoisomerization.[3] In the case of micrometre-scale manipulation of photochromic materials, the surface relief grating (SRG) that results from photoinduced mass migration has attracted considerable attention since the discovery in 1995.[4] In particular, azobenzene polymer is mostly used as a material for SRG formation. Previous studies show that SRG is formed in a broad category of material systems such as amorphous polymer,[5] amorphous low-molecular-weight compounds,[6] crystals,[7] and liquid-crystalline polymers.[8] Moreover, photochromic moieties other than azobenzene, such as spiropyran,[9] diarylethene,[10] and hexaarylbiimidazole,[11] have also been applied for the mass transfer of the film.

We reported the formation of SRG by using a photochromic molecular motor, which shows anomalous isomerization behavior: monodirectional rotation *via* photo and thermal isomerization processes.[12] The photochromic molecular motor has four structures in the isomerization process. Therefore, the trial performed in this study would increase the possibility of applying the mass migration process in SRG formation. Moreover, even after many experimental and theoretical studies, the mechanism of SRG formation is not yet fully understood. We also consider the reported system to be a new model that will aid in understanding the mechanism of SRG formation.

The photoresponsive molecular motor was firstly designed and developed in the 1999,[12a] in which monodirectional rotation was around a central carbon–carbon double bond in a chiral, helical alkene, with each 360° rotation involving four discrete isomerization steps activated by UV light or a change in system temperature (Scheme 1). So far, several types of molecular motors have been developed based on distinct concepts. Based on the previous study, we have chosen and synthesized 9-(2-phenyl-2,3-dihydro-cyclopenta[*a*]naphthalen-1-ylidene)-9*H*-fluorene (**1**), and prepared poly(methyl methacrylate) (PMMA) film added with each isomer for SRG formation.

The sample films (*ca.* 200 nm thickness) were fabricated by casting on a clean glass substrate from toluene solution containing 3 wt% **1**/PMMA (weight ratio 50 : 50). Since the glass transition temperature affects the mass migration phenomena in SRG, we checked the thermal property of the sample by differential scanning calorimetry (DSC) before attempting SRG formation of the film. The second DSC heating curve indicated a T_g value of 70 °C, which is lower than that of PMMA due to the plasticizing effect.



Scheme 1 Photochemical *cis*/*trans* isomerization and thermal helix inversion steps of **1**.[12d]

---

[a] *Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba 278-8510, Japan. E-mail: kokano@rs.noda.tus.ac.jp, yama@rs.noda.tus.ac.jp; Fax: +81 471241501; Tel: +81 471241501*

[b] *RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c1cc14375a

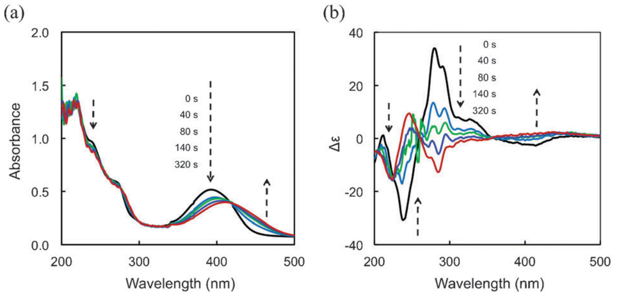


Fig. 1 (a) Changes in the UV-vis absorption spectra of the sample film during irradiation with UV light (220 mW cm^{-2}) at room temperature. (b) Changes in the CD spectra of the sample film containing an (*S*)-isomer (initial state) of **1** by the photoisomerization process.

Photochemical *cis*/*trans* isomerization and the thermal isomerization processes both resulting in a helix inversion were examined in the sample films. The resolution of the enantiomer of **1** was obtained by chiral HPLC (Chiralpak IA column). Fig. 1a shows representative UV-vis spectra of the film as measured for the initial states at 25 °C. Upon irradiation of the film, *cis*/*trans* isomerisation afforded a new isomer, which was monitored by UV-vis spectroscopy as a shift of the absorption around 390 nm to a broad band at higher wavelength. This bathochromic shift is attributed to enhanced twist of the central olefinic bond.[12b,d] The irradiation of the film containing the enantiopure compound **1** at room temperature showed inversion of the major absorption bands in the CD spectrum (Fig. 1b), indicating *cis*/*trans* photoisomerization and simultaneous helix inversion. The photoinduced isomerized CD spectrum was restored to the initial state by the thermal effect, and this tendency was enhanced by an increase in the temperature as shown in Fig. 2. Noticeably, the thermal isomerisation process was much slower in the PMMA than in solution at 25 °C, which means that thermal isomerisation behaviour is restricted in the polymer matrix (see ESI†).

Fig. 3a illustrates the optical setup used for recording holographic gratings in the sample films. Two *s*-polarized beams at 364 nm with an equal intensity of 130 mW cm^{-2} from an Ar^{+} laser were used as writing beams. The interference beams were symmetrically crossed on the film surface at a crossing angle of 14°, leading to an interference pattern with a fringe spacing of 1.5 μm according to $\Lambda = \lambda/(2\sin\theta)$, where λ and θ are the wavelength and the incident angle of the writing laser beams, respectively. The two beams were collimated to a diameter of about 2.0 mm on the film surface. A He–Ne laser beam at 633 nm was used as a probe beam. The grating formation was confirmed in real time by monitoring the intensity of the first-order diffraction beam with a photodiode.

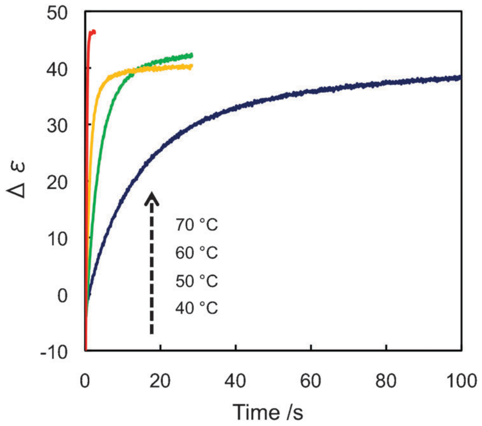


Fig. 2 Thermal relaxation process of the sample films containing an (*S*)-isomer (initial state) of **1** from the photostationary state. These profiles were recorded by CD spectroscopy at 291 nm.

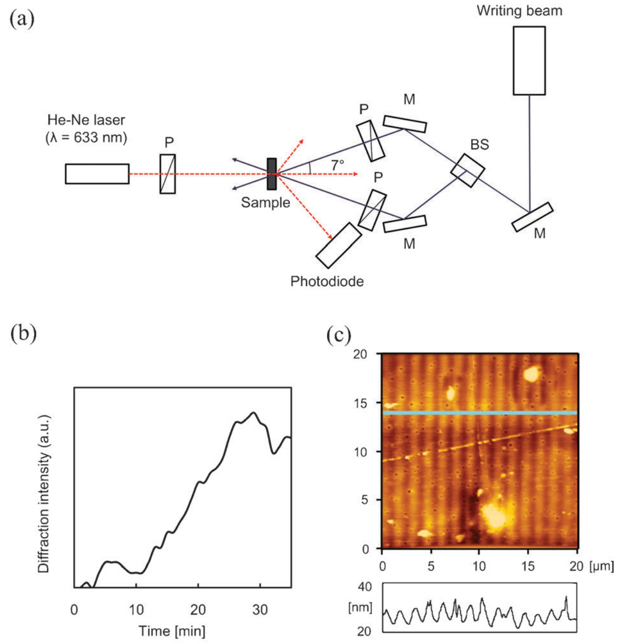


Fig. 3 (a) Schematic illustration of the optical setup for grating formation. BS, M, and P represent the beam splitter, mirror, and polarizer, respectively. The film containing the (*S*)-isomer (initial state) was irradiated with interfered UV beams (364 nm, 130 mW cm^{-2}). (b) Time course profiles of the first-order diffraction of He–Ne beam to evaluate the SRG growth. (c) Topographical AFM image and height profile of the film irradiated for 30 min.

As shown in Fig. 3b, the intensity of diffracted light gradually increased for 10 min irradiation at room temperature, which means that the grating formation occurred due to the difference in the refractive indexes of the bright and dark areas of the interference patterns. Photoisomerization in the sample film was induced immediately after irradiation (Fig. 1). Therefore the timescale between the grating formation and photoisomerization is different. This is probably because the irradiation energy first softens the film surface, and then induces mass migration to form SRG. The result also implies that the gratings comprise mainly SRG rather than refractive index modulation inside the film because modulation of the refractive index occurred immediately for the isomerisation process.[8b] Next, using atomic force microscopy (AFM), we examined the surface morphology of the film after irradiation for 30 min (Fig. 3c). We observed that the irradiation of interference beams results in the formation of SRG on the film surface. Regular surface modulation was achieved with a spatial period of 1.5 μm, which was in accordance with the calculated value. In addition, we observed a peak-to-trough modulation depth of *ca.* 10 nm. Moreover, a similar SRG structure was observed even in the case where (*R*)-isomer in the initial state was used as a dye (see ESI†).

View Article Online

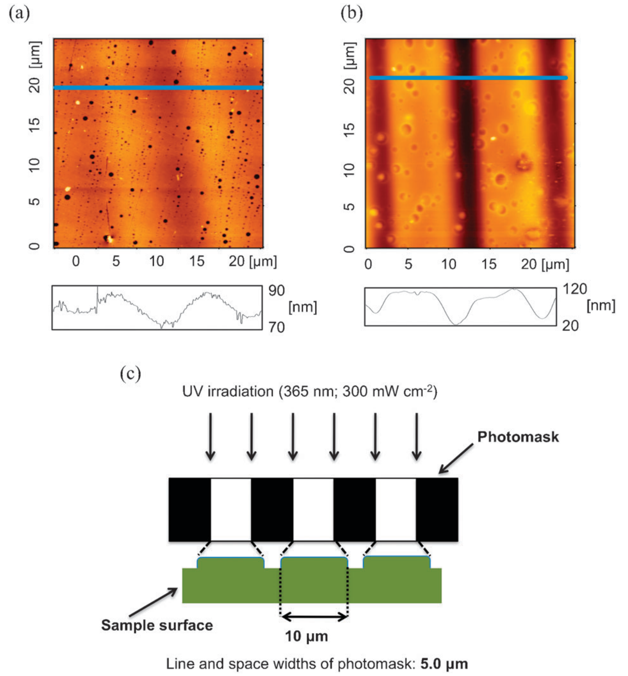


Fig. 4 Top view topographical AFM images and height profiles along the line shown in the film after UV irradiation (365 nm; 300 mW cm^{-2}) with a photomask at room temperature (a) and at 90 °C (b). (c) Possible process of the SRG formation.

An SRG structure of azo-polymer is dependent on polarization of writing beams,[13] because an azobenzene chromophore is aligned by polarization of light (Weigert effect).[14] Therefore, firstly, we measured polarized absorption spectra of a PMMA/molecular motor film after irradiation of polarized UV light at 365 nm (see ESI†). This result shows no anisotropic property of the molecular motor. Next, linearly polarized UV light was used instead of non-polarized one for SRG formation. The depth of SRG formed with linearly polarized UV light showed no difference in one inscribed with non-polarized light.

Based on the above data, the efficient mass migration may occur when the photoirradiation is performed at higher temperatures where the polymer adopts above T_g. Therefore, our focus then shifted to the irradiation experiments using a photomask (5 μm line and space patterns), which enables smooth photo patterning procedures at higher temperatures. Photo patterning with a photomask was achieved with the visible line (365 nm) of an Hg lamp. Upon UV irradiation, a slight grating formation (∼10 nm) was observed at room temperature, whereas an efficient and large mass transfer (∼150 nm) was observed at 90 °C (Fig. 4). These results support the assumption that the mass migration was efficiently caused by photoinduced molecular rotation above T_g. It is noticed that the convex width was 10 μm, whereas the concave width was 3 μm even in the same line and space widths of the used photomask. We observed that the bright areas of strong backlight formed from the photomask were expanded by optical microscopy, which indicates that the bright areas reflect the broader convex region than the concave one. This result implies the mechanism of mass migration of the system. That is, the lateral material transfer occurred from the shaded areas to the irradiated areas (Fig. 4c).

In summary, the phototriggered mass migration behavior was examined using a PMMA film consisting of a photochromic molecular motor. Upon irradiation with interfered beams of an Ar$^+$ laser at 364 nm, SRG is formed on the sample film by photoinduced rotation. In the photo patterning procedure with a photomask, the film also forms SRG. The knowledge obtained in this work will greatly enhance the applicability of materials to the exertion of phototriggered mass transfer systems based on the specific photochromism of molecular rotation.

The authors wish to express their gratitude to Dr Atsushi Shishido for permitting the use of the optical setup required for formation of gratings. This work was partly supported by a CLUSTER (second stage) of the Japan Ministry of Education, Culture, Sports, Science.

Notes and references

1 (*a*) A. Natansohn and P. Rochon, *Chem. Rev.*, 2002, **102**, 4109; (*b*) O. 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*) K. Ichimura, *Chem. Rev.*, 2000, **100**, 1847; (*d*) T. Ikeda, *J. Mater. Chem.*, 2003, **13**, 2037.

2 (*a*) T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi and A. Kanazawa, *Adv. Mater.*, 2003, **15**, 201; (*b*) Y. Yu, M. Nakano and T. Ikeda, *Nature*, 2003, **425**, 145; (*c*) C. J. Barrett, J. Mamiya, K. G. Yager and T. Ikeda, *Soft Matter*, 2007, **3**, 1249; (*d*) M. Camacho-Lopez, H. Finkelmann, P. Palffy and M. Shelley, *Nat. Mater.*, 2004, **3**, 307.

3 (*a*) H. Yu, T. Iyoda and T. Ikeda, *J. Am. Chem. Soc.*, 2006, **128**, 11010; (*b*) Y. Morikawa, T. Kondo, S. Nagaono and T. Seki, *Chem. Mater.*, 2007, **19**, 1540.

4 (*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.

5 (*a*) C. J. Barrett, A. Natansohn and P. 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. Pedersen, P. Johansen, N. Holme and P. Ramanujam, *Phys. Rev. Lett.*, 1998, **80**, 89.

6 H. Nakano, T. Takahashi, T. Tadota and Y. Shirota, *Adv. Mater.*, 2002, **14**, 1157.

7 (*a*) H. Nakano, *J. Phys. Chem. C*, 2008, **112**, 16042; (*b*) L. M. Golenberg, L. Kulikovsky, O. Kulikovska, J. Tomczyk and J. Stumpe, *Langmuir*, 2010, **26**, 2214.

8 (*a*) T. Ubukata, T. Seki and K. Ichimura, *Adv. Mater.*, 2000, **12**, 1675; (*b*) T. Yamamoto, A. Ohashi, S. Yoneyama, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *J. Phys. Chem. B*, 2001, **105**, 2308; (*c*) S. Yoneyama, T. Yamamoto, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *Macromolecules*, 2002, **35**, 8751; (*d*) K. Okano, A. Shishido, O. Tsutsumi and T. Ikeda, *J. Mater. Chem.*, 2005, **15**, 3395.

9 T. Ubutaka, K. Takahashi and Y. Yokoyama, *J. Phys. Org. Chem.*, 2007, **20**, 981.

10 T. Ubutaka, S. Yamaguchi and Y. Yokoyama, *Chem. Lett.*, 2007, 1224.

11 A. Kikuchi, Y. Harada, M. Yagi, T. Ubutaka, Y. Yokoyama and J. Abe, *Chem. Commun.*, 2010, **46**, 2262.

12 (*a*) N. Koumura, R. W. J. Zijistra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152; (*b*) N. Koumura, E. M. Geertsema, M. Gelder, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2002, **124**, 5037; (*c*) M. K. J. ter Wiel, R. A. van Delden, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2003, **125**, 15076; (*d*) J. Vicario, M. Walko, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2006, **128**, 5127; (*e*) M. Klok, N. Boyle, M. T. Pryce, A. Meetsma, W. Browne and B. L. Feringa, *J. Am. Chem. Soc.*, 2008, **130**, 10484; (*f*) G. T. London, G. Carroll, L. T. Fernandez, M. Pollard, P. Rudolf and B. L. Feringa, *Chem. Commun.*, 2009, 1712; (*g*) T. Kudernac, N. Katsonis, W. Browne and B. Feringa, *J. Mater. Chem.*, 2009, **19**, 7168.

13 N. Kawatsuki, E. Uchida and H. Ono, *Appl. Phys. Lett.*, 2003, **83**, 4544.

14 T. Weigert, *Verh. Phys. Ges. Berlin*, 1919, **21**, 485.