2-5-8. Photoinduced Morphological Change and Surface Relief

Overview

Material morphological changes and patterning through photochromic reactions, photopolymerization, and photocrosslinking in thin film have developed rapidly since the 2000s. This section focuses on photoinduced changes in surface morphology and relief formation in photoresponsive thin film systems, introducing recent research. These non-contact, reversible surface deformations induced by photo represent a novel micro/nano-fabrication technique, promising new developments as surface functions for soft materials.

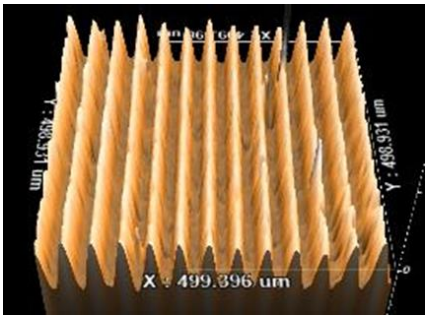

Figure 1. Typical photoinduce surface relief structure (magnifie approximately 200 times vertically).

Current Status and Frontiers

When a polymer film containing the photochromic molecule azobenzene is irradiated with interference or patterned light, the polymer mass migrates according to the light pattern, leading to the formation of a surface relief structure. This phenomenon, known as photoinduced Surface Relief Grating (SRG) or photoinduced mass transfer, was first discovered in Canada and the United States in 1995. Following this initial report, extensive studies were conducted around the year 2000. For an overview up to the mid-2000s, refer to section "2-4-7. Photoinduced Morphological Change and Surface Relief" in the Photochemistry Div Report described in Japanese. URL: https://division.csj.jp/div-report/02/0220407.pdf Even today, many researchers worldwide continue to investigate this phenomenon, and recent studies are presented below.

1. Studies on the mechanism of mass transfer

Since the discovery of photoinduced mass transport, various mechanisms have been proposed. These include pressure changes caused by molecular volume variations resulting from photoisomerization, electromagnetic gradients of light, mean-field theoretical models, anisotropic flow induced by light polarization, anisotropic molecular diffusion, and molecular reorientation due to irradiation with polarized light. However, the precise mechanism is still under debate. In recent years, two groups (Kim *et al.* and Kitamura *et al.*) have demonstrated that the Marangoni effect, arising from surface tension gradients, can serve as a primary driving mechanism of mass transport.

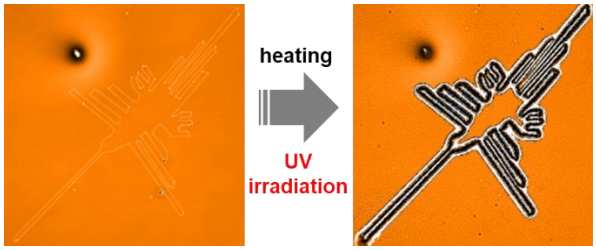

Figure 2. Surface pattern utilizing inkjet drawing and photo-induced Marangoni flow

Kitamura *et al.* constructed bilayer films by transferring a few monolayers (approximately 2–10 nm in thickness) of azobenzene polymers onto a non-

photoresponsive polymer thin film (200 nm thick) using the Langmuir–Schaefer method, followed by irradiation with patterned UV light. As a result, material transport from the non-irradiated regions to the irradiated ones was observed. Remarkably, even when the top azobenzene polymer layer was only ~10 nm thick, surface relief structures as large as ~200 nm could be induced, comparable to those formed in pure azobenzene polymer films. Since the cis isomer of azobenzene is more polar than the trans isomer and therefore possesses higher surface tension, the observed migration from the trans-rich to the cis-rich regions can be interpreted as Marangoni flow. Furthermore, Kitamura *et al.* also demonstrated a microfabrication technique in which a low-surface-tension block copolymer was deposited by inkjet printing onto an azobenzene polymer thin film. Upon UV irradiation, grooves corresponding to the printed patterns were generated via Marangoni flow.

2. Photoinduced Mass Transfer in Systems Other Than Azobenzene

Photoinduced mass transport has also been reported in systems involving photopolymerization, photocrosslinking, and photochromic molecules other than azobenzene, and has been extensively studied in Japan as well. Ubukata et al. observed the formation of SRGs arising from mass transport during the photocrosslinking and photopolymerization of molecules containing bis-anthracene units or diacetylene moieties. In the case of photochromic molecules other than azobenzene, Kawatsuki et al. demonstrated polarization-dependent relief formation by employing polymers bearing N-benzylideneaniline derivatives in the side chains, irradiated with interference light under various polarization conditions. Furthermore, SRG formation has also been reported for low-molecular-weight photochromic molecules such as spirooxazine (Ubukata et al.) and hexa-arylbisimidazole (Kikuchi and Abe et al.). A comprehensive overview of photoinduced SRG formation in various photoresponsive molecules can be found in the recent review by Ubukata, Seki, and co-workers (*Bull. Chem. Soc. Jpn.*, **95**, 138–162 (2022)).

References

1. C. B. Kim, et al., *Macromolecules*, **49**, 7069–7076 (2016).
2. I. Kitamura, et al., *Sci. Rep.*, **10**, 12664 (2020).
3. I. Kitamura, et al., *Sci. Rep.*, **9**, 2556 (2019).
4. T. Ubukata, et al., *ACS Appl. Mater. Interfaces*, **8**, 21974–21978 (2016).
5. N. Kawatsuki, et al., *Macromolecules*, **47**, 324–332 (2014).

Future Perspectives and Directions

Challenges and Prospects for the Next Decade: Key issues to be addressed include elucidating and systematizing the dominant mechanisms of photoinduced mass transport across various material systems, and exploring their suitable applications. Another important goal is the realization of practical systems and devices that exploit reversible surface morphological changes for microfabrication and patterning.

(Author: Shusaku Nagano)