

## Photoresponsive soft material by large-scale molecular ordering of a polymer brush

As exemplified by skeletal muscles, living organisms make use of long-range three-dimensional (3D) molecular orders to achieve particular biological functions. This notion has prompted chemists to develop effective methods for tailoring elaborate molecular assemblies over a macroscopic length scale. Such a technology is considered essential for creating high-performance organic materials and devices. Although several approaches, including the use of shear forces, external electric fields, and patterned surfaces, enable the one-dimensional (1D) macroscopic ordering of liquid crystalline molecules and polymers, no rational molecular design strategy or processing methodology has yet been developed for the 3D ordering of large and/or complex molecules in macroscopic solid materials.

In this report, we describe our recent finding that a one-step hot pressing of a certain graft polymer, sandwiched by uniaxially stretched Teflon sheets, affords a free-standing film, where a 3D molecular order with a remarkably high structural integrity develops widely on its both sides over a macroscopic size regime [1]. The graft polymer that makes the unique structuring event possible is a polymer brush consisting of a polymethacrylate backbone wrapped with densely grafted paraffinic side chains containing three azobenzene units (poly-1, Fig. 1). The azobenzene functionality serves as a mesogenic core of liquid crystalline molecules and is capable of reversible photochemical transformation between its *trans* and *cis* forms with a large structural change.

Poly-1 was prepared by the free-radical polymerization of **1** ( $M_n = 1.5 \times 10^5$  g/mol). This

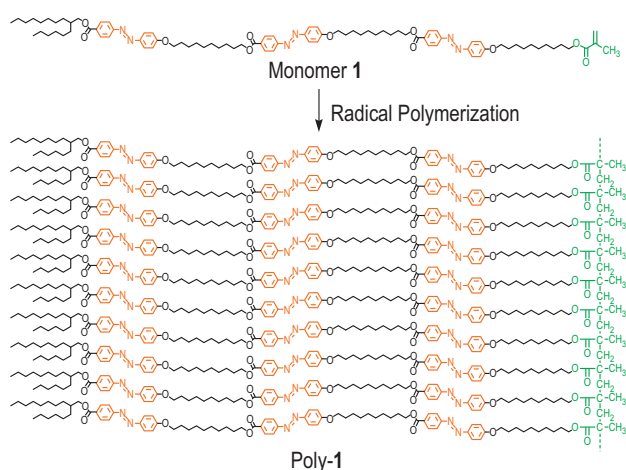


Fig. 1. Molecular formulae of monomer **1** and poly-1.

polymer brush showed two exothermic peaks at 120 and 103°C on cooling from its isotropic melt. To determine the structure of poly-1 at the mesophase, we measured synchrotron radiation small-angle X-ray scattering (SAXS) using beamline BL45XU. The SAXS pattern, thus obtained (Fig. 2(a)), showed multiple reflection peaks assignable to a 2D rectangular lattice (space group;  $P2_1/a$ ) with lattice parameters  $a$  and  $b$  of 218(5) and 147(1) Å, respectively. This observation suggests that poly-1 molecules adopt an elliptically cylindrical structure and align parallel to one another without the entanglement of their side chains.

We found an interesting phenomenon that the polymer molecules, upon hot pressing with commercially available Teflon sheets, orient in a macroscopic regime to yield a free-standing film. When the resultant film was exposed to a synchrotron X-ray beam in a direction perpendicular to the film plane, a through-view 2D SAXS image, characteristic of a rectangular structure ( $P2_1/a$ ), was obtained (Fig. 2(b)). The diffuse spots were successfully

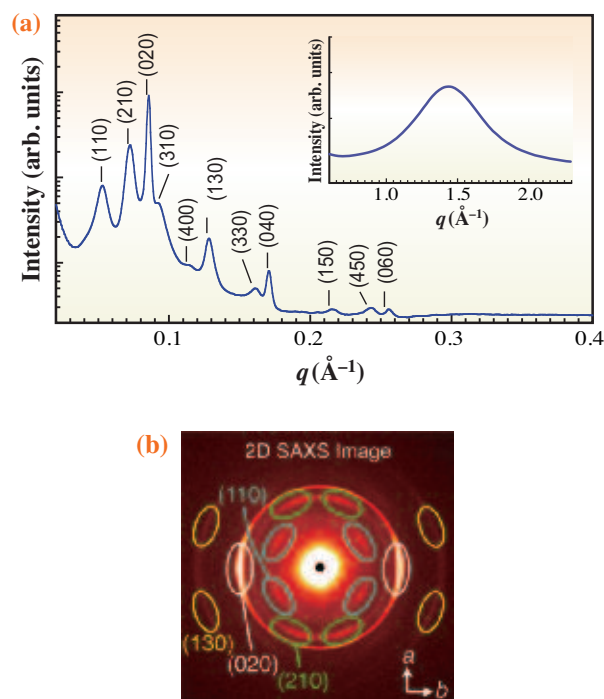


Fig. 2. SAXS data of poly-1. Miller indices are given in parentheses. (a) 1D SAXS pattern of a powdery sample of poly-1 in a capillary, measured at 115°C on cooling from its isotropic melt. (Inset) Scattering profile in wide-angle region. (b) Through-view 2D SAXS images of hot-pressed film of poly-1.



Fig. 3. Schematic illustration of 3D molecular order in hot-pressed polymer brush film.

assigned to the reflections from the  $(hkl) = (110)$ ,  $(210)$ ,  $(020)$ , and  $(130)$  planes. Through detailed structural investigation, we revealed that the hot pressing enables the unidirectional alignment of the polymer brush in such a way that the backbone of the polymer brushes orients perpendicular to the film plane, while the side chains align horizontally along the drawing direction of the Teflon sheets (Fig. 3). The 3D molecular ordering thus observed most likely originates from the polymer brush-mediated structural transfer at the contact interface. In the Teflon sheet, polytetrafluoroethylene (PTFE) molecules are oriented along the drawing direction, and this structural information is transferred to bulk poly-1 at the interface, so that the azobenzene-containing side chains of poly-1 are oriented along the direction of PTFE molecules.

The large-area 3D molecular ordering of poly-1 endows a hot-pressed polymer film with photoactuating capability. Thus, the film rolls up and flattens upon alternate irradiation with UV and visible light (Fig. 4). By detailed investigations, we found that the film possesses competing strains on its both sides. Upon exposure to light, the strain on the photoirradiated side of the film is released, so that the competing strain on the other side prevails, thereby resulting in a photomechanical bending motion.

The present achievement provides a new design concept for photomechanical soft materials and may update the common perception on such materials that the covalent crosslinking of photoactive molecular components is always essential for exerting macroscopic motions. More importantly, the processing method using a polymer brush and Teflon sheets, which enables large-area 3D molecular ordering, has great potential in the development

of high-performance organic materials including electronic materials for thin-film organic transistors and solar cells.

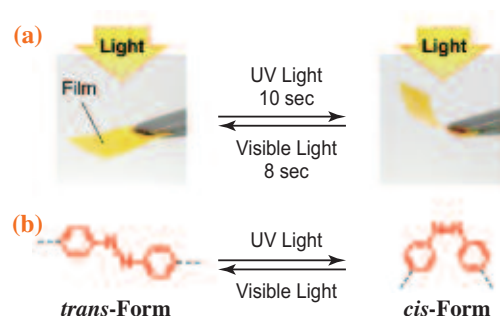


Fig. 4. (a) Photomechanical bending motion of hot-pressed polymer brush film. (b) Structural deformation of azobenzene molecule upon exposure to UV and visible light.

Takashi Kajitani

RIKEN Advanced Science Institute (Wako)

E-mail: kajitani@riken.jp

#### References

- [1] N. Hosono, T. Kajitani, T. Fukushima, K. Ito, S. Sasaki, M. Takata and T. Aida: *Science* **330** (2010) 808.