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# Spontaneous motion observed in highly sensitive surface relief formation system

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**Abstract**

Surface relief gratings formed on a liquid-crystalline azobenzene polymer film known as a highly sensitive system were investigated to obtain deeper insights into polymer migration on the micrometer scale. A surface relief formation was induced with incoherent nonpolarized patterned blue-light using a photomask instead of interference patterns of a coherent laser. Spontaneous lateral migration was observed under the edge of the grating photomask at room temperature even after terminating light irradiation. It was found that interfacial tension and the living *cis* form of azobenzene are essential for inducing spontaneous motion.


*Keywords:* Surface relief gratings; Azobenzene; Liquid-crystalline polymer; Photomask; Atomic force microscopy

## 1. Introduction

The facile, all-optical, and single-step fabrication of a unique regular surface structure has become a new research field of azobenzene (azo) polymers [1–6]. Such a structure is called surface relief grating (SRG) and is constructed using interference patterns of a coherent laser due to polymer chain migration at the micrometer level. Since the first report on the direct photo-inscription of SRGs on azo polymer films [7,8], SRGs have attracted much attention due to their interesting fundamental mechanism and attractive optical device applications.

In the first discovery of SRG, amorphous polymers having a push–pull-type azobenzene side chain showing a relatively high glass transition temperature were employed, and the exposure light dose used for SRG generation was typically on the order of some J cm$^{-2}$. From a practical viewpoint, the advancement of sensitivity for photo-induced polymer migration is a subject of great interest.

Recently, we have demonstrated that transfer efficiency is markedly enhanced by more than three orders in two fluid systems. One is composed of an azo polymer hybridized with a low-mass liquid-crystal molecule [9–11], and the other is a new copolymer having an azobenzene side chain and an oligo(ethylene oxide) side chain as a soft segment [12,13]. In both systems, liquid-crystal molecules and flexible ethylene oxide groups are anticipated to increase film fluidity, and these systems show a liquid-crystalline phase at room temperature. A key means of attaining instant material transfer is pre-UV light irradiation, which induces the *cis*-rich state of azobenzene.

To obtain deeper insights into polymer migration on the micrometer scale in the above-mentioned highly sensitive system, we used patterned light produced using a photomask [14] with wide range of periods (2–50 μm) instead of interference patterns of a coherent laser.

## 2. Experimental

The liquid-crystalline azo polymer having an oligo(ethylene oxide) side chain shown in Scheme 1 was synthesized

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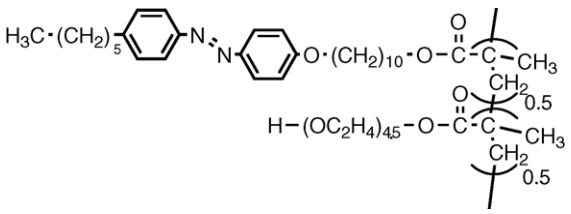

Scheme 1. Chemical structure of azobenzene-functionalized polymer.

as described previously [12]. The average molecular weight ($M_w$) was $3.0 \times 10^4$ ($M_w/M_n = 3.0$).

For preparation of thin dry films, the azo polymer was dissolved in cyclopentanone, and the solution was passed through a 0.2 μm pore filter. It was spin-coated on a cleaned quartz substrate at 2000 rpm for 60 s. The films produced were heated at 333 K under vacuum conditions. The thickness of the films was measured using a DEKTAK3 (Sloan Co.).

The films were pre-irradiated with UV (wavelength; 365 nm) light to a photoequilibrated *cis*-rich state and then patterned light irradiation was performed with blue (wavelength; 436 nm) light through a photomask attached to the film to from surface relief structure. UV and blue-lights were produced using a Hg–Xe lamp through combinations of appropriate glass filters (UV35 + UV36A and Y43 + V44, respectively). The photomask is composed of stripe lines with the same transparent and opaque widths.

The surface relief topologies were observed by atomic force microscopy (AFM) using a Seiko SPA300 module with an SPI 3700 probe station in the cyclic contact mode.

## 3. Results and discussion

Fig. 1 shows an AFM image of the surface relief structure produced by patterned blue-light irradiation through a photomask. Irradiation conditions were set at 1.0 mW cm$^{-2}$ of light power, and 10 min of irradiation time. When the blue-light was shaded completely, only a flat surface was observed as shown on the right-hand side of Fig. 1. On the other hand, when the film was irradiated with patterned light, regular surface modulation was produced, and its spatial period was coincident with that of the photomask as shown on the left-hand side of Fig. 1. When we focused on the cross-sectional topography, we found two hills with different heights within one spatial period of the patterned light. The higher one was produced in the shaded region, and the lower one in the irradiated region. Such a specific structure could be observed in the film irradiated with a patterned light using photomask with a wide period ranging from 10 to 20 μm. Taking account of the fact that polymer migration occurs from the exposed areas to the shaded area in this azo polymer system, the higher hill should be formed by the interflow of the material from both sides of the boundary between the irradiated and shaded regions, and the lower hill could be formed as a result of the remaining azo polymer.

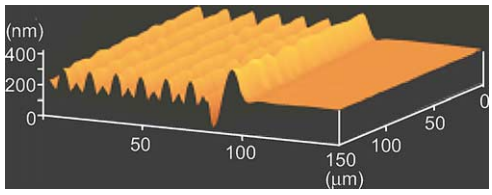


Fig. 1. Atomic force microscopy image of a thin film after irradiation through a photomask.

Interestingly, azo polymer migration continued to proceed even in the dark after terminating the light irradiation. Fig. 2 shows the behavior of spontaneous azo polymer migration with time. Presented time in Fig. 2 means elapsed time from the termination of the irradiation for the formation of the surface relief structure. As shown in Fig. 2, spontaneous motion was only observed at the edge of the stripe region, and it continued for approximately 6 h. Taking note of the lateral positions of the top of the peak and the bottom of the valley as shown by arrows in Fig. 2, it was found that spontaneous motion is directed from the edge of the stripe to the continuous shaded region. This direction is coincident with that of motion occurring during the patterned light irradiation, as speculated from the morphology shown in Fig. 1. The spontaneous azo polymer motion can be ascribed to an asymmetric flow of inelastic fluid induced by light in consideration of both the position where it happened and its direction.

It is worth noting that the height difference between peak and bottom increases against the natural order in the spontaneous motion without supplying energy, as shown in Fig. 2. This fact is inconceivable without consideration of another explanation for this phenomenon. We therefore introduced an aspect ratio to interpret it. Aspect ratio is defined as the ratio of hill height to hill width.

Fig. 3 shows the profile of aspect ratio as a function of elapsed time from the termination of the irradiation. As shown in Fig. 3, aspect ratio decreased simply with elapsed time, and

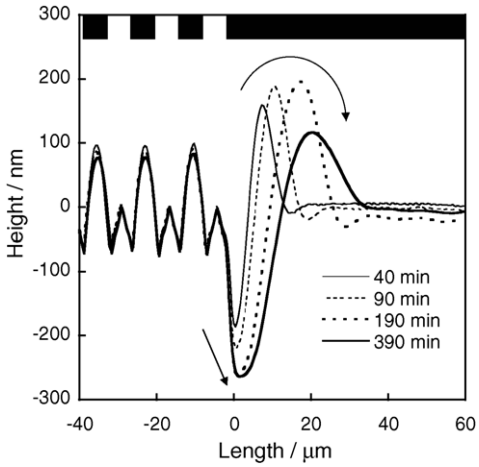


Fig. 2. Change in cross-sectional height profile of the film after terminating blue-light irradiation through a photomask.