

## Two-dimensional manipulation of $\pi$ -conjugated polymer by means of instant mass migration

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Micro-relief structures could be optically inscribed in a spin-coated polymer blend films which consist of liquid crystalline azobenzene polymer and poly(3-dodecylthiophene). The inscriptions were characterized by atomic force microscope and fluorescence microscope. The clear fluorescence patterns drawn by the higher part of the relief structures were observed. We conclude that poly(3-dodecylthiophene) is transferred together with the migration of azobenzene polymer.

Key words: surface relief grating, poly(3-alkylthiophene), patterning, azobenzene, liquid crystalline polymer

### 1. INTRODUCTION

$\pi$ -Conjugated polymers are promising as active materials in many application areas such as microelectronics and photonics. Patterning of  $\pi$ -conjugated polymers have been achieved through some advanced techniques such as micro-molding in capillaries (MIMIC)<sup>1,2</sup>, micro-contact printing ( $\mu$ CP)<sup>3,4</sup>, inkjet printing<sup>5</sup>, mesoscopic dewetting<sup>6</sup> and so on.<sup>7</sup> Most of such techniques required, however, complicated processes. We propose herein a new patterning method of  $\pi$ -conjugated polymers based on photoinduced mass transfer system.

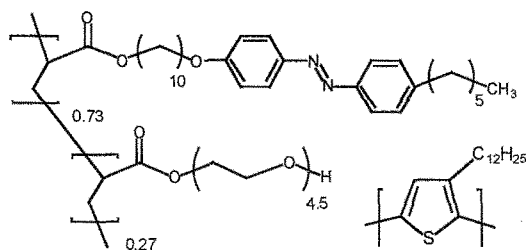
It has been demonstrated that surface relief gratings (SRG) can be optically inscribed on thin films of azobenzene-containing polymers.<sup>8,9</sup> Two research groups discovered the phenomenon in 1995. Since then, this phenomenon is now generally known as a photoinduced surface relief formation (PSR). Sinusoidal undulations on polymer film surface originate from photoinduced polymer chain migration at micrometer levels. Construction of SRG in this technique is advantageous for facile, all-optical, and single step fabrication. In other word, we can obtain large surface relief structures without wet development process.

Potential possibilities for photonic applications such as holographic storage, waveguide and liquid crystal alignment have been realized as soon as the first discovery.<sup>8,9</sup> However the application of PSR technique is limited to attain static use due to the requirement of vast photon dose for generating SRG structures. Various materials for PSR have been produced. In the typical materials, amor-

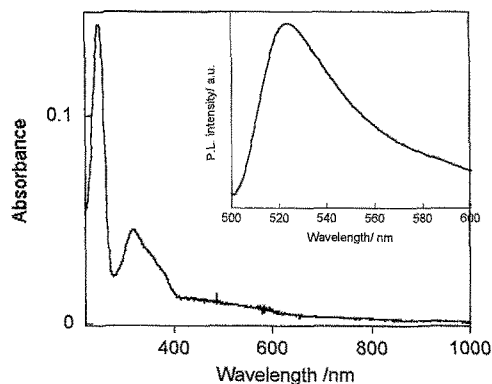
phous azobenzene polymer (pDRIA) films, the total photon dose reaches ca. ten's of  $J\text{ cm}^{-2}$  for clear SRG formation.

In the previous study, we have already shown that highly photosensitive surface relief formation could be accomplished in liquid crystalline azobenzene polymer films.<sup>10, 11</sup> The combination of pre-irradiation treatment and liquid crystalline polymer films led to three orders of magnitude improvement in the photosensitivity for surface relief formation compared to pDRIA. The rapid mass migration in our presented system (instant mass migration) requires a step in which one must pre-expose a film to ultraviolet (UV) light. Without this procedure, no SRG formation is observed at the low intensity exposure that was adopted. Thus, the instant mass migration should be driven by spatially patterned cis-to-trans back-photoisomerization. Furthermore, large topological modulations were only formed under intensity holographic conditions but not under polarization holographic conditions. It was therefore emphasized that only the intensity patterns is essential for the photoinduced rapid mass transfer. The lack of polarization dependence shows marked contrast with that observed for hitherto reported amorphous polymer systems.<sup>12</sup>

Above instant mass migration system provides novel potential for motional functions, for example, soft micro actuators and micro-patterning of other guest materials. Here we focus on the possibility for patterning of  $\pi$ -conjugated polymers using light-driven instant mass migration system as a molecular conveyor.



**Scheme 1.** Chemical structure of polymers.



**Fig. 1.** UV-Vis and emission spectra (insert) of spin-coated polymer blend film on fused silica. The emission spectrum was studied by excitation at 480 nm.

## 2. Experiment

The chemical structures of materials using in this study are shown in scheme 1. The azobenzene-containing polymer for molecular conveyer film was a liquid crystalline azobenzene copolymer having oligo(ethylene oxide) side chain (6Az10Ac-AE4.5) whose synthesis was previously reported. We adopted  $\pi$ -conjugated poly(3-dodecylthiophene) (PDT) as the guest material because PDT have many experimental advantages. Synthesis of PDT is readily achievable utilizing iron trichloride ( $\text{FeCl}_3$ ) as catalyst<sup>13</sup>. The weight-average molecular weight (Mw) was 82000. Furthermore PDT has strong light resistant and dissolves in some organic solvents very well.

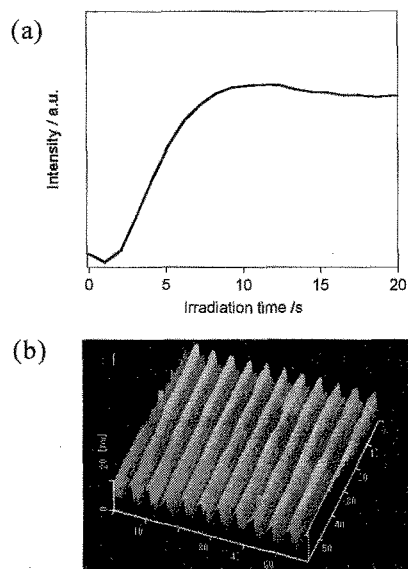
Spin-coated films which consist of 6Az10Ac-AE4.5 and PDT are prepared from a toluene solution containing 2 wt% 6Az10Ac-AE4.5/PDT (1/0.02 mol %). To remove residual solvent, the spin-coated films were heated at 333 K under vacuum conditions. The film thickness was ca. 30 nm as evaluated by atomic force microscope (AFM, SII Nanopics 2100). Phase separation was not admitted in optical microscope observation.

The surface relief gratings were inscribed by two ways: 1) Exposing the blend films to an interference pattern of s-polarized argon ion ( $\text{Ar}^+$ ) laser beams at 488 nm with  $5\text{ mW cm}^{-2}$  or 2) an incoherent non-polarized blue light at 436 nm (i-line of mercury lamp) through a photomask attached to the film. In the holographic recording

experiment, the condition of polarization adopted was pure intensity hologram using s-polarized  $\text{Ar}^+$  laser at 488 nm. The formation of SRG was monitored by measuring the first order diffraction efficiency of probe beam, a low power He-Ne laser beam. The inscriptions were characterized by AFM (SII, Nanopics 2100) and fluorescence microscope (BX51, Olympus).

## 3. Results and Discussion

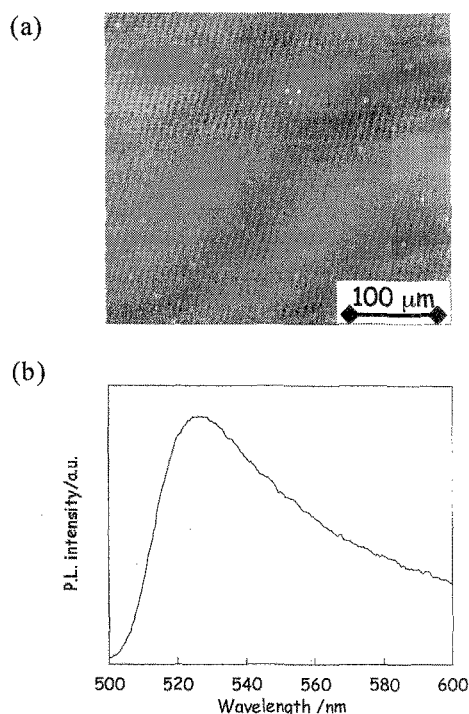
Figure 1 shows the ultraviolet-visible (UV-Vis) absorption spectrum of spin-coated blend film taken with an Agilent, 8453. The UV-Vis spectrum of spin-coated blend films had a broad peak in visible region derived from PDT. The insert shows an emission spectrum with excitation at 480 nm (JASCO, FP-777). The fluorescence spectrum shows a maximum at 530 nm. The same value in PDT film was reported in the literature.<sup>14</sup> Furthermore, a shift of fluorescence maximum wavelength and fluorescence quenching was not observed in trans/cis photoisomerization of azobenzene chromophores. Thus, the mixing of photoisomerizable polymer 6Az10Ac-AE4.5 and PDT does not influence the polymer conformation or intermolecular interactions.



**Fig. 2.** (a) Growth of the first order diffraction intensity with irradiation time. (b) An AFM image of the resulting relief structure after irradiation with  $\text{Ar}^+$  laser at  $5\text{ mW cm}^{-2}$  for 10s.

The spin-coated blend films were first exposed to UV light at 365 nm from mercury lamp and then pure intensity holographic recording was performed with a 488 nm  $\text{Ar}^+$  laser beam. Figure 2(a) displays the growth of the first order diffraction intensity due to SRG formation on the blend films as a function of irradiation time. The change of diffraction intensity was promptly

saturated at 10s. As shown in Fig.2 (b), the sinusoidal surface relief undulation was formed on the spin-coated blend film. The first diffraction efficiency reached ca. 0.5 % and the corresponding modulation depth became ca. 20 nm after exposure to the interferometric Ar<sup>+</sup> laser beam for 10 s. These results indicate that mass migration was almost completed only with such short exposure (in the order of seconds).

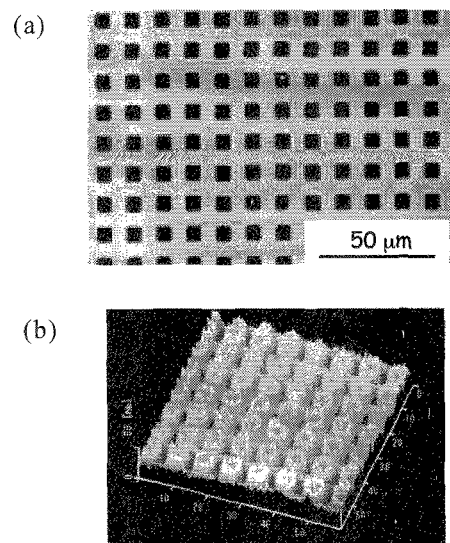


**Fig.3.** Fluorescence micrograph (a) and spectrum (b) of the resulting inscription. The emission spectrum was obtained at excitation at 480 nm.

The clear fluorescent array of line corresponding to the relief structures was observed (Fig.3. (a)). Figure 3. (b) shows the fluorescence spectrum of the inscribed film. The fluorescence spectrum had a maximum at 530 nm in agreement with that measured in unexposed flat film (see Fig. 1.), thus, the mass transport process does not influence the polymer conformation. These results lead to the conclusion that PDT was transferred together with azobenzene polymer with short exposure time.

We could also achieve the photoinduced instant mass migration of PDT by patterned blue incoherent-light irradiation using a photomask instead of interference Ar<sup>+</sup> laser. In our previous work, we conducted two-beam interference experiments under various writing polarization conditions to gain better understandings on the mechanism of our unconventional rapid mass transport system. It is found that the rapid mass migration is promoted only by intensity holographic recording conditions independent of the polarization of the writing beams. This is of great technological advantage for fabrication of on-demand inscriptions

avoiding alignment of complex and expensive optical components. Figure. 4. shows an optical microscopic image of the photomask (a) and the topographic AFM image of the resulting film (b). The tetragonal features of the surface topology evidently indicate that the mass migration of both PDT and azobenzene polymer occurs from the bright regions to the dark ones within the plane.



**Fig.4.** Photograph of a grid type photomask (a) and an AFM image of the resulting relief structure (b) after irradiation with 436 nm light from a mercury lamp ( $4 \text{ mW cm}^{-2}$  for 30 s).

#### 4. Conclusion

We could achieve micropatterning of  $\pi$ -conjugated polymers, poly(3-dodecylthiophene) (PDT) utilizing instant mass migration system. The resulting clear fluorescent array of line was corresponding to the relief structures. This result led to conclusion that PDT was transferred together with azobenzene polymer from the bright regions to the dark ones within the plane with short exposure time.

The present instant mass migration as molecular convey will read to facile processing of periodic microstructures, which may find fascinating applications in photonic device system such as the formation of rewritable or tunable photonic band-gap materials.

#### 5. Acknowledgment

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